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Baratto et al.

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(54) **PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE**

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C01B 3/02 (2006.01)
C01B 3/48 (2006.01)

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(Continued)

(58) **Field of Classification Search**
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(Continued)

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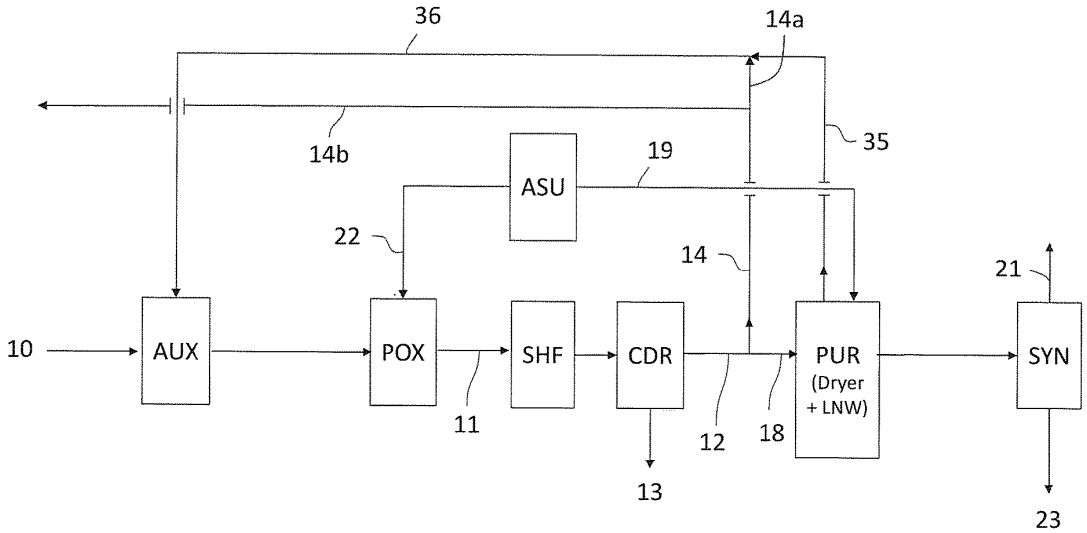
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(57) **ABSTRACT**

Process for the synthesis of ammonia from natural gas comprising conversion of a charge of desulphurized natural gas and steam, with oxygen-enriched air or oxygen, into a synthesis gas, and treatment of the synthesis gas with shift reaction and decarbonation, wherein a part of the CO2-depleted synthesis gas, obtained after decarbonation, is separated and used as fuel fraction for one or more furnaces of the conversion section, and the remaining part of the gas is used to produce ammonia.

23 Claims, 4 Drawing Sheets



(52) **U.S. Cl.**
CPC *C01B 2203/0244* (2013.01); *C01B 2203/0283* (2013.01); *C01B 2203/042* (2013.01); *C01B 2203/0445* (2013.01); *C01B 2203/0475* (2013.01); *C01B 2203/068* (2013.01); *C01B 2203/1241* (2013.01)

(58) **Field of Classification Search**
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See application file for complete search history.

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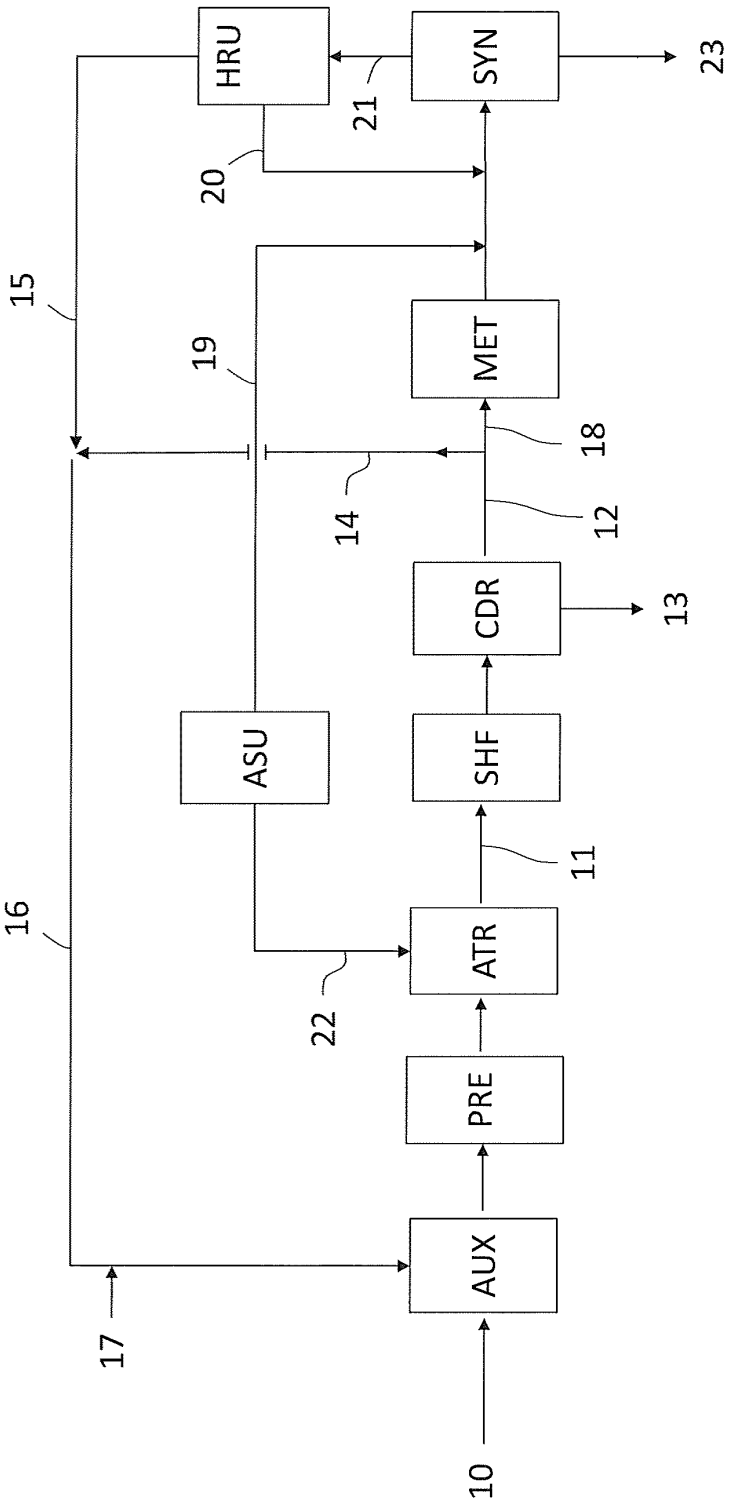

HRU
SYN
23
21
20
15
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MET
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FIG. 1

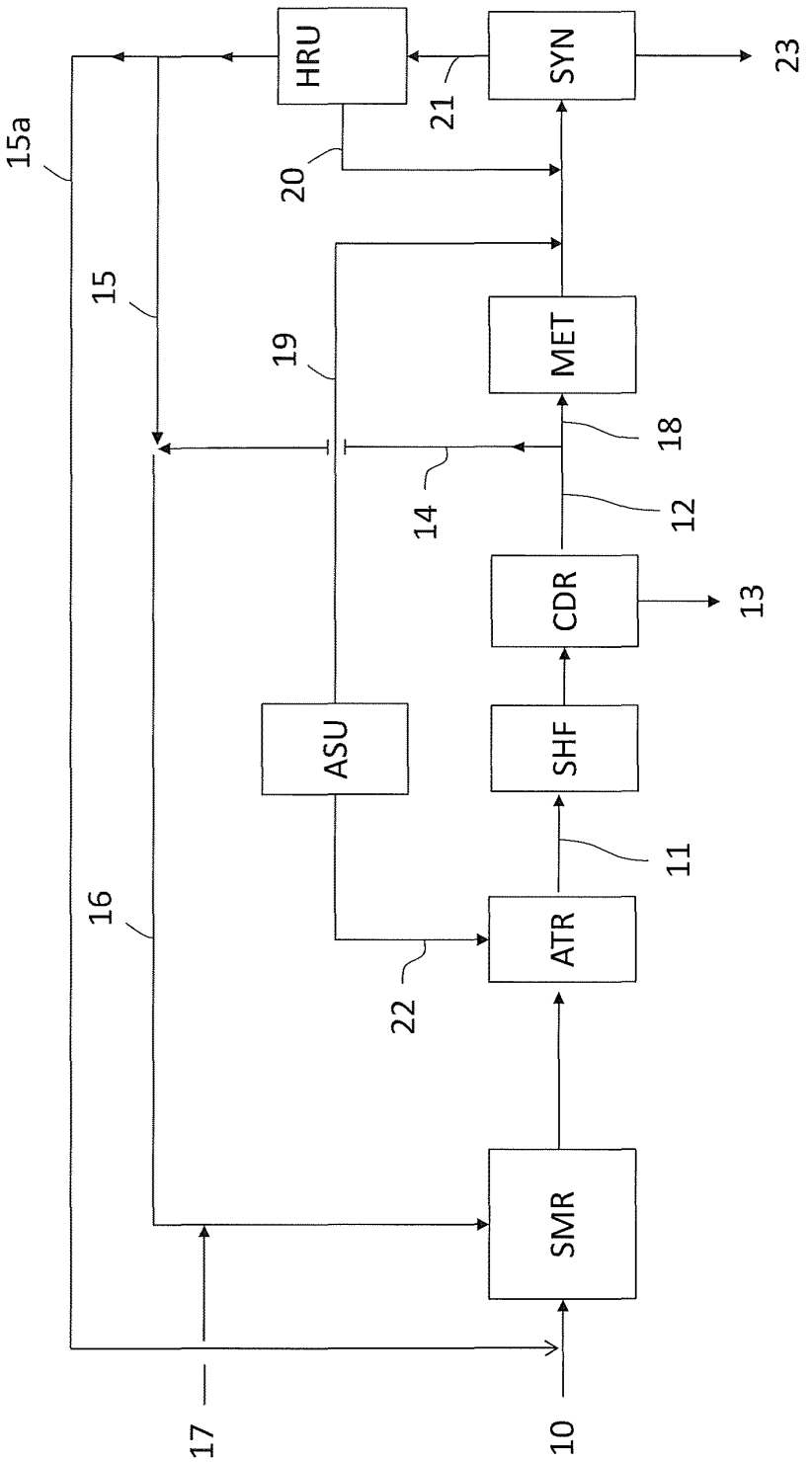

HRU
SYN
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FIG. 2

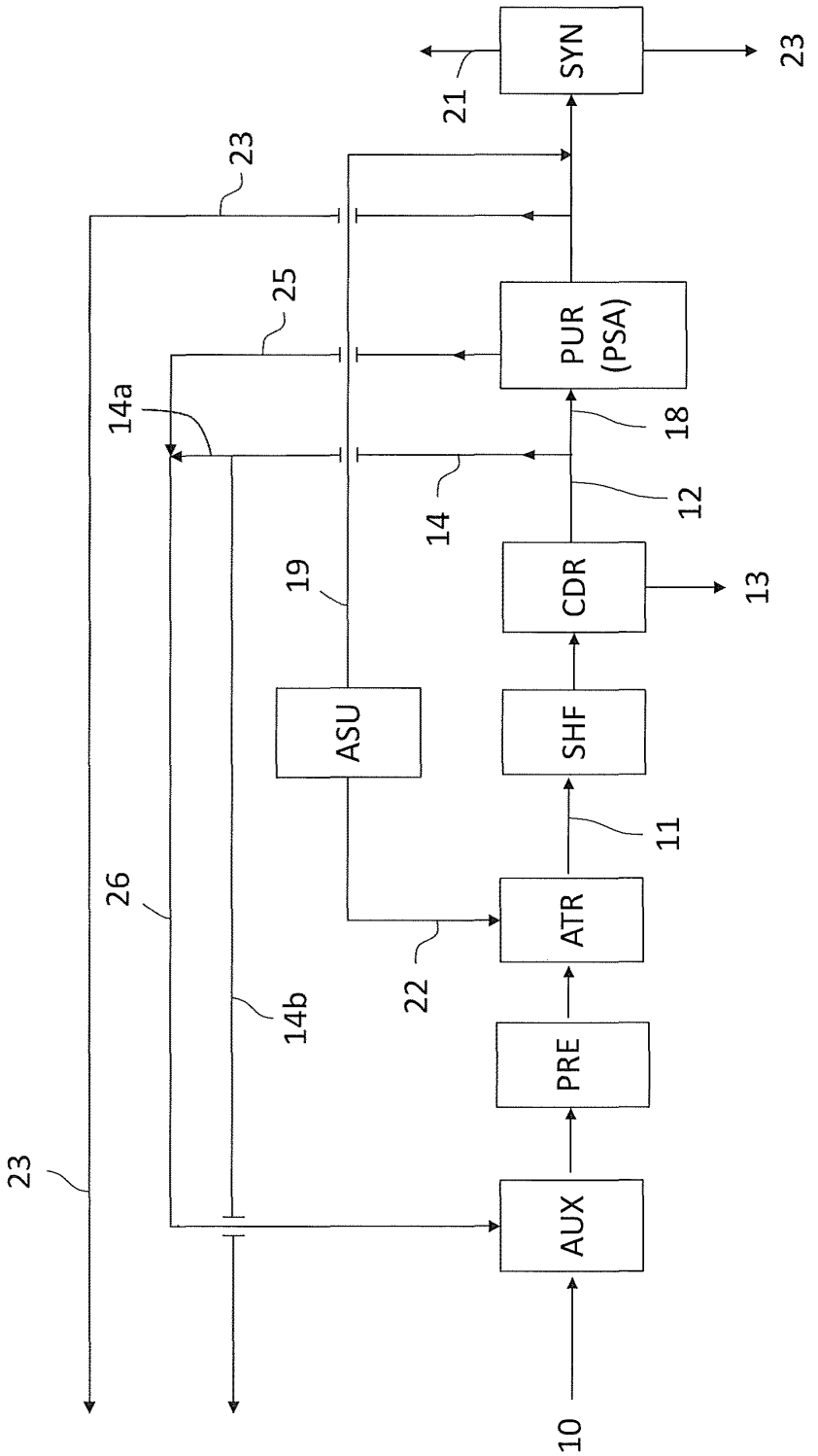

SYN
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23
25
PUR (PSA)
14a
18
14
12
19
CDR
13
ASU
SHF
11
26
ATR
22
14b
PRE
23
AUX
10

FIG. 3

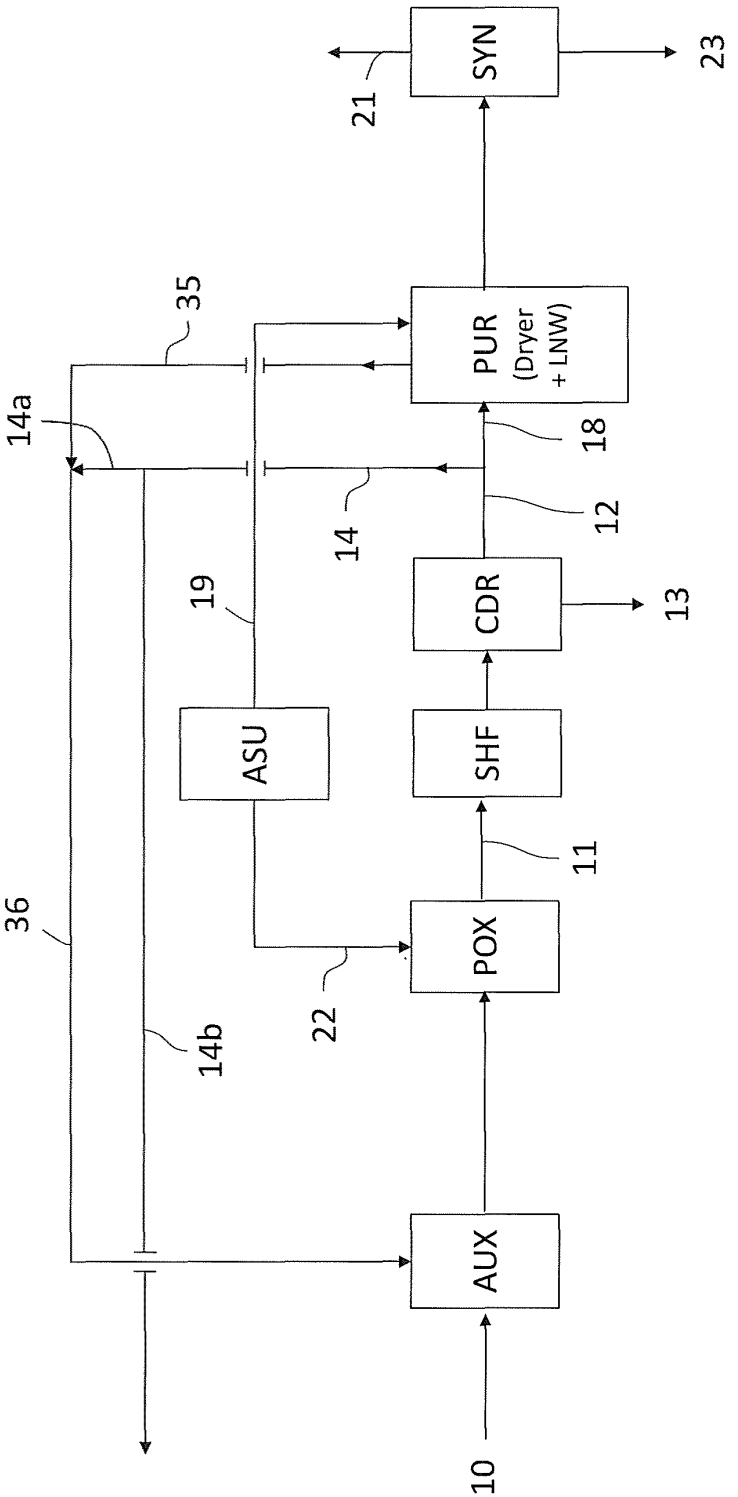

SYN
21
23
PUR
(Dryer
+ LNW)
35
14a
18
14
12
CDR
19
13
ASU
SHF
11
36
POX
22
14b
AUX
10

FIG. 4

PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE

FIELD OF APPLICATION

The invention relates to the field of ammonia synthesis plants fed with natural gas (NG).

PRIOR ART

The ammonia synthesis plants of the type considered here comprise a section adapted to convert the natural gas into a make-up gas containing hydrogen and nitrogen, and a synthesis section wherein said make-up gas reacts catalytically at high pressure to produce ammonia.

The section which generates said make-up gas is referred to in the technical language as the "front end". The term "back end" is instead used to denote the section for ammonia synthesis and the respective cooling section intended to cool the effluent of the synthesis section in order to separate the ammonia.

In the front end, the desulphurized natural gas undergoes reforming, resulting in a gas containing essentially hydrogen, carbon monoxide CO and carbon dioxide CO2. Said gas then undergoes a shift reaction which converts CO into CO2; removal of CO2 (decarbonation) and preferably methanation.

The reforming process, in a common type of plant, comprises primary steam reforming and a subsequent catalytic air-fired secondary reforming. The primary reformer is heated by burners fuelled by a part of the available natural gas. In the secondary reformer the effluent from the primary reformer burns due to contact with the oxygen contained in the air. In some plants other reforming configurations are used, for example an autothermal reformer (ATR) preceded by a furnace for heating the charge, i.e. the gaseous mixture fed to said reformer.

The above described ammonia plants result in significant emissions of CO2 into the atmosphere, overall in the region of 100 million tonnes of CO2 per year. One of the main sources of CO2 emission consists in the combustion fumes of the primary reformer and other burner furnaces if any, for example auxiliary heaters.

For environmental reasons, it is required to minimize the CO2 emissions from the fumes of the NH3 plants. The problem affects in particular the older ammonia plants which are less efficient than the new ones and have greater CO2 flue emissions in relation to the quantity of ammonia produced. It is also necessary that the reduction of the emissions should not increase excessively the costs for production of the ammonia.

According to the present state of the art, the processes for capturing CO2 from fumes are based on washing with solvents (for example the solvent KS-1™ produced by Mitsubishi). The associated plants are, however, costly and complicated, have a high energy consumption and require expensive solvent. Therefore these CO2 capturing processes cannot be applied to the plants considered here since they would increase excessively the costs for production of the ammonia.

In some ammonia synthesis processes of the prior art, part of the fuel may be supplied by a purge flow obtained, for example, from a cryogenic purification section of the synthesis gases or from a PSA unit. Said purge flow may have a reduced CO2 content. However, said purge flow accounts for a small amount of the total fuel and does not solve the problem of the CO2 emissions in the atmosphere.

SUMMARY OF THE INVENTION

The object of the invention is to provide a method for conducting ammonia synthesis processes with CO2 emissions into the atmosphere which are greatly reduced compared to the prior art. Another object of the invention is to provide a method for revamping the existing plants, of the type using air-fed secondary reformers able to reduce drastically the CO2 emissions into the atmosphere.

The objects are achieved with a process and a revamping method according to the claims.

According to the invention, a process for synthesis of ammonia from natural gas comprises:

conversion of a charge of desulphurized natural gas and steam, with oxygen-enriched air or with oxygen, to form a synthesis gas containing hydrogen, CO and CO2;

a treatment of said synthesis gas comprising at least one shift reaction of the carbon monoxide into CO2, and subsequent separation of CO2 from the gas, thus obtaining a CO2-depleted synthesis gas and a CO2-rich gaseous flow containing the CO2 separated from the gas;

optionally, a step for methanation of the synthesis gas and/or addition of nitrogen to the synthesis gas, obtaining a make-up gas containing nitrogen and hydrogen in a suitable molar ratio for ammonia synthesis,

characterized by:

separation of a part of said CO2-depleted synthesis gas, obtaining a fuel fraction of the synthesis gas, wherein said fuel fraction is fed as fuel to at least one furnace.

The invention also relates to a method for revamping a plant originally comprising a reforming section which includes a primary steam reformer and air-fired secondary reformer, and treatment of the synthesis gas comprising a shift reaction of carbon monoxide into carbon dioxide, decarbonation and optionally methanation. The revamping method comprises at least:

providing a flow of enriched air or oxygen and using said flow as an oxidant for the secondary reformer instead of the air;

separating a part of the synthesis gas downstream of decarbonation,

feeding said part of the synthesis gas, which has a reduced CO2 content, as fuel for at least one furnace of the plant.

The term "furnace" is understood as meaning an apparatus chosen from among: a steam reformer or a charge preheater or a steam generator or a steam superheater. These apparatus, which operate by means of combustion, are identified by the term "fired heater". Said furnace in some embodiments forms part of the section for converting the natural gas into synthesis gas. In combined ammonia/urea plants said furnace may form part of the urea section.

The portion of synthesis gas which is separated and sent to said at least one furnace is termed fuel fraction of the gas available after the shift step. Preferably, said fuel fraction is comprised between 1% and 40% of the available gas, more preferably between 10% and 30% and even more preferably between 20% and 30%. For example in a preferred embodiment the fuel fraction is equal to 30%. The remaining part, which is intended to be converted into ammonia, is called process fraction.

It should be noted that said fuel fraction is relatively high, for example about ⅓ of the total. The invention in fact envisages that a non-negligible portion of synthesis gas is allocated to fuel in order to reduce the CO2 emissions. This

results in the need to produce an additional quantity of synthesis gas, but, as will be explained more clearly below with the aid of the examples, this necessity is compensated for by the advantages of the invention.

The separation of the fuel fraction is advantageously performed by splitting a process flow, for example a process gas after shift and decarbonation. As a result of said splitting, the fuel fraction and the remaining part of the gas, also called process fraction, have the same composition.

It should be noted that the present invention envisages deliberately allocating a part of the process flow to the fuel fraction, the fuel fraction being directly separated from the process flow and having the same composition. The prior art, on the other hand, teaches only allocating as fuel any purge streams derived from purification processes and containing methane. The said synthesis gas with a low CO2 content (CO2-depleted syngas) preferably contains no more than 1000 ppm by volume (0.1%) of CO2. Said gas is composed essentially of hydrogen ((H2) with any small residual quantities of CO and CH4, typically less than 2% by volume and preferably less than 1%.

The combustion of said gas is substantially free from production of CO2. In fact, the combustion of the hydrogen does not form CO2, and only the small quantity of CO or CH4, if present, may form CO2.

The invention suggests using a process gas part as fuel for one or more furnaces of the reforming section, differently from the prior art which, for this purpose, uses part of the natural gas, i.e. a hydrocarbon. The process gas part (fuel fraction) is suitably separated after a CO2 removal treatment and, as explained further above, it contains essentially hydrogen which may burn without forming CO2. Consequently it can be understood that the invention allows the CO2 emissions into the atmosphere to be drastically reduced.

Said oxygen-enriched air preferably contains at least 50% oxygen by volume and more preferably at least 90% oxygen by volume and even more preferably at least 95%. The advantages of a high oxygen content in the enriched air are as follows: greater calorific power of the synthesis gas; smaller flow of flue discharge gas; smaller volumetric flow through the apparatus of the conversion section and, consequently, smaller apparatus.

The CO2-depleted synthesis gas preferably forms all—or substantially all—the fuel of the furnaces used for the process. In some embodiments, however, it is preferred to keep a small amount of natural gas which is called "trim fuel" of the furnace. Preferably said small quantity accounts for not more than 15%, more preferably not more than 10%, of the total combustion heat (duty) of the furnace. The trim fuel allows the furnace to be rapidly controlled, for example in order to quickly raise or lower the load if needed.

Said percentage of the combustion heat may be expressed as the product between the flowrate (kg/s or mol/s) and the calorific power (J/kg or J/mol).

According to some embodiments of the invention, methanation of the synthesis gas is performed downstream of decarbonation. The methanation step converts residual CO and CO2 into CH4, consuming H2, in accordance with the reactions $CO+3H2 \rightarrow CH4+H2O$ e $CO2+4H2 \rightarrow CH4+2H2O$.

Preferably, the separation of the fuel fraction from the CO2-depleted synthesis gas is performed before (upstream of) said methanation step.

The advantage of separating the fuel fraction before methanation is that of not oversizing the methanation section of the fuel fraction, and of not losing the methanation heat of the fuel fraction. Moreover, for the same furnace heat requirement and the same gas temperature, the fuel fraction is slightly less if removed before methanation.

There are no disadvantages as regards CO2 emissions into atmosphere, which are the same by using as fuel both the gas upstream of the methanator and the gas downstream of the methanator, for the same flowrate. In case of nitrogen addition, the fuel fraction is separated before adding nitrogen. The advantage is a greater calorific power of the synthesis gas used as fuel, which does not contain nitrogen, or contains a smaller amount thereof.

After separating the fuel fraction, the CO2-depleted synthesis gas may be optionally treated in a purification section comprising, for example, a PSA unit or comprising a dryer followed by a cryogenic unit.

The purification section produces at least one stream of ammonia synthesis gas with a reduced content of inerts, and at least one waste stream containing CO, and CH4. The waste stream may also contain H2 and N2. In some embodiments, at least part of the waste gas of said purification section is used as fuel together with the fuel fraction. Consequently, the fuel fraction may be reduced.

The advantage of the purification unit is that of reducing the inerts content in the make-up gas, resulting in known advantages for the ammonia synthesis, including smaller consumption for circulation and a reduction (or even elimination) of the purge flow of the ammonia synthesis loop.

According to the invention, the fuel fraction is advantageously separated upstream of the purification unit. Consequently, only the synthesis gas portion supplied to the ammonia synthesis undergoes treatment in the purification section which, without having to process the synthesis gas corresponding to the fuel fraction, may be realized with much smaller dimensions. The advantage of separating the fuel fraction upstream of the purification unit is that of avoiding oversizing of the purification unit and the corresponding consumption for the fuel fraction of the synthesis gas. Another advantage is the possibility of controlling separately the fuel fraction and the purification unit.

There is no disadvantage in separating the fuel fraction upstream of the purification from the point of view of the CO2 emissions into atmosphere, since the CO, CO2 and CH4 contained in the synthesis gas of the fuel fraction would be separated by the purification unit to form the waste stream and used as fuel.

Advantageously, the purification unit does not need to have an excessively high hydrogen recovery, because the hydrogen "lost" in the waste gas is used as fuel and does not produce CO2 emissions into atmosphere. The fuel fraction of the synthesis gas is consequently regulated.

Preferably, however, the purification unit has a sufficiently high hydrogen recovery such that the fuel fraction accounts for at least 30%, preferably at least 40%, even more preferably at least 50% of the furnace duty. The applicant has found that this condition is advantageous for the control of the furnace itself independently of the control of the purification unit.

The purification section may comprise selective adsorption of the undesirable components onto a solid. In some embodiments said purification section comprises a PSA (pressure swing adsorption) unit which uses molecular sieves for separating CO, CH4, Ar, H2O and residual CO2. In other embodiments said section comprises at least one dryer for separating residual CO2 and water, followed by a cryogenic unit for separation of CO, CH4 and Ar. The cryogenic separation unit is preferably a Liquid Nitrogen Wash (LNW) unit.

A PSA unit typically produces a single flow of purified product, substantially at the feed pressure, and a single stream of waste gas, at a pressure much lower than the feed pressure. Said waste stream contains CO, CH4, Ar, H2O and residual CO2, and may contain H2 and N2.

If the purification section comprises dryer and LNW, the purified product may emerge as one or more streams, and may already contain H2 and N2 in a suitable ratio for the synthesis of ammonia.

The dryer has a tail gas, product of regeneration of the molecular sieves used for capturing mainly H2O and the traces of residual CO2 contained in the feed, which would freeze during the cryogenic treatment in the LNW unit. The dryer may be regenerated with a nitrogen flow (from the air separation unit). In this case the tail gas containing N2, H2O and CO2 may be discharged into atmosphere or combined with the tail gas of the LNW described below.

The LNW also has at least one tail gas which contains the bottom end product of the LNW absorption column, containing CH4 and CO, in addition to N2 and H2. The discharge gas of the LNW may be conveyed away as fuel.

The tail gas of the LNW may be used at least partly for the regeneration of the dryer before being conveyed away as fuel.

The synthesis gas with a low content of inerts may be conveyed away for ammonia synthesis.

Methanation is an exothermic reaction, but there is not a substantially large amount of reaction heat and it is usually not recovered.

Methanation therefore leaves a small quantity of methane in the synthesis gas (methane slip). The presence of said small quantities of methane in the synthesis gas is not a problem for the purposes of ammonia production, since methane is inert to the synthesis reaction. Methane accumulates in the purge flow of the synthesis loop. However, by using the purge flow of the synthesis loop as fuel, the methane contained therein constitutes a source of CO2, albeit of small entity.

The carbon monoxide contained in the synthesis gas also constitutes a source of CO2, albeit of small entity, both owing to combustion of the synthesis gas used as fuel, and owing to combustion of the waste gas of a purification unit, where present.

In some embodiments of the invention, in order to reduce also this source of CO2 (i.e. the emissions caused by the presence of residual carbon monoxide of the synthesis gas), the process comprises a catalytic purification which selectively converts the CO into CO2 upstream of decarbonation. Selective conversion of the carbon monoxide may be obtained, for example, using the process known as Selectoxo™ which operates with the reaction $CO+\frac{1}{2}O2 \rightarrow CO2$. The oxygen for selective oxidation of the CO may be a part of the mentioned enriched-air or oxygen flow.

An advantage of said selective conversion of CO into CO2 is that at least part of the residual CO from the shift is converted into CO2 and removed during decarbonation. Consequently, the combustion of the synthesis gas, of the synthesis loop purge flow, or of the purification waste gas, produces a smaller quantity of CO2.

According to the invention, the CO2 flue emissions are mainly determined by the CO, CO2 and CH4 content of the synthesis gas downstream of decarbonation, as well as by the optional trim fuel flow which will be described below.

The combustion of said gas is substantially free from CO2 production. In fact, the hydrogen combustion does not form CO2, and only the small quantity of CO or CH4, if present, may form CO2.

The CO2 production is also derived from the combustion of the methane contained in the synthesis loop purge flow.

In case a purification unit is present, CO2 production is also derived from the combustion of CO, CH4 and residual CO2 of the discharge gas.

According to one aspect of the invention, the fuel fraction is produced in excess compared to the fuel required for the conversion section, the quantity of said fuel fraction exceeding that required being exported from the process, and the regulation of the conversion section is performed by modulating the quantity of said fuel fraction directed towards the conversion section and the quantity exported by the process.

The conversion of the natural gas into synthesis gas may be performed using different techniques.

According to some embodiments of the invention, the step of natural gas conversion into synthesis gas comprises primary reforming followed by secondary reforming. In some embodiments, more preferably, the conversion step comprises a catalytic autothermal reforming (ATR), optionally preceded by a preliminary reforming (pre-reforming). An ATR without preliminary reforming is also called "pure ATR". Advantageously, in these embodiments, at least a part of the synthesis gas fuel fraction feeds a furnace for preheating the gas prior to autothermal reforming.

The advantage of using ATR, pure or in combination with a pre-reformer, consists in the smaller heat requirement of the furnace compared to the combination of the ATR with a primary reformer, also considering the heat required for generation and overheating of steam necessary for the process. This is due to the fact that the preheating temperature of the ATR feed and of the optional pre-reformer according to the invention is suitably chosen at a value not greater than 650° C., lower than the output temperature of the primary reformer, and due to the fact that, in the preheating furnace, there is no progression of the steam reforming reaction (which is endothermic).

A pure ATR, or ATR in combination with a pre-reformer, may advantageously operate with a steam/carbon (S/C) ratio less than that of a primary reformer. Preferably, said S/C ratio is not greater than 2, more preferably not greater than 1.5, even more preferably not greater than 1. This also helps reduce the heat required by the furnace for preheating the feed of the ATR and optional pre-reformer.

In the case of ATR without primary reformer, the fuel fraction is preferably comprised between 1 and 30%, more preferably between 10 and 30%, even more preferably between 10 and 20%.

In some embodiments the step for converting the natural gas into synthesis gas comprises a non-catalytic POX (partial oxidation) step. Advantageously, in these embodiments at least a part of the synthesis gas fuel fraction feeds a furnace for preheating the gas before said partial non-catalytic oxidation or for steam generation or steam superheating.

The advantage of using a POX consists in the smaller heat requirement of the furnace compared to the combination of an ATR with a primary reformer, also considering the heat required for generation and overheating of steam necessary for the process. This is due to the fact that the preheating temperature of the POX feed according to the invention is suitably chosen at a value not higher than 500° C., markedly lower than the output temperature of the primary reformer, and due to the fact that in the preheating furnace there is no progression of the steam reforming reaction (which is endothermic). Moreover, POX may advantageously use a S/C ratio lower than that of a primary reformer, preferably not greater than 2, more preferably not greater than 1, even more

preferably not greater than 0.5. This also helps reduce the heat required by the preheating furnace.

In the case of POX, the fuel fraction is preferably comprised between 1 and 30%, more preferably between 10 and 30%, even more preferably between 10 and 20%.

The reduction in the heat required by the preheating furnace for a POX and for a pure ATR compared to an ATR in combination with a primary reformer provides the following advantages: the fuel fraction of the synthesis gas is less, and it is possible to reduce the quantity of trim fuel, therefore lower CO2 flue emissions may be obtained.

Both in the case of POX with optional purification unit of the synthesis gas and in the case of ATR without primary reformer and with optional purification unit of the synthesis gas, it is preferable to select a purification unit with high hydrogen recovery, for example a liquid nitrogen wash, so as to ensure that the fuel fraction of the synthesis gas is sufficiently large to control the furnace independently of control of the purification unit.

Another advantage of the POX and ATR without primary reformer, consequence of both the smaller fuel fraction and the smaller steam/carbon ratio, is the smaller autogenous steam production, which reduces the heat required for the associated overheating, the fuel fraction, the CO2 flue emissions and the total natural gas consumption.

The smaller autogenous steam production may result in a lack of steam for driving the turbines or of electricity for powering the motors of the machines. The missing energy may be conveniently imported from outside the plant as electricity with reduced CO2 emissions, for example generated by renewable sources. It should be pointed out that this synergy is not possible if the process already produces an excess of steam or energy, for example in the case of combination of primary reformer and ATR with a fairly large fuel fraction.

In some embodiments the step of converting the natural gas into synthesis gas also comprises a steam reforming step. Advantageously, in these embodiments at least a part of the synthesis gas fuel fraction feeds the burners of the reformer.

A part of the fuel fraction may be allocated, in some embodiments, to furnaces for the production and/or superheating of steam.

The invention also allows to produce the electricity necessary for the synthesis of ammonia or of its derivatives (for example urea) with low emissions of CO2, using as fuel CO2-depleted synthesis gas, for example in the following ways:

- expansion in a turbo generator of a flow of steam produced in a steam generator or steam superheater, fed by the CO2-depleted synthesis gas as fuel;
- combustion in a gas turbine or in a gas engine, fed by the CO2-depleted synthesis gas as fuel.

Generally, in ammonia processes, a purging gas is extracted from the ammonia synthesis loop, in order to remove the inert substances from the synthesis loop, and said purging gas is treated with a process for recovery of the hydrogen contained in it (HRU). Said recovery process generates a hydrogen-rich gas which may be reused for synthesis and a tail gas containing most of the methane initially contained in the purging gas. The methane in the tail gas is practically all that contained in the process fraction of the synthesis gas. Normally said tail gas, given its relatively high methane content, is used exclusively as fuel. This use of tail gas, however, generates CO2 emissions.

According to one aspect of the invention at least a part of said tail gas is recycled as process gas during the natural gas conversion step, for example during the reforming or partial oxidation step. An associated advantage is a further reduction in the CO2 emissions.

In some embodiments a part of the said CO2-depleted synthesis gas is treated in a nitrogen (N2) separation unit, preferably a membrane unit, obtaining a nitrogen-depleted synthesis gas and a nitrogen-rich flow; at least a part of the nitrogen-depleted synthesis gas (preferably all of it) is used as fuel; the remaining part is fed to the ammonia synthesis together with the nitrogen-rich flow.

This configuration is particularly advantageous if the O2-enriched air does not have a very high purity (for example less than 95% of O2) and/or if the natural gas contains nitrogen. Three benefits are obtained: an increase in the calorific power of the fuel gas, a reduction in the flow of combustion fumes (and the power of the respective ID fan) and conservation of the nitrogen which is a reagent for the ammonia. The membrane nitrogen separation unit is further preferred because said unit may operate using the pressure difference between the synthesis gas (produced at high pressure) and the combustion in the furnace (which occurs at atmospheric pressure). Moreover, the nitrogen-rich flow, which is used for synthesis, does not lose pressure.

The configuration described above, which envisages separation of the nitrogen from the synthesis gas, is applicable also in a conventional process, with primary steam reformer and secondary air-fired reformer, resulting in the advantage that it is not required to modify or enlarge the air compressor. However, with a secondary air-fired reformer and without modifying the compressor, and therefore without being able to increase the air flow, the additional fraction of synthesis gas (required as fuel) would have to be produced by increasing the capacity of the primary reformer and/or installing a gas-heated reformer (GHR), both solutions being very costly. For these reasons, the nitrogen separation described is particularly preferred in combination with the use of the enriched air during conversion of the natural gas into synthesis gas.

In some embodiments, it is envisaged expanding, with production of mechanical work, the CO2-depleted synthesis gas after optionally heating it.

Said gas is available at a pressure higher than the pressure required for combustion in a furnace and therefore it may be expanded in a suitable machine, such as an expander or a turbine, producing mechanical work. For example, said expansion may be from about 25 bar to about 3 bar. The gas has a high specific volume given that it comprises essentially H2 and for this reason its expansion may generate a considerable amount of power. The power obtained may cover partly the process requirements, making it more efficient.

In some embodiments the shift step comprises two steps at different temperatures, for example preferably one high-temperature shift (HTS), for example carried out using an iron-based catalyst, followed by a low-temperature shift (LTS) or medium-temperature shift (MTS), for example carried out using a copper-based catalyst. The associated advantage is that of obtaining the maximum conversion of the CO into CO2, which will then be separated during the decarbonation step, so as to obtain the minimum residual CO content in the synthesis gas used as fuel. Since the CO is a source of CO2, during combustion, the advantage of minimizing the CO2 flue emissions is obtained.

In some embodiments, in which a relatively low overall S/C ratio is used, for example <2.7, the shift preferably comprises two steps in series carried out over catalyst suitable to operate with a low steam content, for example a copper-based catalyst. In this configuration, the first step

consists of a medium temperature shift (MTS), which is preferably pseudo-isothermal and operates in the temperature range of 200-320° C., and the second step is a low temperature shift (LTS) operating in the temperature range 180-250° C.

The conversion of the natural gas into synthesis gas, for example by means of reforming, is preferably performed at a pressure lower than 50 bar, more preferably lower than 40 bar, and even more preferably lower than 30 bar.

Generally the prior art teaches the preference for high conversion pressures, in order to increase the capacity of the conversion section (front end) and reduce the consumption of synthesis gas compression. The present invention is instead preferably implemented with low conversion pressures in order to obtain the maximum conversion of the methane, since the steam reforming reaction is favoured at a lower pressure, so as to have the minimum residual methane content in the synthesis gas used as fuel. Since the methane is a source of CO2, during combustion, the advantage of minimizing the CO2 flue emissions is obtained.

In the case of ATR, a high methane conversion is also obtained by operating at a relatively high output temperature, >950° C., preferably >1000° C., even more preferably >1030° C.

In the case of POX, a high methane conversion is also obtained by operating at a relatively high output temperature, >1200° C., preferably >1300° C.

In some embodiments the overall steam/carbon (S/C) ratio during conversion is greater than 2.0, preferably greater than 2.2 and more preferably greater than 2.7. Generally the prior art teaches a preference for low S/C ratios in order to increase the capacity of the conversion section (front end). The invention instead envisages a relatively high S/C ratio in order to maximize the conversion of the methane and the CO during the shift step and reduce the concentration of CH4 and CO in the synthesis gas. Since the methane and CO are a source of CO2, during combustion, the advantage of minimizing the CO2 flue emissions is obtained.

In the case of pure ATR (optionally in combination with pre-reformer) or POX, the invention employs a S/C ratio not higher than 2 in the reforming section. Preferably further steam is added downstream of the reforming and upstream of the shift, until an overall S/C ratio greater than 2, and preferably greater than 2.4, is reached so as to promote the progression of the shift reaction and the associated conversion of the carbon monoxide.

The use of the trim fuel solves the problem of rapidly controlling the furnace, but at the cost of increasing the CO2 emissions into the atmosphere. For some configurations of the invention, for example those comprising a steam reformer, the trim fuel represents the greatest contribution to the CO2 emissions in the atmosphere. This will be illustrated in the examples.

In a preferred embodiment of the invention, the trim fuel is not used and the fuel of the furnace is only the synthesis gas. The fuel fraction is consequently greater than in the case where the trim fuel is used, because it is required to provide also the combustion heat of the trim fuel with the fuel fraction.

In a first embodiment, the fuel fraction has a combustion heat substantially corresponding to the heat required by the furnace. In order to rapidly control the furnace, for example in order to quickly raise or lower the load when needed, the flowrate of the fuel fraction is suitably raised or lowered. This control, however, has the undesirable effect of varying the flowrate of the make-up gas, and therefore the production. In order to re-establish the initial production, it is necessary to increase or reduce the total flowrate of natural gas fed to the reforming section, which in turn requires control of the furnace. It may be understood how this procedure is operationally undesirable.

According to one aspect of the invention: the fuel fraction is produced in an overabundant amount with respect to the requirement of said at least one furnace, i.e. a surplus of synthesis gas to be used as fuel is produced with respect to the corresponding quantity of heat required by the furnace, and the surplus of fuel synthesis gas is exported from the process, i.e. is not used either as fuel fraction or as process fraction. The availability of synthesis gas in excess (for use as fuel) allows to rapidly regulate said at least one furnace without using, or using to a lesser degree, the trim fuel, with a further advantage in terms of reduction of the CO2 emissions.

For example, the surplus may be:

exported as a further product (for example as hydrogen or as CO2-depleted fuel for consumption outside the ammonia plant) or

conveyed to a storage buffer, or

flared.

In order to rapidly control the furnace, for example in order to quickly raise or lower the load in the case of need, the flowrate of the synthesis gas surplus is suitably lowered or raised, without affecting either the fuel fraction or the process fraction.

The surplus of fuel synthesis gas may be taken from the fuel fraction, and therefore have the same composition and pressure as the fuel synthesis gas.

Alternatively, if a purification unit (for example a PSA unit) or a methanation unit is present, the surplus of fuel synthesis gas may be collected downstream of purification or methanation, so as to obtain greater purity of the surplus exported.

The surplus fuel may be separated from the tail gas of purification (PSA, or dryer+LNW), even though said solution is less preferred for two reasons:

the tail gas has a low pressure, therefore a compression is required to export said tail gas (with considerable energy expenditure and plant cost);

the tail gas contains CO, CO2 and CH4 in a concentration much greater than both the fuel synthesis gas and the purification product, therefore it has a less desirable composition.

The quantity of the surplus fuel synthesis gas is preferably >2%, more preferably >4%, and even more preferably >6% of the fuel fraction. If the surplus of the fuel synthesis gas is not exported, its quantity is preferably not greater than 15% of the fuel fraction, and even more preferably not greater than 10% of the fuel fraction, in order to prevent an excessive consumption thereof.

The invention obtains CO2 emissions which are less than 0.5 t/t (tonnes of CO2 emitted per tonne of ammonia produced); in preferred embodiments of the invention the emissions are less than 0.3 t/t or less than 0.2 t/t.

As will be illustrated in the examples, in some preferred embodiments the CO2 emissions may reach values less than 0.1 t/t or even 0.05 t/t, corresponding to a CO2 capture value close to 99%.

As regards the plant, the furnaces are advantageously equipped with dual-fuel burners able to burn both natural gas and synthesis gas. The invention may require the installation of an air separation unit (ASU) for the production of the enriched air and optionally nitrogen.

The invention may also be applied to ammonia/urea processes and plants. An ammonia/urea plant is a plant

comprising a first ammonia synthesis section and a second section for synthesis of urea from ammonia and CO2, wherein at least a part of the ammonia produced in the first section feeds the second section. In this case also the CO2 separated during the decarbonation step feeds advantageously said second urea synthesis section.

The main advantages of the invention are listed below.

The separation of the CO2 is performed from a synthesis gas which has a high concentration of CO2 (15-25% mol) and is at a relatively high pressure, and therefore the separation of CO2 from this flow is much easier and requires a lower energy consumption than CO2 separated from combustion fumes.

The system according to the invention does not require solvent in order to capture CO2 from fumes.

The use of oxygen-enriched air gives rise to various advantages:

- it increases the heat value of the synthesis gas;
- combustion of the synthesis gas generates less fumes than the combustion of natural gas, for the same amount of heat released, because the combustion of hydrogen (contained in the synthesis gas) occurs with a reduction of the number of mols, unlike the combustion of methane, so that the convective current of the reformer is smaller and requires an induced draft (ID) fan which is less powerful;
- it limits the flue loss of nitrogen (which is a reagent), avoiding wastage of energy for N2 separation and compression; the generation of nitrogen for synthesis must not be increased;
- it allows a high temperature for conversion of the natural gas to be maintained, free from the constraint of avoiding the introduction of excessive nitrogen in relation to the stoichiometry of the NH3 synthesis (typical of conventional air-fired processes) with a high conversion of the methane resulting in minimal CO2 emissions.

In conventional plants with a secondary air-fed reformer, the process air is fed to said secondary reformer in stoichiometric quantities, i.e. in the quantity required to reach a H/N ratio of about 3 in the make-up gas. This means that the air flowrate (in particular the quantity of oxygen introduced into the reformer) cannot be freely chosen, for example in order to achieve full conversion of the NG.

Instead, if the oxidant and the nitrogen are separately fed to the process, it is possible to choose the flowrate of oxidant so as to obtain complete conversion of the natural gas and optionally add, downstream, the nitrogen which is needed for the desired make-up gas composition. The advantage of full conversion is to produce a synthesis gas with a smaller methane content and therefore lower CO2 emissions.

Another advantage of the invention is that the greater flowrate of gas in the front end allows more heat to be recovered and more steam to be generated. The greater quantity of steam produced in the front end limits the duty of the respective auxiliary steam-generating apparatus; an advantage is that the fuel consumption (and potential source of CO2 emissions) is represented only by the primary reformer or fired heater. If the fuel of the reformer is replaced with synthesis gas (and if necessary the associated burners replaced) a substantial elimination or zeroing of the CO2 emissions is obtained.

Another advantage is that the invention does not require necessarily separation of hydrogen from the CO2-depleted syngas, i.e. purification of the CO2-depleted syngas into a gas which is rich in H2 and a waste gas, in order to obtain low CO2 emissions into the atmosphere. The CO2-depleted syngas may be used directly for ammonia synthesis after possible methanation.

In some embodiments it may be advantageous to perform a syngas gas purification in order to reduce the overall energy consumption of the process.

When applied to revamping of plants, the invention achieves significant synergies which allows the CO2 emissions to be reduced without production losses, limiting modifications and costs. This is because the invention:

- reduces greatly the gas flowrate in the front end, and therefore the associated apparatus and (secondary, shift reaction, decarbonation or methanation) piping are suitable for a greater capacity;
- said greater capacity corresponds to the synthesis gas to be used as fuel;
- a high output temperature from the secondary reformer may be used (obtaining complete conversion of the methane), because the nitrogen is added separately from the oxygen; therefore the method according to the invention produces extra gas to be used as fuel without requiring costly modifications of the primary reformer, even when said reformer is substantially at the limit of its capacity;
- the CO2 removal section is de-bottlenecked because the invention increases the partial CO2 pressure and reduces the gas flowrate in the absorber;
- the combustion of the CO2-depleted syngas generates fewer fumes than the NG so that the convective current of the reformer and ID fan are less charged;
- it is necessary to modify only the front end, while the backend (synthesis gas compressor, ammonia synthesis, refrigerating section) is substantially unchanged.
- the process does not require intense purification of the synthesis gas in order to remove the inert components, it being sufficient to use the methanator (often the existing one); in particular, it is not necessary to perform any separation of the synthesis gas into an H2 and waste gas flow.

DESCRIPTION OF THE FIGURES

FIG. **1** shows a first embodiment of the invention.

FIG. **2** shows a second embodiment.

FIG. **3** shows a third embodiment.

FIG. **4** shows a fourth embodiment.

DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

FIG. **1** shows a process according to a mode of implementing the invention based on an oxygen autothermal reformer ATR and pre-reformer.

The blocks in FIG. **1** denote the following systems or apparatus:

AUX charge pre-heater furnace and auxiliary boiler
PRE pre-reformer
ATR autothermal reformer
POX partial oxidation reactor
SHF shift section
CDR CO2 removal section (decarbonation)
MET methanator
SYN synthesis section
HRU hydrogen recovery section
ASU air separation (fractioning) section

A charge **10** comprising natural gas and steam is preheated in AUX and converted into a synthesis gas **11** via the

reformers PRE and ATR. The autothermal reformer ATR operates with a flow **22** of enriched air or oxygen.

The synthesis gas, which contains H2, CO and CO2, undergoes a shift reaction in SHF and then removal of CO2 in CDR. The section SHF may comprise shift treatments at different temperatures. The section CDR operates for example with chemical/physical washing of the gas using an aqueous amine solution.

The section CDR produces a CO2-depleted syngas **12** and a flow **13** of CO2 which may be sequestered or used for other process purposes, for example in order to produce urea.

Preferably the synthesis gas **12** has the following composition: 98% H2, 1% CO+CH4, 0.1% CO2, Ar+N2 0.9%.

A part **14** of said CO2-depleted syngas **12** is used as fuel in a furnace in the front end, for example in a charge heater (AUX block). The remaining part **18** of synthesis gas is further treated in the methanator MET.

In the example, the fuel fraction **14** of synthesis gas, together with a tail gas **15** of the HRU section, feeds one or more users of the block AUX via the fuel line **16**. Optionally a suitable quantity of natural gas **17** (trim gas) is added to the gas **16**.

Nitrogen **18** from the air separation section ASU is added to the process fraction **18** of the synthesis gas, after it has passed inside the methanator (optional).

The gas thus obtained, together with a flow of hydrogen **20** recovered from the HRU section, feeds the synthesis section SYN. Said synthesis section produces ammonia **23** and a flow **21** of purging gas treated in the section HRU for recovery of the hydrogen contained inside it.

The separation section ASU produces, in addition to the nitrogen **19**, also the flow **22** of enriched air or oxygen for the autothermal reformer ATR.

FIG. **2** shows a process according to a preferred mode of implementing the invention based on primary reforming and ATR.

The block SMR in FIG. **1** denotes the primary reformer (or steam reformer) plus auxiliary apparatus, for example steam generators. The remaining symbols in FIG. **2** correspond to the symbols in FIG. **1** and therefore the description is not repeated.

FIG. **2** also shows an optional line **15***a* for recycling part of the tail gas **15** from the unit HRU for feeding the primary reformer SMR.

FIG. **3** shows an ATR-based process, similar to FIG. **1**, but comprising a purification of the process fraction of the synthesis gas in a section PUR, which in this example comprises a PSA unit.

The fuel fraction **14** separated from the CO2-depleted synthesis gas **12** is divided into a first portion **14***a* used as fuel in a furnace in the front end, for example in the block AUX, and a second portion **14***b* exported as excess fuel. The remaining part **18** of synthesis gas is further treated in the PSA unit.

A portion **23** of the effluent of the PSA unit is (optionally) exported as excess fuel. Said portion **23** has a greater hydrogen purity than the gas portion **14***b*.

In the example shown in FIG. **3**, the portion **14***a* of synthesis gas separated as fuel fraction, together with a tail gas **25** of the PSA unit, feeds one or more users of the block AUX via the fuel line **26**.

FIG. **4** shows a process based on POX, comprising purification of the process fraction of the synthesis gas in a section PUR comprising dryer and LNW (liquid nitrogen wash).

In a similar manner to the embodiment shown in FIG. **3**, also in this case the fuel fraction **14** separated from the CO2-depleted synthesis gas **12** is split into a first portion **14***a* used as fuel for example in the block AUX, and a second portion **14***b* exported as excess fuel. Said portion **14***a*, together with a tail gas **35** of the section PUR, feeds one or more users of the block AUX via the fuel line **36**. Said tail gas **35** results from the combination of the tail gas of the LNW and of the dryer.

The process according to the invention allows to produce ammonia with emissions of CO2 of about 0.1 t/t compared to about 0.7 t/t in the prior art.

All the configurations illustrated may be the result of revamping of an ammonia plant with air-fed secondary reformer.

In one embodiment, the revamping procedure comprises essentially the following steps:

installing the ASU unit in order to generate the flow **22** of oxygen or enriched air;

modifying the secondary reformer in order to accept said flow **22** instead of air;

increasing the fraction of natural gas intended for the process and reducing the fraction of natural gas intended for fuel;

revamping the existing section for desulphurization of the natural gas so as to increase the capacity thereof owing to the greater process gas flowrate;

revamping the existing section CDR so as to increase the capacity thereof owing to the greater quantity of CO2 to be separated.

It can be understood that the revamping does not require costly modifications to the reformer, the exchangers and piping of the front end and the shift section. This is due to the fact that the volumetric flowrate of the gas through the front end does not increase, despite the generation of the additional gas fraction (fuel fraction).

EXAMPLE

The following Table 1 refers to a plant with a capacity of 3000 metric tonnes per day (MTD) of ammonia produced.

Table 1 compares the following options:

(1) Plant of the prior art with primary reformer and air-fed secondary reformer.

(2) Plant of the prior art, as per option (1), with capturing of the CO2 from the fumes of the primary reformer.

(3) Plant according to the invention, as per FIG. **1**.

(4) Plant according to the invention, as per FIG. **2**.

TABLE 1

		Option			
		(1) Prior art	(2) Prior art	(3) Inv.	(4) Inv.
NH3 production	MTD	3000	3000	3000	3000
Net Natural Gas consumption based on gas LHV (FEED + FUEL-Steam exported e.g. to urea)	Gcal/t NH3	6.7	7.4	7.0	6.9
	Gcal/t NH3		+0.7	+0.3	+0.2

TABLE 1-continued

		Option			
		(1) Prior art	(2) Prior art	(3) Inv.	(4) Inv.
CO2 captured in process	MTD	3600	3600	5200	5100
CO2 to atmosphere (contained in flue gas)	MTD	2100	200	200	200
CO2 to atmosphere (contained in flue gas)	t/t NH3	0.7	0.1	0.1	0.1
Main Equipment size					
Total fired heater duty (reformer/fired heater + auxiliary boiler)	%	100	120	75	105
Process CO2 removal capacity	%	100	100	145	140
ASU O2 capacity	%	n/a	n/a	100	60
Flowrate of front end (secondary output/ATR)	%	100	100	120	97

The table shows that the process according to the invention (option 3) requires a front end suitable for producing also the gas fraction to be used as fuel in the furnaces; in fact the quantity of CO2 captured in the process amounts to 5200 MTD compared to 3600 for options (1) and (2), and the synthesis gas flowrate in the front end is about 20% more than FIGS. **1** and **2**. Despite this, the consumption of the plant is much less than that of option (2) (7.0 instead of 7.4 Gcal/MT) and is competitive with the plant without capturing according to option (1). The total duty of the furnaces is only 75% of option (1).

In option (4) the energy consumption obtained is less than in option (3), i.e. equal to 6.9 Gcal/MT, and also the cost of the plant is less. This because, in option (4), the quantity of CO2 separated in the process is less than in option (3); the duty of the furnaces is greater than in (3), but is comparable with that of options (1) and (2); the oxygen consumption is markedly less than (3); the flowrate in the front end is markedly less than (3) and comparable with (1) and (2).

The examples show how the novel process is more efficient and competitive than the prior art.

The example also shows the advantage of modifying a plant operating as per option (1), preferably implementing option (4). In fact, in this case the duty of the furnaces and the flowrate of the gases remain substantially unvaried, while the CO2 emissions are reduced. The invention thus achieves the object of minimizing the CO2 emissions of a conventional plant without losing ammonia production.

The following Table 2 refers to a plant with a capacity of 3000 metric tonnes per day (MTD) of ammonia produced, which is self-sufficient from the point of view of the steam and electric power. The process comprises the consumption relating to the compression of the CO2 sequestered up to the pressure of 100 bar. For each process, the natural gas consumption and the CO2 emissions indicated also consider the superheated steam production in AUX for driving all the turbines, and the production of the electric power necessary for the process.

Table 2 compares the following options:

(1) Plant according to the invention, with SMR+ATR as per FIG. **2**, in the following variants:

a. with the overall S/C ratio=2.7, shift composed of HTS and LTS, methanator, trim fuel with flowrate corresponding to 10% of the duty required by the furnace;

b. as for 1 a, but without trim fuel.

(2) Plant according to the invention, with pre-reformer+ATR as per FIG. **3**, in the following variants:

a. with the overall S/C ratio=2, shift composed of MTS and LTS, PSA, trim fuel with flowrate corresponding to 10% of the duty required by the furnace;

b. as for 2a, without trim fuel, with the Selectoxo™ process downstream of SHF and upstream of CDR for converting the residual CO.

(3) Plant according to the invention, with POX, as per FIG. **4**, in the variants:

a. with the overall S/C ratio=2, shift composed of MTS and LTS, LNW dryer, trim fuel with flowrate corresponding to 10% of required duty of the furnace;

b. as for 2a, without trim fuel, with selective catalytic oxidation of CO (Selectoxo™ process) downstream of the shift reaction and upstream of the CO2 removal.

TABLE 2

	1a: SMR + ATR	1b SMR + ATR	2a ATR	2b ATR	3a POX	3b POX
Daily production of NH3, MTD	3000	3000	3000	3000	3000	3000
Daily throughput of sequestered CO2, MTD	5600	5800	5100	5300	5350	5600
Net consumption of natural gas (for Example 1a), dimensionless	100%	100%	93%	93%	95%	95%

TABLE 2-continued

	1a: SMR + ATR	1b SMR + ATR	2a ATR	2b ATR	3a POX	3b POX
CO2 emissions into atmosphere per unit of ammonia produced, t CO2/t NH3	0.15	0.075	0.17	0.10	0.15	0.05
Distribution of the CO2 emissions						
trim fuel	50%	zero	20%	zero	20%	zero
CH4 slip in the process gas	15%	29%	40%	79%	30%	63%
CO slip in the process gas	34%	69%	39%	19%	49%	34%
CO2 slip in the process gas	1%	2%	1%	2%	1%	3%

In Table 2:

"Trim fuel" as defined in the patent;

"CH4 slip in the process gas" is the residual methane content of the synthesis gas produced in the front end (i.e. in SMR+ATR in option 1, in the pre-reformer+ATR in option 2, POX in option 3), quantified upstream of optional methanation.

"CO slip in the process gas" is the residual carbon monoxide content of the synthesis gas downstream of the shift section;

"CO2 slip in the process gas" is the residual carbon dioxide content of the synthesis gas downstream of the CO2 removal section;

Several comments may be made in view of Table 2:

- In the case of SMR+ATR in option 1a, the trim fuel provides the greatest percentage of the CO2 emissions; avoiding the trim fuel by exporting surplus fuel enables the emissions to be significantly reduced to less than 0.1 t/t, as shown in the Table for option 1b; at the same time, the quantity of sequestered CO2 increases from 5600 to 5800 MTD.
- In the case of SMR+ATR, the CO slip in the process gas provides the second greatest percentage of the CO2 emissions in option 1a, and provides the greatest percentage in option 1b; application of the Selectoxo process to option 1a or 1b would significantly reduce the CO2 emissions; the CH4 slip in the process gas and the CO2 slip in the process gas provides a smaller percentage of the CO2 emissions.
- The overall energy consumption of the options based on ATR and POX+purification (2 and 3) is decidedly lower than that of the options based on SMR+ATR (1a and 1b); this is mainly due to the synthesis gas purification (which improves the efficiency of the synthesis section and avoids the purge); the quantity of CO2 sequestered in these options (2a, 3a; or 2b, 3b) is consequently less than in options 1a or 1b.
- The emissions due to the use of the trim fuel in options 2a (ATR) and 3a are of about 20% of the total emissions, much less than in option 1a, by way of confirmation of the fact that the heat required by the furnace in these two options is much less than in option 1a.
- In the embodiments with ATR or POX, the residual CO and CH4 are of higher relevance owing to the lower S/C ratio at which ATR and POX operate compared to SMR+ATR; POX operates at a higher temperature than ATR, which results in a smaller residual amount of CH4, but in a greater residual amount of CO.
- In both the options 2b and 3b, the improvement achieved by selective oxidation of CO, in order to reduce the CO slip, and by avoiding trim fuel, is evident.
- It should be noted that both POX and ATR achieve very low emissions—as low as 0.05 for POX and 0.1 for ATR—comparable with those achieved by SMR+ATR, but with lower energy consumption, and therefore preferable.

The above example shows how the invention is able to achieve extremely low CO2 emission levels, corresponding to almost total capture (>98%), while maintaining competitive energy consumption levels.

The invention claimed is:

1. A process for synthesis of ammonia from natural gas, the process comprising:

conversion of a charge of desulphurized natural gas and steam, with oxygen-enriched air or with oxygen, into a synthesis gas containing hydrogen, CO and CO2, in a conversion section;

treatment of said synthesis gas including at least a shift reaction of the carbon monoxide into CO2, and subsequent separation of CO2 from the gas, thus obtaining a CO2-depleted synthesis gas and a CO2-rich gaseous flow containing the CO2 separated from the gas;

separation of a part of said CO2-depleted synthesis gas as fuel fraction, wherein said fuel fraction is fed as fuel to at least one furnace and wherein said separation of the fuel fraction includes the split of said CO2-depleted synthesis gas into at least a first stream and a second stream, said first and second streams having the same composition, wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia.

2. The process of claim **1**, wherein the first stream forms the fuel fraction and the second stream is the process gas intended for the synthesis of ammonia after further purification.

3. The process of claim **1**, wherein said fuel fraction is between 1% and 40% of the total amount of said CO2-depleted syngas.

4. The process of claim **1**, wherein said fuel fraction is between 10% and 30% of the total amount of said CO2-depleted syngas.

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5. The process of claim 1, further comprising a step for methanation of the synthesis gas and/or addition of nitrogen to the synthesis gas.

6. The process of claim 5, wherein said fuel fraction is separated upstream of the methanation step or upstream of the nitrogen addition step.

7. The process of claim 1, wherein said CO2-depleted syngas contains no more than 1000 ppm by volume of CO2.

8. The process of claim 1, wherein said enriched air contains at least 50% oxygen.

9. The process of claim 1, wherein said enriched air contains at least 90% oxygen.

10. The process of claim 1, wherein said fuel fraction of the synthesis gas feeds one or more of the following apparatuses: a steam production and/or superheating furnace; one or more burners of a primary steam reformer; or one or more furnaces for pre-heating the charge of an autothermal reformer or partial oxidation reactor or natural-gas desulphurization section.

11. The process of claim 1, wherein: a purge gas of the ammonia synthesis process, containing hydrogen and methane, is treated so as to recover the hydrogen contained in the purge gas, obtaining a hydrogen-rich gas and a tail gas containing methane; at least part of said tail gas is recycled as process gas and subjected to said step of conversion of the natural gas into synthesis gas.

12. The process of claim 1, wherein: a part of said CO2-depleted syngas is treated in a unit for separation of nitrogen, obtaining a first stream of nitrogen-depleted syngas and a second nitrogen-enriched stream; at least one part of said first stream, is used as fuel; any remaining part of said first stream is fed to the synthesis of ammonia together with the second stream.

13. The process of claim 1, further comprising a step of expansion, with production of mechanical work, of the CO2-depleted syngas, after heating the CO2-depleted syngas.

14. The process of claim 1, wherein the overall steam/carbon ratio in the conversion step is greater than 2.0.

15. The process of claim 1, wherein the overall steam/carbon ratio in the conversion step is greater than 2.4.

16. The process of claim 1, wherein the overall steam/carbon ratio in the conversion step is greater than 2.7.

17. The process of claim 1, wherein

said synthesis gas fuel fraction forms all of the fuel of the furnaces used in the conversion section, or

an amount of natural gas is provided as trim fuel, said trim fuel accounting for not more than 15% of the total combustion heat.

18. The process of claim 1, wherein:

the fuel fraction is produced in excess with respect to the fuel necessary for the conversion section, the quantity of said fuel fraction exceeding that required being exported from the process; and

regulation of the conversion section is performed by modulating the quantity of said fuel fraction directed towards the conversion section and the quantity exported from the process.

19. The process of claim 1, wherein:

the conversion of the natural gas charge into synthesis gas includes a step of autothermal reforming, or a step of partial oxidation;

said step of autothermal reforming or partial oxidation is performed with a steam/carbon ratio not greater than 2.

20. The process of claim 1, wherein the conversion of the natural gas into synthesis gas includes primary reforming of the natural gas in the presence of steam and secondary reforming performed with said oxygen flow or enriched air.

21. A method for revamping a plant for synthesis of ammonia from natural gas or ammonia/urea plant, wherein the plant includes a reforming section that includes a primary steam reformer and an air-fired secondary reformer, and a section for treatment of the synthesis gas by a shift reaction of carbon monoxide into carbon dioxide, and decarbonation; the method comprising:

providing a flow of enriched air or oxygen and using said flow as oxidant, instead of air, for the secondary reformer;

separating a part of the synthesis gas, downstream of decarbonation, for use as fuel fraction, and allocating a remaining process fraction of the synthesis gas for ammonia conversion;

feeding said fuel fraction of the gas, which has a reduced CO2 content, as fuel for at least one furnace of the plant.

22. The method of claim 21, further comprising installing an air separation unit so as to provide said oxygen or enriched air flow, wherein said separation unit also provides a nitrogen flow which is added to the process fraction of the synthesis gas in order to obtain the desired H2/N2 ratio.

23. The method of claim 21, wherein the section for treatment of the synthesis gas by the shift reaction of carbon monoxide includes methanation.

* * * * *

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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
96/000,424		1128618	283386WOUS01_495230-44	9950

116407 7590 04/12/2023
Dorsey & Whitney / UT GENERAL
111 South Main Street
21st Floor
Salt Lake City, UT 84111-2176

EXAMINER	
ART UNIT	PAPER NUMBER
3991	
MAIL DATE	DELIVERY MODE
04/12/2023	PAPER

Please find below and/or attached an Office communication concerning this application or proceeding.

The time period for reply, if any, is set in the attached communication.

ATTACHMENT TO THE
NOTICE OF NONCOMPLIANT SUPPLEMENTAL EXAMINATION REQUEST

I. Specifically, the original request is not compliant with:

Box 8. (from page 1 of this Notice):

The detailed explanation of the relevance of the Items of Information is not compliant with 37 C.F.R. § 1.610(b)(5).

1. The Original Request does not adequately set forth the relevance and manner of applying the Items of Information to the dependent claims 6, 13, 18 and 22-23.

In the detailed explanation of the relevance of the Items of Information Patent Owner only references independent claims 1 and 21 and dependent claims 2-5, 7-12, 14-17 and 19-21 and does not mention dependent claims 6, 13, 18 and 22-23. Therefore, it is unclear how any of the items of information is applied to claims 6, 13, 18 and 22-23.

MPEP § 2811.01 I. expressly states that "[a] separate, detailed explanation is also required for each dependent claim for which supplemental examination is requested." Additionally, the same paragraph provides exemplary wording that a patent owner may use if the patent owner desires to rely on the required explanation under 37 C.F.R. § 1.610(b)(5) of the parental claim. In particular, patent owner does not clearly describe that the subject dependent claim(s) include all of the limitations of the subject independent claim(s).

One way to correct this defect would be to specifically apply at least one Item of Information to each of claims 6, 13, 18 and 22-23.

2. Furthermore, a request for supplemental examination must stand on its own. A request for supplemental examination cannot be made, and the requirements for a detailed explanation pursuant to 37 CFR 1.610(b)(5) cannot be satisfied, by incorporating by reference a paper from another proceeding. The detailed explanation must reflect the opinion of the patent owner, and not that of a third party (including a patent examiner). 35 U.S.C. 257(a) specifies that a patent owner may request supplemental examination. For this reason, the detailed explanation required under 37 CFR 1.610(b)(5) must be drafted by the patent owner, and must reflect the opinion of the patent owner, i.e., what the patent owner believes is the relevance of each item of information, and what the patent owner believes is the manner of applying each item of information to each claim of the patent for which supplemental examination is requested. [Emphasis added.] MPEP § 2811.01(II). Therefore, Patent owner is reminded that the discussion of the items of information, required by 37 CFR 1.610(b)(5) must reflect *the opinion of the patent owner*, and cannot not solely rely upon the analysis in Office actions or responses filed in patent applications.

To correct these informalities, it is recommended that Patent Owner apply the references cited in the European Office Communication to the claims in the 37 CFR 1.610(b)(5) detailed explanation. Further, if the Patent Owner discusses the references cited in the office actions, then Patent Owner should consider whether or not the office actions need be included as items of information since the combination of references applied in said office actions are now discussed in the 37 CFR 1.610(b)(5) detailed explanation.

3. Patent Owner has not applied all of the items of information to the claims. 37 CFR 1.610(b)(5) requires that the detailed explanation must include for each item of information and explanation of how the item of information may be applied to each claim. As discussed in MPEP 2811.01(I) "A general statement of relevance that is not tied to any particular claim limitation is not sufficient to meet the requirement." Specifically, item D4 (Urea Product Expansion by Newly Developed CO2 Recovery Process from Primary Reformer Flue Gas) is discussed on page 20 of the request as "may be relevant to independent claim 1" but is not applied to the limitations of the claims.

II. Patent Owner's Recourse

The patent owner is given **ONE (1) opportunity** to file a corrected request, should the patent owner so desire. See MPEP § 2812.03.

In order to obtain a filing date for the request papers, the patent owner must, within 15 days of the mailing date of this notice, file a corrected request which properly addresses all of the defects set forth in this notice and which satisfies all of the requirements of 37 C.F.R. §§ 1.605, 1.610, and 1.615. For further guidance on filing a corrected request, see MPEP § 2812.03.

A complete, corrected request that will replace the originally-filed request must be submitted. In other words, the patent owner must not submit a "supplemental" or corrected portion of the request and must include all of the components that the patent owner intends to include as part of the request, such as, for example, the request itself, copies of each of the items of information, a copy of the patent for which supplemental examination is requested, any transmittal sheet, a submission in compliance with 37 CFR 3.73(c), etc.. See MPEP § 2812.03. However, if all applicable fees have already been paid, these fees do not have to be resubmitted with the corrected request.

If the corrected request properly addresses all of the defects set forth in this notice and satisfies all of the requirements of 37 CFR 1.605, 1.610, and 1.615, *the date of the receipt of the corrected request* will be the filing date of the supplemental examination proceeding.

If the corrected request filed in response to this notice *fails* to cure the defects identified in this notice, or introduces a new defect, the request will not be granted a filing date, and the processing of the request will be terminated. See MPEP § 2812.04.

The complete, corrected request submission must be filed as follow-on paper(s) in proceeding control number 96/000,424. Any follow-on papers that do not contain this particular control number may be

treated as a separate request for supplemental examination and may have new fees charged accordingly.

General inquiries related to this notice should be directed to the Central Reexamination Unit at (571) 272-7705. Specific inquiries relating to the policies and procedures reflected in this notice should be directed to Eileen Lillis, Supervisory Patent Reexamination Specialist, at (571) 272-6928.

/EILEEN D LILLIS/
SPRS, Art Unit 3993

Notice of Noncompliant Supplemental Examination Request (37 CFR 1.610(d))	Application No. 96/000,424	Patent Under Reexamination 11286168	
	Examiner Eileen D Lillis	Central Reexamination Unit 3993	AIA Status Yes

The Central Reexamination Unit (CRU) in the United States Patent and Trademark Office (USPTO) has received a request for supplemental examination on 16 February 2023. The request cannot be processed, because the below-identified requirements for a supplemental examination request have not been satisfied. If a fully compliant request is not received within 15 days of the mailing date of this notice, then 1) the processing of the request will be terminated, and 2) the request will not be considered, will not be made part of the official record, and will remain closed from public view. **A filing date will NOT be assigned** to the request until the deficiencies noted below are corrected (37 CFR 1.610(d)), and the filing date of the request will be the receipt date of the corrected request that meets all applicable requirements:

The following items required by 37 CFR 1.610(a) and (b) are missing:

☐ 1. The fee for filing the request, as set forth in 37 CFR 1.20(k)(1).

☐ 2. The fee for reexamination ordered as a result of a supplemental examination proceeding, as set forth in 37 CFR 1.20(k)(2).

☐ 3. The applicable document size fees for non-patent documents as set forth in 37 CFR 1.20(k)(3). Specifically:

- ☐ (i). The fee set forth in 37 CFR 1.20(k)(3)(i) for each non-patent document between 21 - 50 pages in length.
- ☐ (ii). The fee set forth in 37 CFR 1.20(k)(3)(ii) for each additional 50 pages of the non-patent document, or a fraction thereof. This fee is charged in addition to the fee under 37 CFR 1.20(k)(3)(i).

☐ 4. An identification of the number of the patent for which supplemental examination is requested.

☐ 5. A list of the items of information that are requested to be considered, reconsidered or corrected. Where appropriate, the list must meet the requirements of § 1.98(b).

☐ 6. A list identifying any other prior or concurrent post-patent Office proceedings involving the patent for which supplemental examination is being requested.

☐ 7. An identification of each claim of the patent for which supplemental examination is being requested.

☑ 8. A separate, detailed explanation of the relevance and manner of applying each item of information to each claim of the patent for which supplemental examination is being requested.

☐ 9. A legible copy of the patent for which supplemental examination is requested and a legible copy of any disclaimer or certificate issued for the patent.

☐ 10. A legible copy of each item of information submitted as part of the request (other than U.S. patents or U.S. patent application publications, or items of information that form part of the discussion within the body of the request pursuant to 37 CFR 1.605(b)), accompanied by an English language translation of all the necessary and pertinent parts of any non-English language item of information.

☐ 11. A summary of the relevant portions of any submitted document, other than the request, that is over 50 pages in length. The summary must include citations to the particular pages containing the relevant portions.

☐ 12. An identification of the owner(s) of the entire right, title, and interest in the patent requested to be examined.

☐ 13. A submission by the patent owner in compliance with 37 CFR 3.73(c) establishing the entirety of the ownership in the patent requested to be examined.

☐ 14. Other: _____

☑ 15. Explanation of above item(s) and/or identification and explanation of other additional defects: See attached.

For inquiries regarding this supplemental examination, contact the Central Reexamination Unit at (571) 272-7705.

/MICHAEL FUELLING/ Supervisory Patent Examiner, Art Unit 3992	/EILEEN D LILLIS/ SPRS, Art Unit 3993

US011286168B2

(12) **United States Patent**
Baratto et al.

(10) **Patent No.: US 11,286,168 B2**
(45) **Date of Patent: Mar. 29, 2022**

(54) **PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE**

(71) Applicant: **CASALE SA**, Lugano (CH)

(72) Inventors: **Francesco Baratto**, Como (IT); **Raffaele Ostuni**, Lugano (CH)

(73) Assignee: **Casale SA**, Lugano (CH)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 66 days.

(21) Appl. No.: **16/485,695**

(22) PCT Filed: **Jan. 31, 2018**

(86) PCT No.: **PCT/EP2018/052358**
§ 371 (c)(1),
(2) Date: **Aug. 13, 2019**

(87) PCT Pub. No.: **WO2018/149641**
PCT Pub. Date: **Aug. 23, 2018**

(65) **Prior Publication Data**

US 2020/0055738 A1 Feb. 20, 2020

(30) **Foreign Application Priority Data**

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Oct. 6, 2017 (EP) 17195305

(51) **Int. Cl.**
C01C 1/04 (2006.01)
C01B 3/02 (2006.01)
C01B 3/48 (2006.01)

(52) **U.S. Cl.**
CPC ***C01C 1/04*** (2013.01); ***C01B 3/025*** (2013.01); ***C01B 3/48*** (2013.01);
(Continued)

(58) **Field of Classification Search**
CPC .. C01C 1/04; C01B 3/025; C01B 3/48; C01B 2203/0244; C01B 2203/0283;
(Continued)

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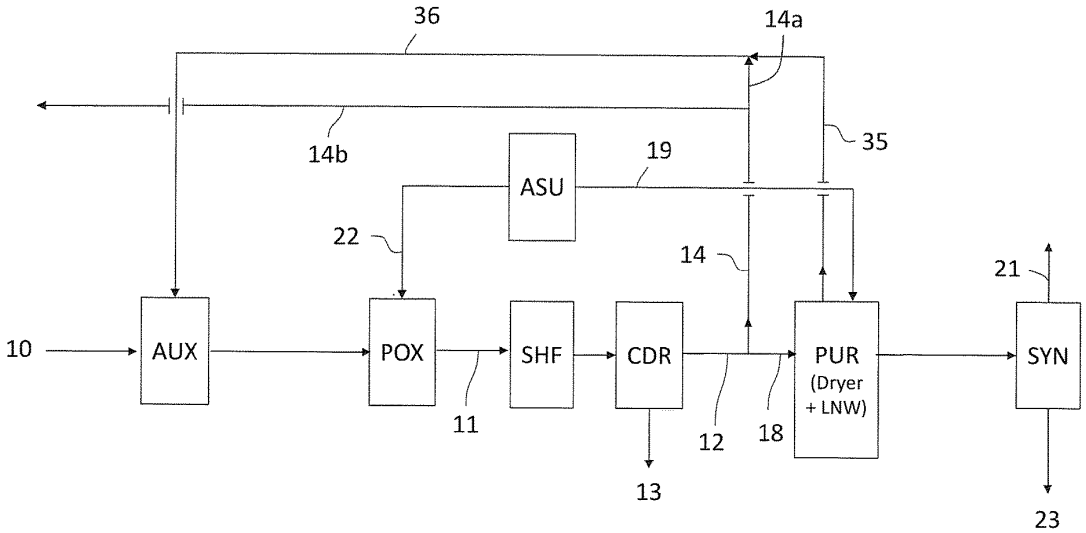
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(Continued)

Primary Examiner — Jafar F Parsa
(74) *Attorney, Agent, or Firm* — Dorsey & Whitney LLP

(57) **ABSTRACT**

Process for the synthesis of ammonia from natural gas comprising conversion of a charge of desulphurized natural gas and steam, with oxygen-enriched air or oxygen, into a synthesis gas, and treatment of the synthesis gas with shift reaction and decarbonation, wherein a part of the CO2-depleted synthesis gas, obtained after decarbonation, is separated and used as fuel fraction for one or more furnaces of the conversion section, and the remaining part of the gas is used to produce ammonia.

23 Claims, 4 Drawing Sheets



(52) **U.S. Cl.**
CPC *C01B 2203/0244* (2013.01); *C01B 2203/0283* (2013.01); *C01B 2203/042* (2013.01); *C01B 2203/0445* (2013.01); *C01B 2203/0475* (2013.01); *C01B 2203/068* (2013.01); *C01B 2203/1241* (2013.01)

(58) **Field of Classification Search**
CPC C01B 2203/042; C01B 2203/0445; C01B 2203/068; C01B 2203/0827; C01B 2203/86
See application file for complete search history.

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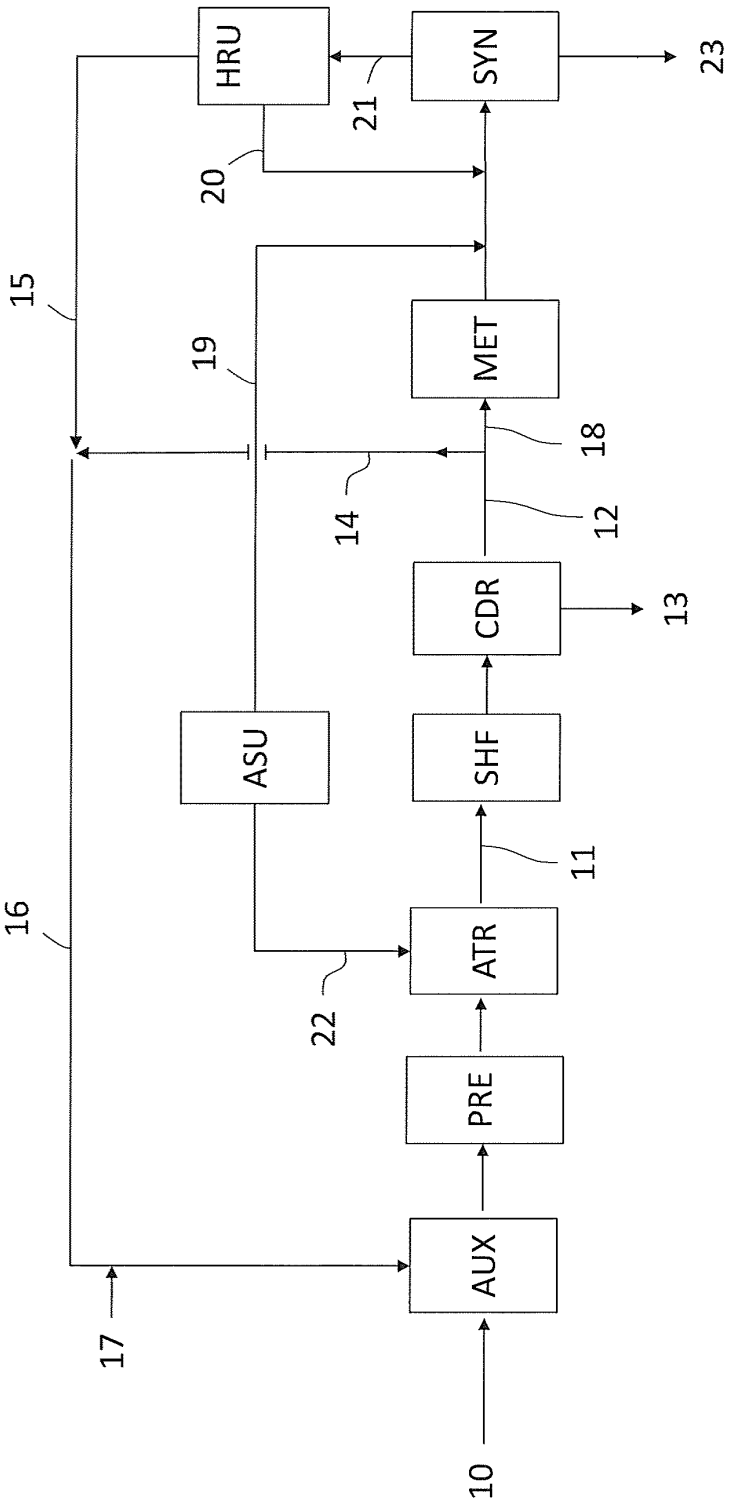

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FIG. 1

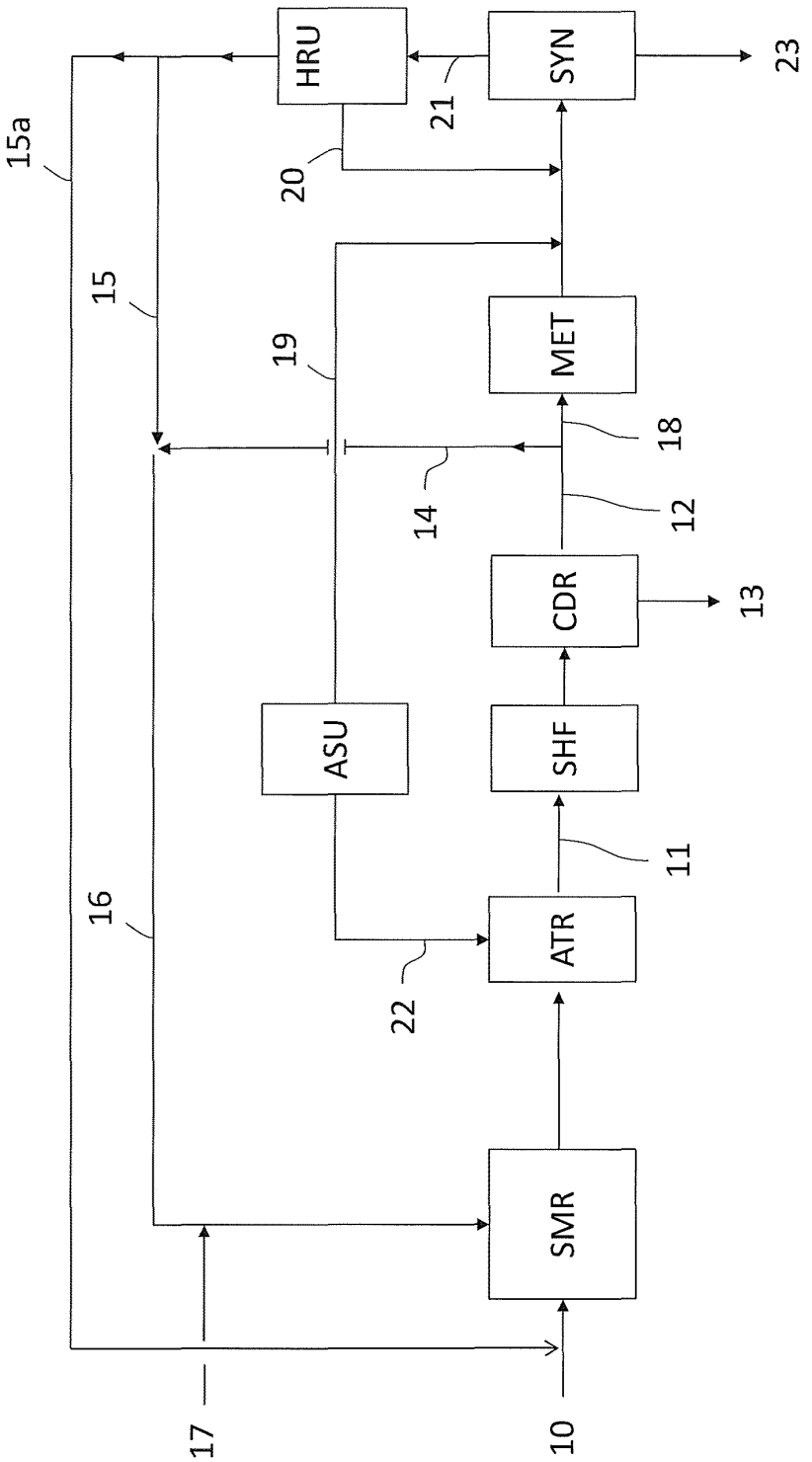

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FIG. 2

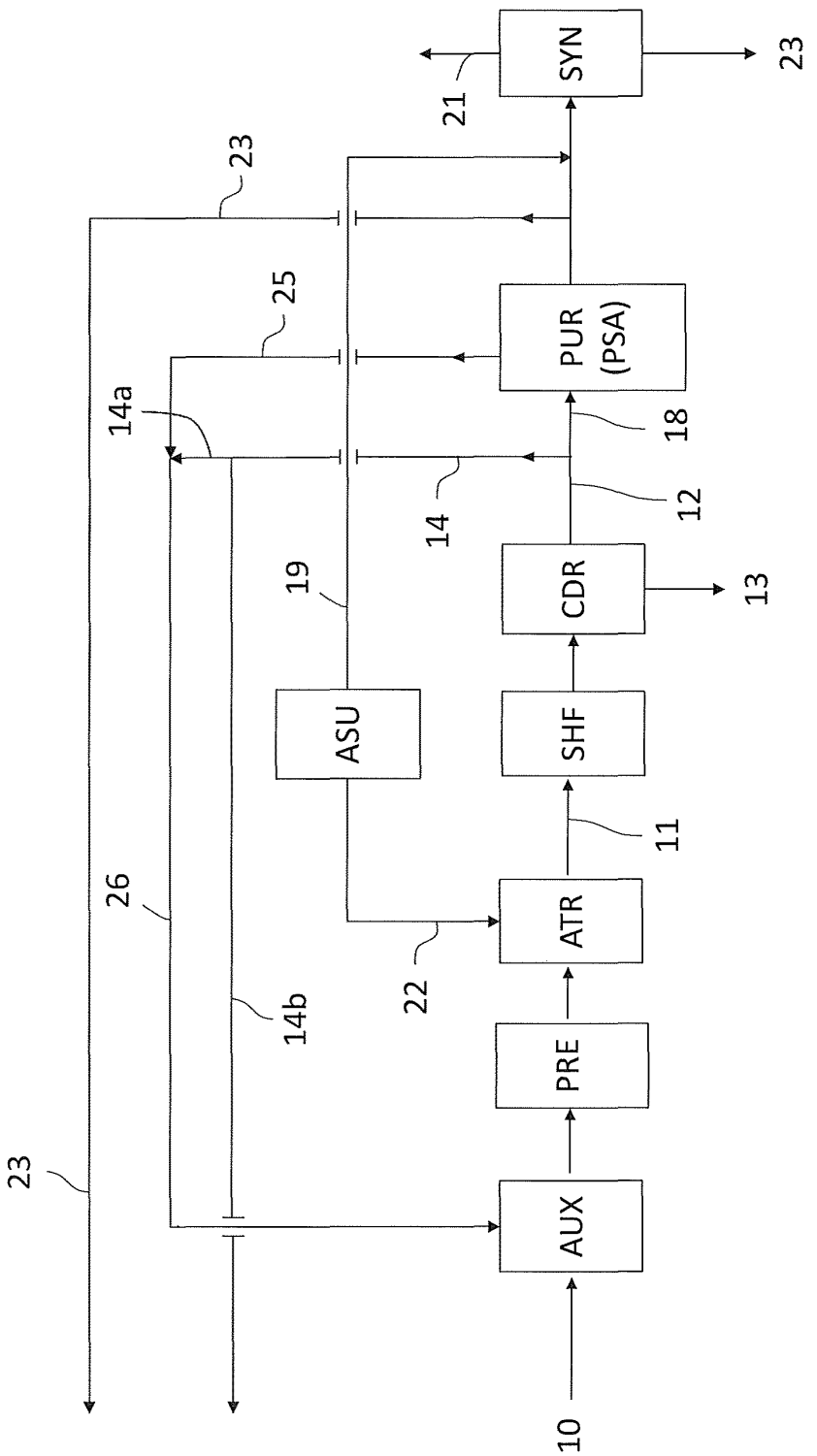

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AUX
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FIG. 3

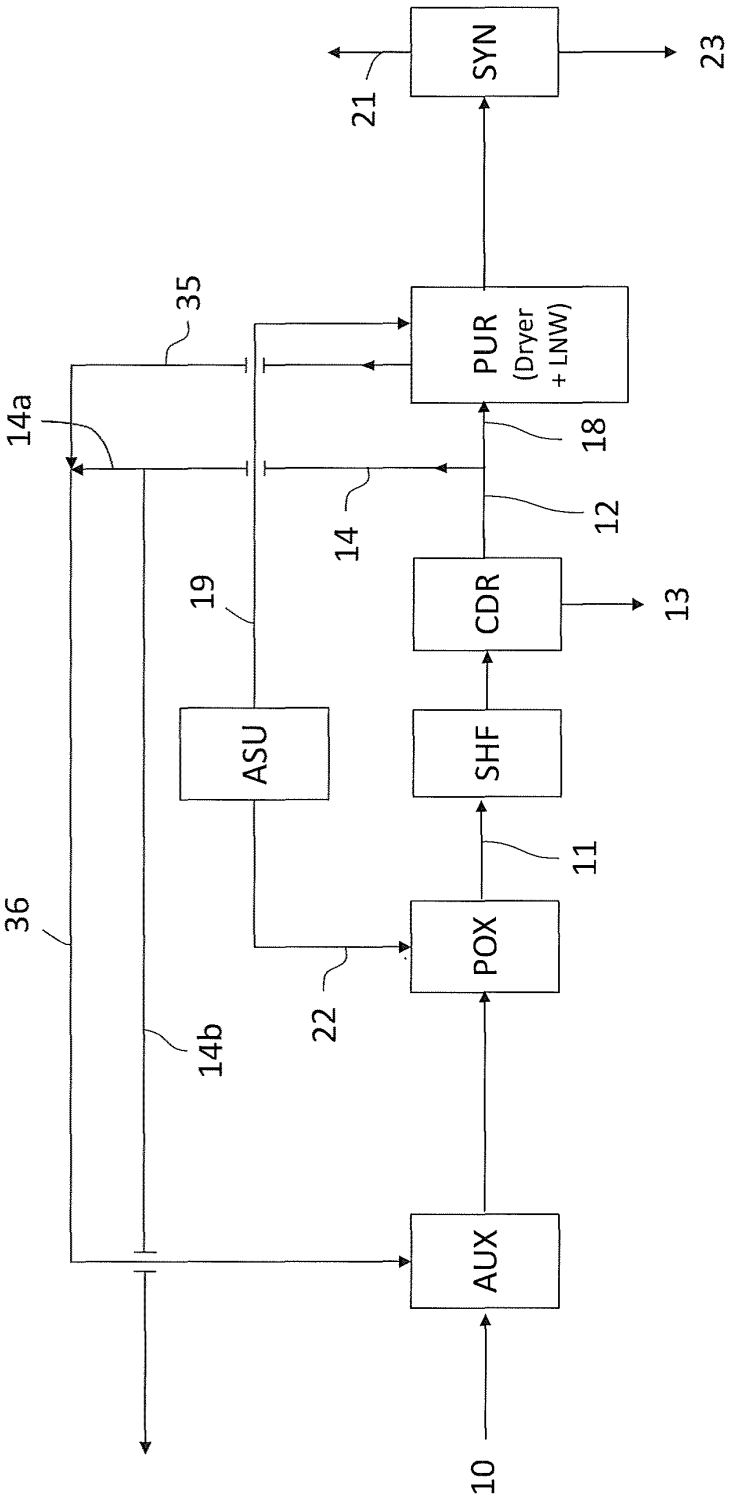

SYN
21
23
PUR
(Dryer
+ LNW)
35
14a
18
14
12
CDR
19
13
ASU
SHF
11
36
POX
22
14b
AUX
10

FIG. 4

PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE

FIELD OF APPLICATION

The invention relates to the field of ammonia synthesis plants fed with natural gas (NG).

PRIOR ART

The ammonia synthesis plants of the type considered here comprise a section adapted to convert the natural gas into a make-up gas containing hydrogen and nitrogen, and a synthesis section wherein said make-up gas reacts catalytically at high pressure to produce ammonia.

The section which generates said make-up gas is referred to in the technical language as the "front end". The term "back end" is instead used to denote the section for ammonia synthesis and the respective cooling section intended to cool the effluent of the synthesis section in order to separate the ammonia.

In the front end, the desulphurized natural gas undergoes reforming, resulting in a gas containing essentially hydrogen, carbon monoxide CO and carbon dioxide CO2. Said gas then undergoes a shift reaction which converts CO into CO2; removal of CO2 (decarbonation) and preferably methanation.

The reforming process, in a common type of plant, comprises primary steam reforming and a subsequent catalytic air-fired secondary reforming. The primary reformer is heated by burners fuelled by a part of the available natural gas. In the secondary reformer the effluent from the primary reformer burns due to contact with the oxygen contained in the air. In some plants other reforming configurations are used, for example an autothermal reformer (ATR) preceded by a furnace for heating the charge, i.e. the gaseous mixture fed to said reformer.

The above described ammonia plants result in significant emissions of CO2 into the atmosphere, overall in the region of 100 million tonnes of CO2 per year. One of the main sources of CO2 emission consists in the combustion fumes of the primary reformer and other burner furnaces if any, for example auxiliary heaters.

For environmental reasons, it is required to minimize the CO2 emissions from the fumes of the NH3 plants. The problem affects in particular the older ammonia plants which are less efficient than the new ones and have greater CO2 flue emissions in relation to the quantity of ammonia produced. It is also necessary that the reduction of the emissions should not increase excessively the costs for production of the ammonia.

According to the present state of the art, the processes for capturing CO2 from fumes are based on washing with solvents (for example the solvent KS-1™ produced by Mitsubishi). The associated plants are, however, costly and complicated, have a high energy consumption and require expensive solvent. Therefore these CO2 capturing processes cannot be applied to the plants considered here since they would increase excessively the costs for production of the ammonia.

In some ammonia synthesis processes of the prior art, part of the fuel may be supplied by a purge flow obtained, for example, from a cryogenic purification section of the synthesis gases or from a PSA unit. Said purge flow may have a reduced CO2 content. However, said purge flow accounts for a small amount of the total fuel and does not solve the problem of the CO2 emissions in the atmosphere.

SUMMARY OF THE INVENTION

The object of the invention is to provide a method for conducting ammonia synthesis processes with CO2 emissions into the atmosphere which are greatly reduced compared to the prior art. Another object of the invention is to provide a method for revamping the existing plants, of the type using air-fed secondary reformers able to reduce drastically the CO2 emissions into the atmosphere.

The objects are achieved with a process and a revamping method according to the claims.

According to the invention, a process for synthesis of ammonia from natural gas comprises:

conversion of a charge of desulphurized natural gas and steam, with oxygen-enriched air or with oxygen, to form a synthesis gas containing hydrogen, CO and CO2;

a treatment of said synthesis gas comprising at least one shift reaction of the carbon monoxide into CO2, and subsequent separation of CO2 from the gas, thus obtaining a CO2-depleted synthesis gas and a CO2-rich gaseous flow containing the CO2 separated from the gas;

optionally, a step for methanation of the synthesis gas and/or addition of nitrogen to the synthesis gas, obtaining a make-up gas containing nitrogen and hydrogen in a suitable molar ratio for ammonia synthesis,

characterized by:

separation of a part of said CO2-depleted synthesis gas, obtaining a fuel fraction of the synthesis gas, wherein said fuel fraction is fed as fuel to at least one furnace.

The invention also relates to a method for revamping a plant originally comprising a reforming section which includes a primary steam reformer and air-fired secondary reformer, and treatment of the synthesis gas comprising a shift reaction of carbon monoxide into carbon dioxide, decarbonation and optionally methanation. The revamping method comprises at least:

providing a flow of enriched air or oxygen and using said flow as an oxidant for the secondary reformer instead of the air;

separating a part of the synthesis gas downstream of decarbonation,

feeding said part of the synthesis gas, which has a reduced CO2 content, as fuel for at least one furnace of the plant.

The term "furnace" is understood as meaning an apparatus chosen from among: a steam reformer or a charge preheater or a steam generator or a steam superheater. These apparatus, which operate by means of combustion, are identified by the term "fired heater". Said furnace in some embodiments forms part of the section for converting the natural gas into synthesis gas. In combined ammonia/urea plants said furnace may form part of the urea section.

The portion of synthesis gas which is separated and sent to said at least one furnace is termed fuel fraction of the gas available after the shift step. Preferably, said fuel fraction is comprised between 1% and 40% of the available gas, more preferably between 10% and 30% and even more preferably between 20% and 30%. For example in a preferred embodiment the fuel fraction is equal to 30%. The remaining part, which is intended to be converted into ammonia, is called process fraction.

It should be noted that said fuel fraction is relatively high, for example about ⅓ of the total. The invention in fact envisages that a non-negligible portion of synthesis gas is allocated to fuel in order to reduce the CO2 emissions. This

results in the need to produce an additional quantity of synthesis gas, but, as will be explained more clearly below with the aid of the examples, this necessity is compensated for by the advantages of the invention.

The separation of the fuel fraction is advantageously performed by splitting a process flow, for example a process gas after shift and decarbonation. As a result of said splitting, the fuel fraction and the remaining part of the gas, also called process fraction, have the same composition.

It should be noted that the present invention envisages deliberately allocating a part of the process flow to the fuel fraction, the fuel fraction being directly separated from the process flow and having the same composition. The prior art, on the other hand, teaches only allocating as fuel any purge streams derived from purification processes and containing methane. The said synthesis gas with a low CO2 content (CO2-depleted syngas) preferably contains no more than 1000 ppm by volume (0.1%) of CO2. Said gas is composed essentially of hydrogen ((H2) with any small residual quantities of CO and CH4, typically less than 2% by volume and preferably less than 1%.

The combustion of said gas is substantially free from production of CO2. In fact, the combustion of the hydrogen does not form CO2, and only the small quantity of CO or CH4, if present, may form CO2.

The invention suggests using a process gas part as fuel for one or more furnaces of the reforming section, differently from the prior art which, for this purpose, uses part of the natural gas, i.e. a hydrocarbon. The process gas part (fuel fraction) is suitably separated after a CO2 removal treatment and, as explained further above, it contains essentially hydrogen which may burn without forming CO2. Consequently it can be understood that the invention allows the CO2 emissions into the atmosphere to be drastically reduced.

Said oxygen-enriched air preferably contains at least 50% oxygen by volume and more preferably at least 90% oxygen by volume and even more preferably at least 95%. The advantages of a high oxygen content in the enriched air are as follows: greater calorific power of the synthesis gas; smaller flow of flue discharge gas; smaller volumetric flow through the apparatus of the conversion section and, consequently, smaller apparatus.

The CO2-depleted synthesis gas preferably forms all—or substantially all—the fuel of the furnaces used for the process. In some embodiments, however, it is preferred to keep a small amount of natural gas which is called "trim fuel" of the furnace. Preferably said small quantity accounts for not more than 15%, more preferably not more than 10%, of the total combustion heat (duty) of the furnace. The trim fuel allows the furnace to be rapidly controlled, for example in order to quickly raise or lower the load if needed.

Said percentage of the combustion heat may be expressed as the product between the flowrate (kg/s or mol/s) and the calorific power (J/kg or J/mol).

According to some embodiments of the invention, methanation of the synthesis gas is performed downstream of decarbonation. The methanation step converts residual CO and CO2 into CH4, consuming H2, in accordance with the reactions $CO+3H2 \rightarrow CH4+H2O$ e $CO2+4H2 \rightarrow CH4+2H2O$.

Preferably, the separation of the fuel fraction from the CO2-depleted synthesis gas is performed before (upstream of) said methanation step.

The advantage of separating the fuel fraction before methanation is that of not oversizing the methanation section of the fuel fraction, and of not losing the methanation heat of the fuel fraction. Moreover, for the same furnace heat requirement and the same gas temperature, the fuel fraction is slightly less if removed before methanation.

There are no disadvantages as regards CO2 emissions into atmosphere, which are the same by using as fuel both the gas upstream of the methanator and the gas downstream of the methanator, for the same flowrate. In case of nitrogen addition, the fuel fraction is separated before adding nitrogen. The advantage is a greater calorific power of the synthesis gas used as fuel, which does not contain nitrogen, or contains a smaller amount thereof.

After separating the fuel fraction, the CO2-depleted synthesis gas may be optionally treated in a purification section comprising, for example, a PSA unit or comprising a dryer followed by a cryogenic unit.

The purification section produces at least one stream of ammonia synthesis gas with a reduced content of inerts, and at least one waste stream containing CO, and CH4. The waste stream may also contain H2 and N2. In some embodiments, at least part of the waste gas of said purification section is used as fuel together with the fuel fraction. Consequently, the fuel fraction may be reduced.

The advantage of the purification unit is that of reducing the inerts content in the make-up gas, resulting in known advantages for the ammonia synthesis, including smaller consumption for circulation and a reduction (or even elimination) of the purge flow of the ammonia synthesis loop.

According to the invention, the fuel fraction is advantageously separated upstream of the purification unit. Consequently, only the synthesis gas portion supplied to the ammonia synthesis undergoes treatment in the purification section which, without having to process the synthesis gas corresponding to the fuel fraction, may be realized with much smaller dimensions. The advantage of separating the fuel fraction upstream of the purification unit is that of avoiding oversizing of the purification unit and the corresponding consumption for the fuel fraction of the synthesis gas. Another advantage is the possibility of controlling separately the fuel fraction and the purification unit.

There is no disadvantage in separating the fuel fraction upstream of the purification from the point of view of the CO2 emissions into atmosphere, since the CO, CO2 and CH4 contained in the synthesis gas of the fuel fraction would be separated by the purification unit to form the waste stream and used as fuel.

Advantageously, the purification unit does not need to have an excessively high hydrogen recovery, because the hydrogen "lost" in the waste gas is used as fuel and does not produce CO2 emissions into atmosphere. The fuel fraction of the synthesis gas is consequently regulated.

Preferably, however, the purification unit has a sufficiently high hydrogen recovery such that the fuel fraction accounts for at least 30%, preferably at least 40%, even more preferably at least 50% of the furnace duty. The applicant has found that this condition is advantageous for the control of the furnace itself independently of the control of the purification unit.

The purification section may comprise selective adsorption of the undesirable components onto a solid. In some embodiments said purification section comprises a PSA (pressure swing adsorption) unit which uses molecular sieves for separating CO, CH4, Ar, H2O and residual CO2. In other embodiments said section comprises at least one dryer for separating residual CO2 and water, followed by a cryogenic unit for separation of CO, CH4 and Ar. The cryogenic separation unit is preferably a Liquid Nitrogen Wash (LNW) unit.

A PSA unit typically produces a single flow of purified product, substantially at the feed pressure, and a single stream of waste gas, at a pressure much lower than the feed pressure. Said waste stream contains CO, CH4, Ar, H2O and residual CO2, and may contain H2 and N2.

If the purification section comprises dryer and LNW, the purified product may emerge as one or more streams, and may already contain H2 and N2 in a suitable ratio for the synthesis of ammonia.

The dryer has a tail gas, product of regeneration of the molecular sieves used for capturing mainly H2O and the traces of residual CO2 contained in the feed, which would freeze during the cryogenic treatment in the LNW unit. The dryer may be regenerated with a nitrogen flow (from the air separation unit). In this case the tail gas containing N2, H2O and CO2 may be discharged into atmosphere or combined with the tail gas of the LNW described below.

The LNW also has at least one tail gas which contains the bottom end product of the LNW absorption column, containing CH4 and CO, in addition to N2 and H2. The discharge gas of the LNW may be conveyed away as fuel.

The tail gas of the LNW may be used at least partly for the regeneration of the dryer before being conveyed away as fuel.

The synthesis gas with a low content of inerts may be conveyed away for ammonia synthesis.

Methanation is an exothermic reaction, but there is not a substantially large amount of reaction heat and it is usually not recovered.

Methanation therefore leaves a small quantity of methane in the synthesis gas (methane slip). The presence of said small quantities of methane in the synthesis gas is not a problem for the purposes of ammonia production, since methane is inert to the synthesis reaction. Methane accumulates in the purge flow of the synthesis loop. However, by using the purge flow of the synthesis loop as fuel, the methane contained therein constitutes a source of CO2, albeit of small entity.

The carbon monoxide contained in the synthesis gas also constitutes a source of CO2, albeit of small entity, both owing to combustion of the synthesis gas used as fuel, and owing to combustion of the waste gas of a purification unit, where present.

In some embodiments of the invention, in order to reduce also this source of CO2 (i.e. the emissions caused by the presence of residual carbon monoxide of the synthesis gas), the process comprises a catalytic purification which selectively converts the CO into CO2 upstream of decarbonation. Selective conversion of the carbon monoxide may be obtained, for example, using the process known as Selectoxo™ which operates with the reaction $CO+\frac{1}{2}O2 \rightarrow CO2$. The oxygen for selective oxidation of the CO may be a part of the mentioned enriched-air or oxygen flow.

An advantage of said selective conversion of CO into CO2 is that at least part of the residual CO from the shift is converted into CO2 and removed during decarbonation. Consequently, the combustion of the synthesis gas, of the synthesis loop purge flow, or of the purification waste gas, produces a smaller quantity of CO2.

According to the invention, the CO2 flue emissions are mainly determined by the CO, CO2 and CH4 content of the synthesis gas downstream of decarbonation, as well as by the optional trim fuel flow which will be described below.

The combustion of said gas is substantially free from CO2 production. In fact, the hydrogen combustion does not form CO2, and only the small quantity of CO or CH4, if present, may form CO2.

The CO2 production is also derived from the combustion of the methane contained in the synthesis loop purge flow.

In case a purification unit is present, CO2 production is also derived from the combustion of CO, CH4 and residual CO2 of the discharge gas.

According to one aspect of the invention, the fuel fraction is produced in excess compared to the fuel required for the conversion section, the quantity of said fuel fraction exceeding that required being exported from the process, and the regulation of the conversion section is performed by modulating the quantity of said fuel fraction directed towards the conversion section and the quantity exported by the process.

The conversion of the natural gas into synthesis gas may be performed using different techniques.

According to some embodiments of the invention, the step of natural gas conversion into synthesis gas comprises primary reforming followed by secondary reforming. In some embodiments, more preferably, the conversion step comprises a catalytic autothermal reforming (ATR), optionally preceded by a preliminary reforming (pre-reforming). An ATR without preliminary reforming is also called "pure ATR". Advantageously, in these embodiments, at least a part of the synthesis gas fuel fraction feeds a furnace for preheating the gas prior to autothermal reforming.

The advantage of using ATR, pure or in combination with a pre-reformer, consists in the smaller heat requirement of the furnace compared to the combination of the ATR with a primary reformer, also considering the heat required for generation and overheating of steam necessary for the process. This is due to the fact that the preheating temperature of the ATR feed and of the optional pre-reformer according to the invention is suitably chosen at a value not greater than 650° C., lower than the output temperature of the primary reformer, and due to the fact that, in the preheating furnace, there is no progression of the steam reforming reaction (which is endothermic).

A pure ATR, or ATR in combination with a pre-reformer, may advantageously operate with a steam/carbon (S/C) ratio less than that of a primary reformer. Preferably, said S/C ratio is not greater than 2, more preferably not greater than 1.5, even more preferably not greater than 1. This also helps reduce the heat required by the furnace for preheating the feed of the ATR and optional pre-reformer.

In the case of ATR without primary reformer, the fuel fraction is preferably comprised between 1 and 30%, more preferably between 10 and 30%, even more preferably between 10 and 20%.

In some embodiments the step for converting the natural gas into synthesis gas comprises a non-catalytic POX (partial oxidation) step. Advantageously, in these embodiments at least a part of the synthesis gas fuel fraction feeds a furnace for preheating the gas before said partial non-catalytic oxidation or for steam generation or steam superheating.

The advantage of using a POX consists in the smaller heat requirement of the furnace compared to the combination of an ATR with a primary reformer, also considering the heat required for generation and overheating of steam necessary for the process. This is due to the fact that the preheating temperature of the POX feed according to the invention is suitably chosen at a value not higher than 500° C., markedly lower than the output temperature of the primary reformer, and due to the fact that in the preheating furnace there is no progression of the steam reforming reaction (which is endothermic). Moreover, POX may advantageously use a S/C ratio lower than that of a primary reformer, preferably not greater than 2, more preferably not greater than 1, even more

preferably not greater than 0.5. This also helps reduce the heat required by the preheating furnace.

In the case of POX, the fuel fraction is preferably comprised between 1 and 30%, more preferably between 10 and 30%, even more preferably between 10 and 20%.

The reduction in the heat required by the preheating furnace for a POX and for a pure ATR compared to an ATR in combination with a primary reformer provides the following advantages: the fuel fraction of the synthesis gas is less, and it is possible to reduce the quantity of trim fuel, therefore lower CO2 flue emissions may be obtained.

Both in the case of POX with optional purification unit of the synthesis gas and in the case of ATR without primary reformer and with optional purification unit of the synthesis gas, it is preferable to select a purification unit with high hydrogen recovery, for example a liquid nitrogen wash, so as to ensure that the fuel fraction of the synthesis gas is sufficiently large to control the furnace independently of control of the purification unit.

Another advantage of the POX and ATR without primary reformer, consequence of both the smaller fuel fraction and the smaller steam/carbon ratio, is the smaller autogenous steam production, which reduces the heat required for the associated overheating, the fuel fraction, the CO2 flue emissions and the total natural gas consumption.

The smaller autogenous steam production may result in a lack of steam for driving the turbines or of electricity for powering the motors of the machines. The missing energy may be conveniently imported from outside the plant as electricity with reduced CO2 emissions, for example generated by renewable sources. It should be pointed out that this synergy is not possible if the process already produces an excess of steam or energy, for example in the case of combination of primary reformer and ATR with a fairly large fuel fraction.

In some embodiments the step of converting the natural gas into synthesis gas also comprises a steam reforming step. Advantageously, in these embodiments at least a part of the synthesis gas fuel fraction feeds the burners of the reformer.

A part of the fuel fraction may be allocated, in some embodiments, to furnaces for the production and/or superheating of steam.

The invention also allows to produce the electricity necessary for the synthesis of ammonia or of its derivatives (for example urea) with low emissions of CO2, using as fuel CO2-depleted synthesis gas, for example in the following ways:

- expansion in a turbo generator of a flow of steam produced in a steam generator or steam superheater, fed by the CO2-depleted synthesis gas as fuel;
- combustion in a gas turbine or in a gas engine, fed by the CO2-depleted synthesis gas as fuel.

Generally, in ammonia processes, a purging gas is extracted from the ammonia synthesis loop, in order to remove the inert substances from the synthesis loop, and said purging gas is treated with a process for recovery of the hydrogen contained in it (HRU). Said recovery process generates a hydrogen-rich gas which may be reused for synthesis and a tail gas containing most of the methane initially contained in the purging gas. The methane in the tail gas is practically all that contained in the process fraction of the synthesis gas. Normally said tail gas, given its relatively high methane content, is used exclusively as fuel. This use of tail gas, however, generates CO2 emissions.

According to one aspect of the invention at least a part of said tail gas is recycled as process gas during the natural gas conversion step, for example during the reforming or partial oxidation step. An associated advantage is a further reduction in the CO2 emissions.

In some embodiments a part of the said CO2-depleted synthesis gas is treated in a nitrogen (N2) separation unit, preferably a membrane unit, obtaining a nitrogen-depleted synthesis gas and a nitrogen-rich flow; at least a part of the nitrogen-depleted synthesis gas (preferably all of it) is used as fuel; the remaining part is fed to the ammonia synthesis together with the nitrogen-rich flow.

This configuration is particularly advantageous if the O2-enriched air does not have a very high purity (for example less than 95% of O2) and/or if the natural gas contains nitrogen. Three benefits are obtained: an increase in the calorific power of the fuel gas, a reduction in the flow of combustion fumes (and the power of the respective ID fan) and conservation of the nitrogen which is a reagent for the ammonia. The membrane nitrogen separation unit is further preferred because said unit may operate using the pressure difference between the synthesis gas (produced at high pressure) and the combustion in the furnace (which occurs at atmospheric pressure). Moreover, the nitrogen-rich flow, which is used for synthesis, does not lose pressure.

The configuration described above, which envisages separation of the nitrogen from the synthesis gas, is applicable also in a conventional process, with primary steam reformer and secondary air-fired reformer, resulting in the advantage that it is not required to modify or enlarge the air compressor. However, with a secondary air-fired reformer and without modifying the compressor, and therefore without being able to increase the air flow, the additional fraction of synthesis gas (required as fuel) would have to be produced by increasing the capacity of the primary reformer and/or installing a gas-heated reformer (GHR), both solutions being very costly. For these reasons, the nitrogen separation described is particularly preferred in combination with the use of the enriched air during conversion of the natural gas into synthesis gas.

In some embodiments, it is envisaged expanding, with production of mechanical work, the CO2-depleted synthesis gas after optionally heating it.

Said gas is available at a pressure higher than the pressure required for combustion in a furnace and therefore it may be expanded in a suitable machine, such as an expander or a turbine, producing mechanical work. For example, said expansion may be from about 25 bar to about 3 bar. The gas has a high specific volume given that it comprises essentially H2 and for this reason its expansion may generate a considerable amount of power. The power obtained may cover partly the process requirements, making it more efficient.

In some embodiments the shift step comprises two steps at different temperatures, for example preferably one high-temperature shift (HTS), for example carried out using an iron-based catalyst, followed by a low-temperature shift (LTS) or medium-temperature shift (MTS), for example carried out using a copper-based catalyst. The associated advantage is that of obtaining the maximum conversion of the CO into CO2, which will then be separated during the decarbonation step, so as to obtain the minimum residual CO content in the synthesis gas used as fuel. Since the CO is a source of CO2, during combustion, the advantage of minimizing the CO2 flue emissions is obtained.

In some embodiments, in which a relatively low overall S/C ratio is used, for example <2.7, the shift preferably comprises two steps in series carried out over catalyst suitable to operate with a low steam content, for example a copper-based catalyst. In this configuration, the first step

consists of a medium temperature shift (MTS), which is preferably pseudo-isothermal and operates in the temperature range of 200-320° C., and the second step is a low temperature shift (LTS) operating in the temperature range 180-250° C.

The conversion of the natural gas into synthesis gas, for example by means of reforming, is preferably performed at a pressure lower than 50 bar, more preferably lower than 40 bar, and even more preferably lower than 30 bar.

Generally the prior art teaches the preference for high conversion pressures, in order to increase the capacity of the conversion section (front end) and reduce the consumption of synthesis gas compression. The present invention is instead preferably implemented with low conversion pressures in order to obtain the maximum conversion of the methane, since the steam reforming reaction is favoured at a lower pressure, so as to have the minimum residual methane content in the synthesis gas used as fuel. Since the methane is a source of CO2, during combustion, the advantage of minimizing the CO2 flue emissions is obtained.

In the case of ATR, a high methane conversion is also obtained by operating at a relatively high output temperature, >950° C., preferably >1000° C., even more preferably >1030° C.

In the case of POX, a high methane conversion is also obtained by operating at a relatively high output temperature, >1200° C., preferably >1300° C.

In some embodiments the overall steam/carbon (S/C) ratio during conversion is greater than 2.0, preferably greater than 2.2 and more preferably greater than 2.7. Generally the prior art teaches a preference for low S/C ratios in order to increase the capacity of the conversion section (front end). The invention instead envisages a relatively high S/C ratio in order to maximize the conversion of the methane and the CO during the shift step and reduce the concentration of CH4 and CO in the synthesis gas. Since the methane and CO are a source of CO2, during combustion, the advantage of minimizing the CO2 flue emissions is obtained.

In the case of pure ATR (optionally in combination with pre-reformer) or POX, the invention employs a S/C ratio not higher than 2 in the reforming section. Preferably further steam is added downstream of the reforming and upstream of the shift, until an overall S/C ratio greater than 2, and preferably greater than 2.4, is reached so as to promote the progression of the shift reaction and the associated conversion of the carbon monoxide.

The use of the trim fuel solves the problem of rapidly controlling the furnace, but at the cost of increasing the CO2 emissions into the atmosphere. For some configurations of the invention, for example those comprising a steam reformer, the trim fuel represents the greatest contribution to the CO2 emissions in the atmosphere. This will be illustrated in the examples.

In a preferred embodiment of the invention, the trim fuel is not used and the fuel of the furnace is only the synthesis gas. The fuel fraction is consequently greater than in the case where the trim fuel is used, because it is required to provide also the combustion heat of the trim fuel with the fuel fraction.

In a first embodiment, the fuel fraction has a combustion heat substantially corresponding to the heat required by the furnace. In order to rapidly control the furnace, for example in order to quickly raise or lower the load when needed, the flowrate of the fuel fraction is suitably raised or lowered. This control, however, has the undesirable effect of varying the flowrate of the make-up gas, and therefore the production. In order to re-establish the initial production, it is necessary to increase or reduce the total flowrate of natural gas fed to the reforming section, which in turn requires control of the furnace. It may be understood how this procedure is operationally undesirable.

According to one aspect of the invention: the fuel fraction is produced in an overabundant amount with respect to the requirement of said at least one furnace, i.e. a surplus of synthesis gas to be used as fuel is produced with respect to the corresponding quantity of heat required by the furnace, and the surplus of fuel synthesis gas is exported from the process, i.e. is not used either as fuel fraction or as process fraction. The availability of synthesis gas in excess (for use as fuel) allows to rapidly regulate said at least one furnace without using, or using to a lesser degree, the trim fuel, with a further advantage in terms of reduction of the CO2 emissions.

For example, the surplus may be:

exported as a further product (for example as hydrogen or as CO2-depleted fuel for consumption outside the ammonia plant) or

conveyed to a storage buffer, or

flared.

In order to rapidly control the furnace, for example in order to quickly raise or lower the load in the case of need, the flowrate of the synthesis gas surplus is suitably lowered or raised, without affecting either the fuel fraction or the process fraction.

The surplus of fuel synthesis gas may be taken from the fuel fraction, and therefore have the same composition and pressure as the fuel synthesis gas.

Alternatively, if a purification unit (for example a PSA unit) or a methanation unit is present, the surplus of fuel synthesis gas may be collected downstream of purification or methanation, so as to obtain greater purity of the surplus exported.

The surplus fuel may be separated from the tail gas of purification (PSA, or dryer+LNW), even though said solution is less preferred for two reasons:

the tail gas has a low pressure, therefore a compression is required to export said tail gas (with considerable energy expenditure and plant cost);

the tail gas contains CO, CO2 and CH4 in a concentration much greater than both the fuel synthesis gas and the purification product, therefore it has a less desirable composition.

The quantity of the surplus fuel synthesis gas is preferably >2%, more preferably >4%, and even more preferably >6% of the fuel fraction. If the surplus of the fuel synthesis gas is not exported, its quantity is preferably not greater than 15% of the fuel fraction, and even more preferably not greater than 10% of the fuel fraction, in order to prevent an excessive consumption thereof.

The invention obtains CO2 emissions which are less than 0.5 t/t (tonnes of CO2 emitted per tonne of ammonia produced); in preferred embodiments of the invention the emissions are less than 0.3 t/t or less than 0.2 t/t.

As will be illustrated in the examples, in some preferred embodiments the CO2 emissions may reach values less than 0.1 t/t or even 0.05 t/t, corresponding to a CO2 capture value close to 99%.

As regards the plant, the furnaces are advantageously equipped with dual-fuel burners able to burn both natural gas and synthesis gas. The invention may require the installation of an air separation unit (ASU) for the production of the enriched air and optionally nitrogen.

The invention may also be applied to ammonia/urea processes and plants. An ammonia/urea plant is a plant

comprising a first ammonia synthesis section and a second section for synthesis of urea from ammonia and CO2, wherein at least a part of the ammonia produced in the first section feeds the second section. In this case also the CO2 separated during the decarbonation step feeds advantageously said second urea synthesis section.

The main advantages of the invention are listed below.

The separation of the CO2 is performed from a synthesis gas which has a high concentration of CO2 (15-25% mol) and is at a relatively high pressure, and therefore the separation of CO2 from this flow is much easier and requires a lower energy consumption than CO2 separated from combustion fumes.

The system according to the invention does not require solvent in order to capture CO2 from fumes.

The use of oxygen-enriched air gives rise to various advantages:

- it increases the heat value of the synthesis gas;
- combustion of the synthesis gas generates less fumes than the combustion of natural gas, for the same amount of heat released, because the combustion of hydrogen (contained in the synthesis gas) occurs with a reduction of the number of mols, unlike the combustion of methane, so that the convective current of the reformer is smaller and requires an induced draft (ID) fan which is less powerful;
- it limits the flue loss of nitrogen (which is a reagent), avoiding wastage of energy for N2 separation and compression; the generation of nitrogen for synthesis must not be increased;
- it allows a high temperature for conversion of the natural gas to be maintained, free from the constraint of avoiding the introduction of excessive nitrogen in relation to the stoichiometry of the NH3 synthesis (typical of conventional air-fired processes) with a high conversion of the methane resulting in minimal CO2 emissions.

In conventional plants with a secondary air-fed reformer, the process air is fed to said secondary reformer in stoichiometric quantities, i.e. in the quantity required to reach a H/N ratio of about 3 in the make-up gas. This means that the air flowrate (in particular the quantity of oxygen introduced into the reformer) cannot be freely chosen, for example in order to achieve full conversion of the NG.

Instead, if the oxidant and the nitrogen are separately fed to the process, it is possible to choose the flowrate of oxidant so as to obtain complete conversion of the natural gas and optionally add, downstream, the nitrogen which is needed for the desired make-up gas composition. The advantage of full conversion is to produce a synthesis gas with a smaller methane content and therefore lower CO2 emissions.

Another advantage of the invention is that the greater flowrate of gas in the front end allows more heat to be recovered and more steam to be generated. The greater quantity of steam produced in the front end limits the duty of the respective auxiliary steam-generating apparatus; an advantage is that the fuel consumption (and potential source of CO2 emissions) is represented only by the primary reformer or fired heater. If the fuel of the reformer is replaced with synthesis gas (and if necessary the associated burners replaced) a substantial elimination or zeroing of the CO2 emissions is obtained.

Another advantage is that the invention does not require necessarily separation of hydrogen from the CO2-depleted syngas, i.e. purification of the CO2-depleted syngas into a gas which is rich in H2 and a waste gas, in order to obtain low CO2 emissions into the atmosphere. The CO2-depleted syngas may be used directly for ammonia synthesis after possible methanation.

In some embodiments it may be advantageous to perform a syngas gas purification in order to reduce the overall energy consumption of the process.

When applied to revamping of plants, the invention achieves significant synergies which allows the CO2 emissions to be reduced without production losses, limiting modifications and costs. This is because the invention:

- reduces greatly the gas flowrate in the front end, and therefore the associated apparatus and (secondary, shift reaction, decarbonation or methanation) piping are suitable for a greater capacity;
- said greater capacity corresponds to the synthesis gas to be used as fuel;
- a high output temperature from the secondary reformer may be used (obtaining complete conversion of the methane), because the nitrogen is added separately from the oxygen; therefore the method according to the invention produces extra gas to be used as fuel without requiring costly modifications of the primary reformer, even when said reformer is substantially at the limit of its capacity;
- the CO2 removal section is de-bottlenecked because the invention increases the partial CO2 pressure and reduces the gas flowrate in the absorber;
- the combustion of the CO2-depleted syngas generates fewer fumes than the NG so that the convective current of the reformer and ID fan are less charged;
- it is necessary to modify only the front end, while the backend (synthesis gas compressor, ammonia synthesis, refrigerating section) is substantially unchanged.
- the process does not require intense purification of the synthesis gas in order to remove the inert components, it being sufficient to use the methanator (often the existing one); in particular, it is not necessary to perform any separation of the synthesis gas into an H2 and waste gas flow.

DESCRIPTION OF THE FIGURES

FIG. **1** shows a first embodiment of the invention.
FIG. **2** shows a second embodiment.
FIG. **3** shows a third embodiment.
FIG. **4** shows a fourth embodiment.

DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

FIG. **1** shows a process according to a mode of implementing the invention based on an oxygen autothermal reformer ATR and pre-reformer.

The blocks in FIG. **1** denote the following systems or apparatus:

AUX charge pre-heater furnace and auxiliary boiler
PRE pre-reformer
ATR autothermal reformer
POX partial oxidation reactor
SHF shift section
CDR CO2 removal section (decarbonation)
MET methanator
SYN synthesis section
HRU hydrogen recovery section
ASU air separation (fractioning) section

A charge **10** comprising natural gas and steam is preheated in AUX and converted into a synthesis gas **11** via the

reformers PRE and ATR. The autothermal reformer ATR operates with a flow **22** of enriched air or oxygen.

The synthesis gas, which contains H2, CO and CO2, undergoes a shift reaction in SHF and then removal of CO2 in CDR. The section SHF may comprise shift treatments at different temperatures. The section CDR operates for example with chemical/physical washing of the gas using an aqueous amine solution.

The section CDR produces a CO2-depleted syngas **12** and a flow **13** of CO2 which may be sequestered or used for other process purposes, for example in order to produce urea.

Preferably the synthesis gas **12** has the following composition: 98% H2, 1% CO+CH4, 0.1% CO2, Ar+N2 0.9%.

A part **14** of said CO2-depleted syngas **12** is used as fuel in a furnace in the front end, for example in a charge heater (AUX block). The remaining part **18** of synthesis gas is further treated in the methanator MET.

In the example, the fuel fraction **14** of synthesis gas, together with a tail gas **15** of the HRU section, feeds one or more users of the block AUX via the fuel line **16**. Optionally a suitable quantity of natural gas **17** (trim gas) is added to the gas **16**.

Nitrogen **18** from the air separation section ASU is added to the process fraction **18** of the synthesis gas, after it has passed inside the methanator (optional).

The gas thus obtained, together with a flow of hydrogen **20** recovered from the HRU section, feeds the synthesis section SYN. Said synthesis section produces ammonia **23** and a flow **21** of purging gas treated in the section HRU for recovery of the hydrogen contained inside it.

The separation section ASU produces, in addition to the nitrogen **19**, also the flow **22** of enriched air or oxygen for the autothermal reformer ATR.

FIG. **2** shows a process according to a preferred mode of implementing the invention based on primary reforming and ATR.

The block SMR in FIG. **1** denotes the primary reformer (or steam reformer) plus auxiliary apparatus, for example steam generators. The remaining symbols in FIG. **2** correspond to the symbols in FIG. **1** and therefore the description is not repeated.

FIG. **2** also shows an optional line **15***a* for recycling part of the tail gas **15** from the unit HRU for feeding the primary reformer SMR.

FIG. **3** shows an ATR-based process, similar to FIG. **1**, but comprising a purification of the process fraction of the synthesis gas in a section PUR, which in this example comprises a PSA unit.

The fuel fraction **14** separated from the CO2-depleted synthesis gas **12** is divided into a first portion **14***a* used as fuel in a furnace in the front end, for example in the block AUX, and a second portion **14***b* exported as excess fuel. The remaining part **18** of synthesis gas is further treated in the PSA unit.

A portion **23** of the effluent of the PSA unit is (optionally) exported as excess fuel. Said portion **23** has a greater hydrogen purity than the gas portion **14***b*.

In the example shown in FIG. **3**, the portion **14***a* of synthesis gas separated as fuel fraction, together with a tail gas **25** of the PSA unit, feeds one or more users of the block AUX via the fuel line **26**.

FIG. **4** shows a process based on POX, comprising purification of the process fraction of the synthesis gas in a section PUR comprising dryer and LNW (liquid nitrogen wash).

In a similar manner to the embodiment shown in FIG. **3**, also in this case the fuel fraction **14** separated from the CO2-depleted synthesis gas **12** is split into a first portion **14***a* used as fuel for example in the block AUX, and a second portion **14***b* exported as excess fuel. Said portion **14***a*, together with a tail gas **35** of the section PUR, feeds one or more users of the block AUX via the fuel line **36**. Said tail gas **35** results from the combination of the tail gas of the LNW and of the dryer.

The process according to the invention allows to produce ammonia with emissions of CO2 of about 0.1 t/t compared to about 0.7 t/t in the prior art.

All the configurations illustrated may be the result of revamping of an ammonia plant with air-fed secondary reformer.

In one embodiment, the revamping procedure comprises essentially the following steps:

installing the ASU unit in order to generate the flow **22** of oxygen or enriched air;

modifying the secondary reformer in order to accept said flow **22** instead of air;

increasing the fraction of natural gas intended for the process and reducing the fraction of natural gas intended for fuel;

revamping the existing section for desulphurization of the natural gas so as to increase the capacity thereof owing to the greater process gas flowrate;

revamping the existing section CDR so as to increase the capacity thereof owing to the greater quantity of CO2 to be separated.

It can be understood that the revamping does not require costly modifications to the reformer, the exchangers and piping of the front end and the shift section. This is due to the fact that the volumetric flowrate of the gas through the front end does not increase, despite the generation of the additional gas fraction (fuel fraction).

EXAMPLE

The following Table 1 refers to a plant with a capacity of 3000 metric tonnes per day (MTD) of ammonia produced.

Table 1 compares the following options:

(1) Plant of the prior art with primary reformer and air-fed secondary reformer.

(2) Plant of the prior art, as per option (1), with capturing of the CO2 from the fumes of the primary reformer.

(3) Plant according to the invention, as per FIG. **1**.

(4) Plant according to the invention, as per FIG. **2**.

TABLE 1

		Option			
		(1) Prior art	(2) Prior art	(3) Inv.	(4) Inv.
NH3 production	MTD	3000	3000	3000	3000
Net Natural Gas consumption based on gas LHV (FEED + FUEL-Steam exported e.g. to urea)	Gcal/t NH3	6.7	7.4	7.0	6.9
	Gcal/t NH3		+0.7	+0.3	+0.2

TABLE 1-continued

		Option			
		(1) Prior art	(2) Prior art	(3) Inv.	(4) Inv.
CO2 captured in process	MTD	3600	3600	5200	5100
CO2 to atmosphere (contained in flue gas)	MTD	2100	200	200	200
CO2 to atmosphere (contained in flue gas)	t/t NH3	0.7	0.1	0.1	0.1
Main Equipment size					
Total fired heater duty (reformer/fired heater + auxiliary boiler)	%	100	120	75	105
Process CO2 removal capacity	%	100	100	145	140
ASU O2 capacity	%	n/a	n/a	100	60
Flowrate of front end (secondary output/ATR)	%	100	100	120	97

The table shows that the process according to the invention (option 3) requires a front end suitable for producing also the gas fraction to be used as fuel in the furnaces; in fact the quantity of CO2 captured in the process amounts to 5200 MTD compared to 3600 for options (1) and (2), and the synthesis gas flowrate in the front end is about 20% more than FIGS. **1** and **2**. Despite this, the consumption of the plant is much less than that of option (2) (7.0 instead of 7.4 Gcal/MT) and is competitive with the plant without capturing according to option (1). The total duty of the furnaces is only 75% of option (1).

In option (4) the energy consumption obtained is less than in option (3), i.e. equal to 6.9 Gcal/MT, and also the cost of the plant is less. This because, in option (4), the quantity of CO2 separated in the process is less than in option (3); the duty of the furnaces is greater than in (3), but is comparable with that of options (1) and (2); the oxygen consumption is markedly less than (3); the flowrate in the front end is markedly less than (3) and comparable with (1) and (2).

The examples show how the novel process is more efficient and competitive than the prior art.

The example also shows the advantage of modifying a plant operating as per option (1), preferably implementing option (4). In fact, in this case the duty of the furnaces and the flowrate of the gases remain substantially unvaried, while the CO2 emissions are reduced. The invention thus achieves the object of minimizing the CO2 emissions of a conventional plant without losing ammonia production.

The following Table 2 refers to a plant with a capacity of 3000 metric tonnes per day (MTD) of ammonia produced, which is self-sufficient from the point of view of the steam and electric power. The process comprises the consumption relating to the compression of the CO2 sequestered up to the pressure of 100 bar. For each process, the natural gas consumption and the CO2 emissions indicated also consider the superheated steam production in AUX for driving all the turbines, and the production of the electric power necessary for the process.

Table 2 compares the following options:

(1) Plant according to the invention, with SMR+ATR as per FIG. **2**, in the following variants:

a. with the overall S/C ratio=2.7, shift composed of HTS and LTS, methanator, trim fuel with flowrate corresponding to 10% of the duty required by the furnace;

b. as for 1 a, but without trim fuel.

(2) Plant according to the invention, with pre-reformer+ATR as per FIG. **3**, in the following variants:

a. with the overall S/C ratio=2, shift composed of MTS and LTS, PSA, trim fuel with flowrate corresponding to 10% of the duty required by the furnace;

b. as for 2a, without trim fuel, with the Selectoxo™ process downstream of SHF and upstream of CDR for converting the residual CO.

(3) Plant according to the invention, with POX, as per FIG. **4**, in the variants:

a. with the overall S/C ratio=2, shift composed of MTS and LTS, LNW dryer, trim fuel with flowrate corresponding to 10% of required duty of the furnace;

b. as for 2a, without trim fuel, with selective catalytic oxidation of CO (Selectoxo™ process) downstream of the shift reaction and upstream of the CO2 removal.

TABLE 2

	1a: SMR + ATR	1b SMR + ATR	2a ATR	2b ATR	3a POX	3b POX
Daily production of NH3, MTD	3000	3000	3000	3000	3000	3000
Daily throughput of sequestered CO2, MTD	5600	5800	5100	5300	5350	5600
Net consumption of natural gas (for Example 1a), dimensionless	100%	100%	93%	93%	95%	95%

TABLE 2-continued

	1a: SMR + ATR	1b SMR + ATR	2a ATR	2b ATR	3a POX	3b POX
CO2 emissions into atmosphere per unit of ammonia produced, t CO2/t NH3	0.15	0.075	0.17	0.10	0.15	0.05
Distribution of the CO2 emissions						
trim fuel	50%	zero	20%	zero	20%	zero
CH4 slip in the process gas	15%	29%	40%	79%	30%	63%
CO slip in the process gas	34%	69%	39%	19%	49%	34%
CO2 slip in the process gas	1%	2%	1%	2%	1%	3%

In Table 2:

"Trim fuel" as defined in the patent;

"CH4 slip in the process gas" is the residual methane content of the synthesis gas produced in the front end (i.e. in SMR+ATR in option 1, in the pre-reformer+ATR in option 2, POX in option 3), quantified upstream of optional methanation.

"CO slip in the process gas" is the residual carbon monoxide content of the synthesis gas downstream of the shift section;

"CO2 slip in the process gas" is the residual carbon dioxide content of the synthesis gas downstream of the CO2 removal section;

Several comments may be made in view of Table 2:

- In the case of SMR+ATR in option 1a, the trim fuel provides the greatest percentage of the CO2 emissions; avoiding the trim fuel by exporting surplus fuel enables the emissions to be significantly reduced to less than 0.1 t/t, as shown in the Table for option 1b; at the same time, the quantity of sequestered CO2 increases from 5600 to 5800 MTD.
- In the case of SMR+ATR, the CO slip in the process gas provides the second greatest percentage of the CO2 emissions in option 1a, and provides the greatest percentage in option 1b; application of the Selectoxo process to option 1a or 1b would significantly reduce the CO2 emissions; the CH4 slip in the process gas and the CO2 slip in the process gas provides a smaller percentage of the CO2 emissions.
- The overall energy consumption of the options based on ATR and POX+purification (2 and 3) is decidedly lower than that of the options based on SMR+ATR (1a and 1b); this is mainly due to the synthesis gas purification (which improves the efficiency of the synthesis section and avoids the purge); the quantity of CO2 sequestered in these options (2a, 3a; or 2b, 3b) is consequently less than in options 1a or 1b.
- The emissions due to the use of the trim fuel in options 2a (ATR) and 3a are of about 20% of the total emissions, much less than in option 1a, by way of confirmation of the fact that the heat required by the furnace in these two options is much less than in option 1a.
- In the embodiments with ATR or POX, the residual CO and CH4 are of higher relevance owing to the lower S/C ratio at which ATR and POX operate compared to SMR+ATR; POX operates at a higher temperature than ATR, which results in a smaller residual amount of CH4, but in a greater residual amount of CO.
- In both the options 2b and 3b, the improvement achieved by selective oxidation of CO, in order to reduce the CO slip, and by avoiding trim fuel, is evident.
- It should be noted that both POX and ATR achieve very low emissions—as low as 0.05 for POX and 0.1 for ATR—comparable with those achieved by SMR+ATR, but with lower energy consumption, and therefore preferable.

The above example shows how the invention is able to achieve extremely low CO2 emission levels, corresponding to almost total capture (>98%), while maintaining competitive energy consumption levels.

The invention claimed is:

1. A process for synthesis of ammonia from natural gas, the process comprising:

conversion of a charge of desulphurized natural gas and steam, with oxygen-enriched air or with oxygen, into a synthesis gas containing hydrogen, CO and CO2, in a conversion section;

treatment of said synthesis gas including at least a shift reaction of the carbon monoxide into CO2, and subsequent separation of CO2 from the gas, thus obtaining a CO2-depleted synthesis gas and a CO2-rich gaseous flow containing the CO2 separated from the gas;

separation of a part of said CO2-depleted synthesis gas as fuel fraction, wherein said fuel fraction is fed as fuel to at least one furnace and wherein said separation of the fuel fraction includes the split of said CO2-depleted synthesis gas into at least a first stream and a second stream, said first and second streams having the same composition, wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia.

2. The process of claim **1**, wherein the first stream forms the fuel fraction and the second stream is the process gas intended for the synthesis of ammonia after further purification.

3. The process of claim **1**, wherein said fuel fraction is between 1% and 40% of the total amount of said CO2-depleted syngas.

4. The process of claim **1**, wherein said fuel fraction is between 10% and 30% of the total amount of said CO2-depleted syngas.

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5. The process of claim 1, further comprising a step for methanation of the synthesis gas and/or addition of nitrogen to the synthesis gas.

6. The process of claim 5, wherein said fuel fraction is separated upstream of the methanation step or upstream of the nitrogen addition step.

7. The process of claim 1, wherein said CO2-depleted syngas contains no more than 1000 ppm by volume of CO2.

8. The process of claim 1, wherein said enriched air contains at least 50% oxygen.

9. The process of claim 1, wherein said enriched air contains at least 90% oxygen.

10. The process of claim 1, wherein said fuel fraction of the synthesis gas feeds one or more of the following apparatuses: a steam production and/or superheating furnace; one or more burners of a primary steam reformer; or one or more furnaces for pre-heating the charge of an autothermal reformer or partial oxidation reactor or natural-gas desulphurization section.

11. The process of claim 1, wherein: a purge gas of the ammonia synthesis process, containing hydrogen and methane, is treated so as to recover the hydrogen contained in the purge gas, obtaining a hydrogen-rich gas and a tail gas containing methane; at least part of said tail gas is recycled as process gas and subjected to said step of conversion of the natural gas into synthesis gas.

12. The process of claim 1, wherein: a part of said CO2-depleted syngas is treated in a unit for separation of nitrogen, obtaining a first stream of nitrogen-depleted syngas and a second nitrogen-enriched stream; at least one part of said first stream, is used as fuel; any remaining part of said first stream is fed to the synthesis of ammonia together with the second stream.

13. The process of claim 1, further comprising a step of expansion, with production of mechanical work, of the CO2-depleted syngas, after heating the CO2-depleted syngas.

14. The process of claim 1, wherein the overall steam/carbon ratio in the conversion step is greater than 2.0.

15. The process of claim 1, wherein the overall steam/carbon ratio in the conversion step is greater than 2.4.

16. The process of claim 1, wherein the overall steam/carbon ratio in the conversion step is greater than 2.7.

17. The process of claim 1, wherein

said synthesis gas fuel fraction forms all of the fuel of the furnaces used in the conversion section, or

an amount of natural gas is provided as trim fuel, said trim fuel accounting for not more than 15% of the total combustion heat.

18. The process of claim 1, wherein:

the fuel fraction is produced in excess with respect to the fuel necessary for the conversion section, the quantity of said fuel fraction exceeding that required being exported from the process; and

regulation of the conversion section is performed by modulating the quantity of said fuel fraction directed towards the conversion section and the quantity exported from the process.

19. The process of claim 1, wherein:

the conversion of the natural gas charge into synthesis gas includes a step of autothermal reforming, or a step of partial oxidation;

said step of autothermal reforming or partial oxidation is performed with a steam/carbon ratio not greater than 2.

20. The process of claim 1, wherein the conversion of the natural gas into synthesis gas includes primary reforming of the natural gas in the presence of steam and secondary reforming performed with said oxygen flow or enriched air.

21. A method for revamping a plant for synthesis of ammonia from natural gas or ammonia/urea plant, wherein the plant includes a reforming section that includes a primary steam reformer and an air-fired secondary reformer, and a section for treatment of the synthesis gas by a shift reaction of carbon monoxide into carbon dioxide, and decarbonation; the method comprising:

providing a flow of enriched air or oxygen and using said flow as oxidant, instead of air, for the secondary reformer;

separating a part of the synthesis gas, downstream of decarbonation, for use as fuel fraction, and allocating a remaining process fraction of the synthesis gas for ammonia conversion;

feeding said fuel fraction of the gas, which has a reduced CO2 content, as fuel for at least one furnace of the plant.

22. The method of claim 21, further comprising installing an air separation unit so as to provide said oxygen or enriched air flow, wherein said separation unit also provides a nitrogen flow which is added to the process fraction of the synthesis gas in order to obtain the desired H2/N2 ratio.

23. The method of claim 21, wherein the section for treatment of the synthesis gas by the shift reaction of carbon monoxide includes methanation.

* * * * *

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(12) **United States Patent**
Licht et al.

(10) **Patent No.: US 8,137,422 B2**
(45) **Date of Patent: Mar. 20, 2012**

(54) **STEAM-HYDROCARBON REFORMING WITH REDUCED CARBON DIOXIDE EMISSIONS**

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(73) Assignee: **Air Products and Chemicals, Inc.**, Allentown, PA (US)

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C01B 3/34 (2006.01)
C10J 3/46 (2006.01)

(52) **U.S. Cl.** ..... **48/197 R**; 48/198.1; 48/198.3; 423/650; 423/651; 423/652; 423/655; 252/373

(58) **Field of Classification Search** ..... 48/197 R, 48/198.1, 198.3; 423/650, 651, 652, 655; 252/373

See application file for complete search history.

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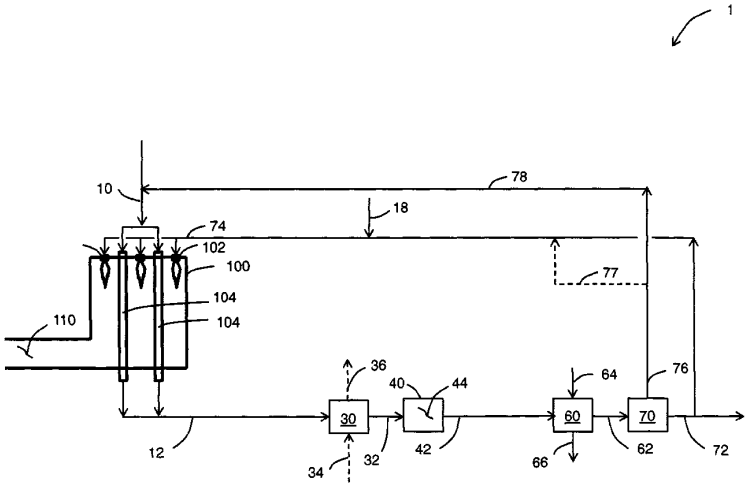
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(74) *Attorney, Agent, or Firm* — Bryan C. Hoke, Jr.

(57) **ABSTRACT**

A process for producing a hydrogen-containing product gas with reduced carbon dioxide emissions compared to conventional hydrogen production processes. A hydrocarbon and steam are reformed in a reformer and the resulting reformate stream is shifted in one or more shift reactors. The shifted mixture is scrubbed to remove carbon dioxide to form a carbon dioxide-depleted stream. The carbon dioxide-depleted stream is separated to form a hydrogen-containing product gas and a by-product gas. A portion of the hydrogen containing product gas is used as a fuel in the reformer and a portion of the by-product gas is recycled back into the process. The process may optionally include reforming in a pre-reformer and/or an oxygen secondary reformer.

12 Claims, 4 Drawing Sheets



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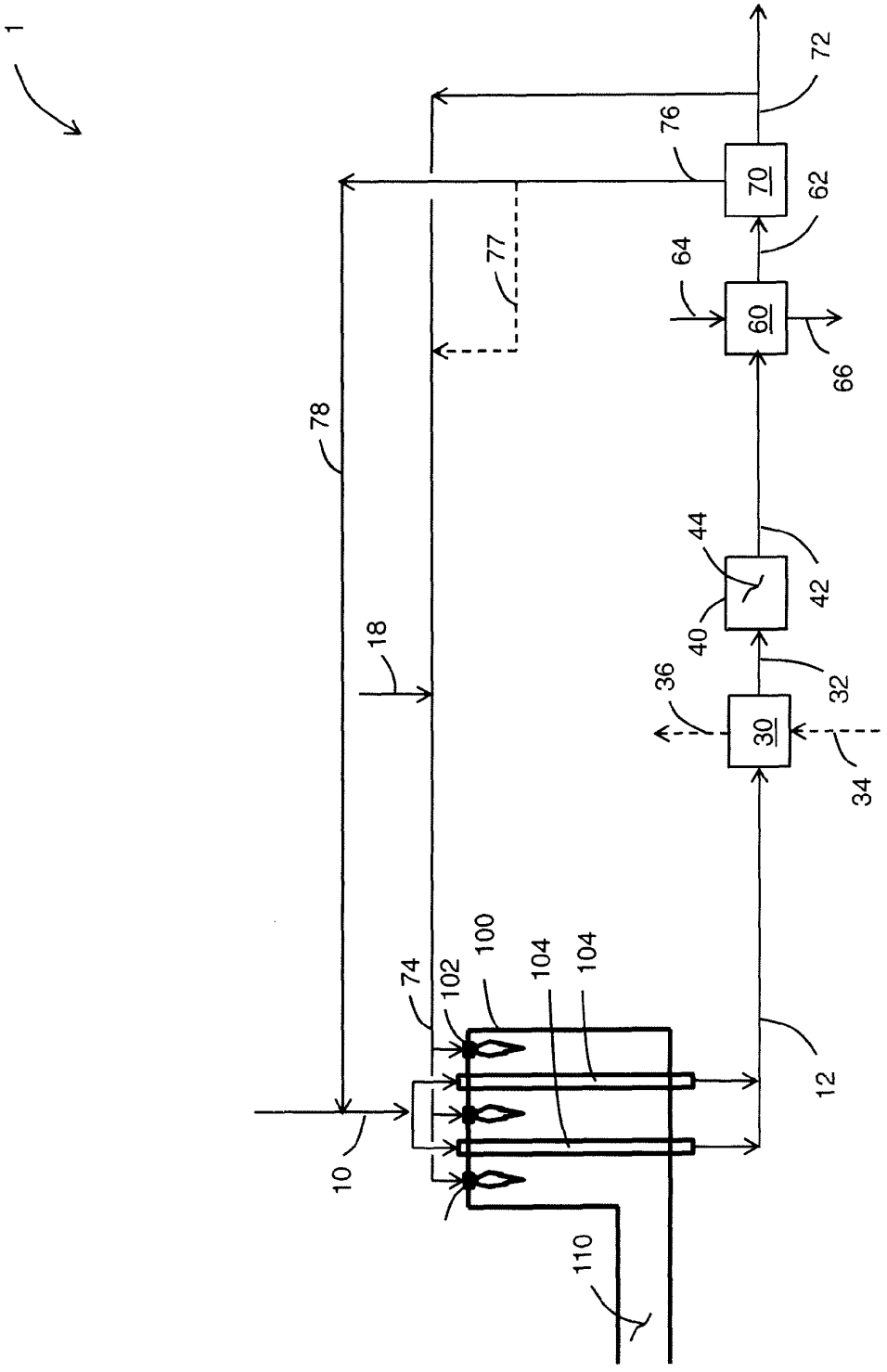

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FIG. 1

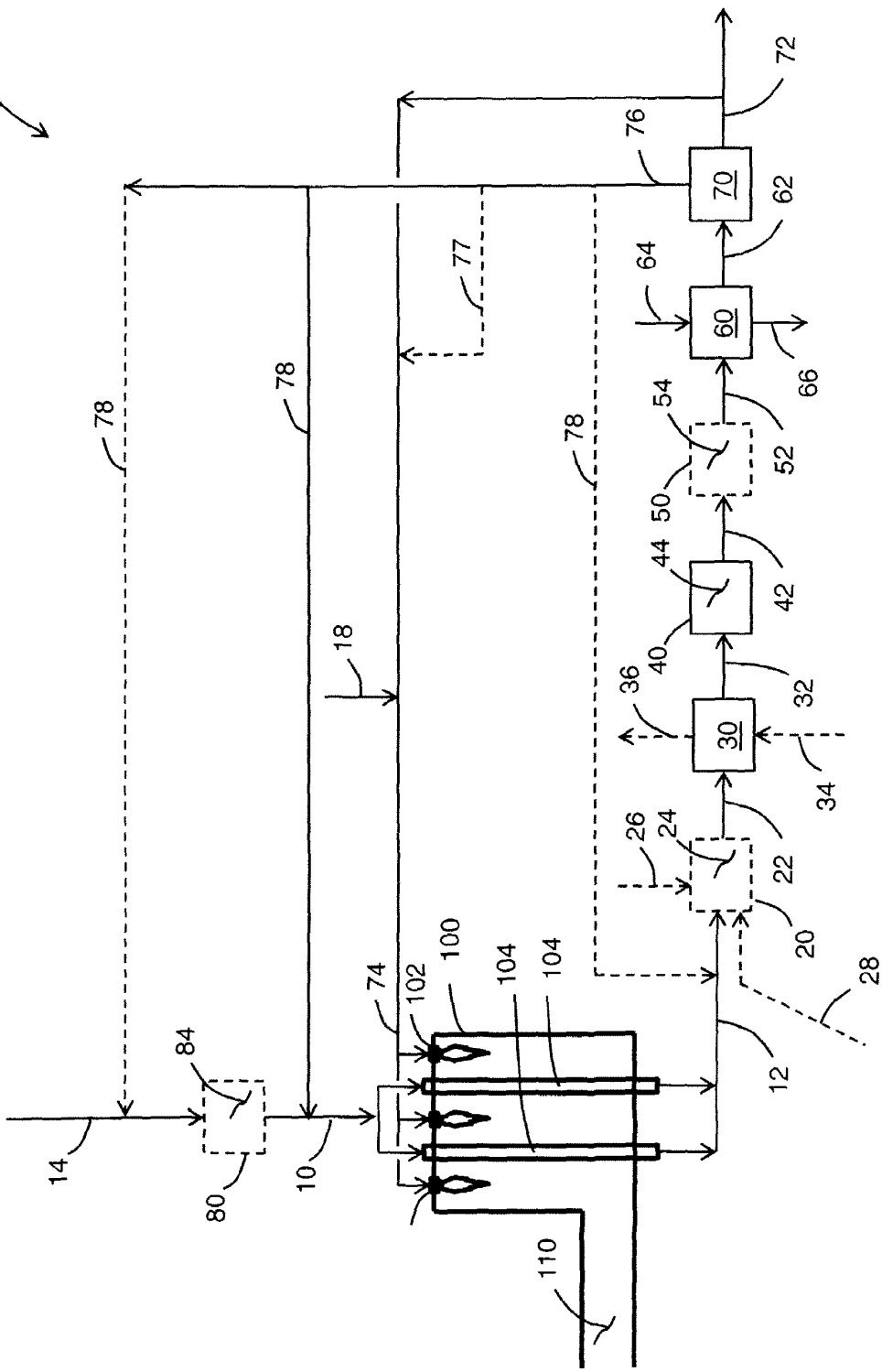

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FIG. 2

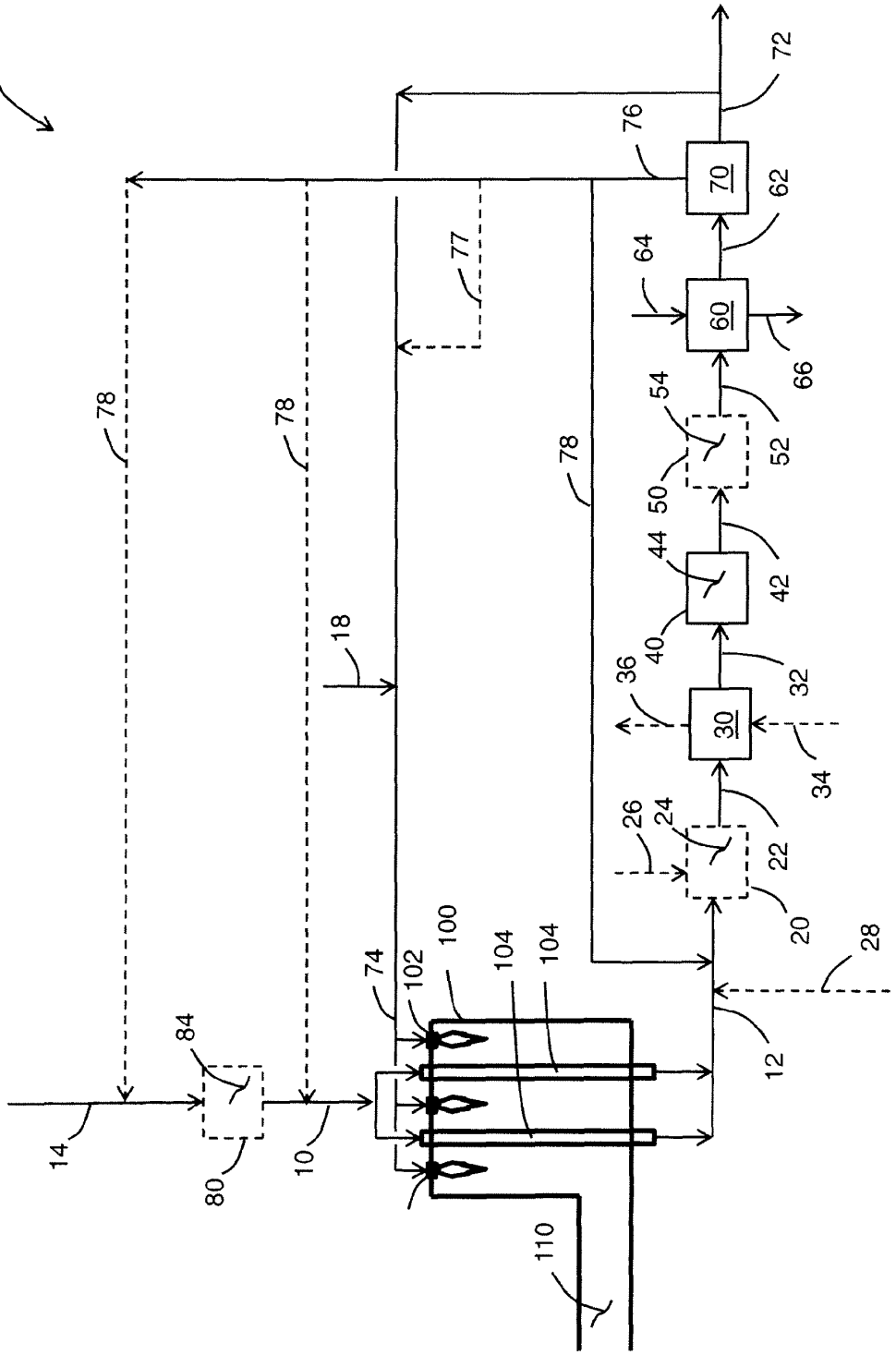

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FIG. 3

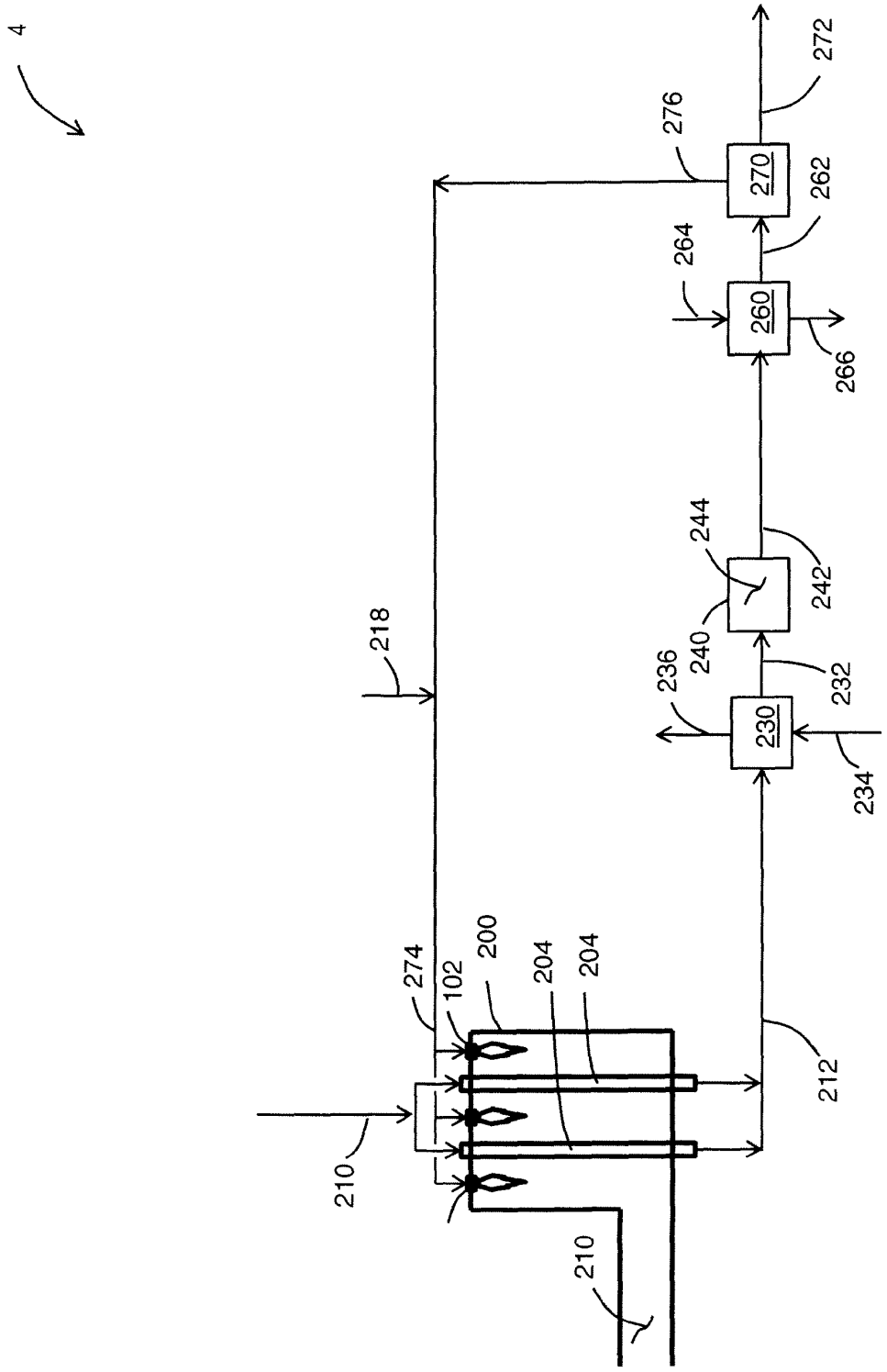


FIG. 4 Prior Art

STEAM-HYDROCARBON REFORMING WITH REDUCED CARBON DIOXIDE EMISSIONS

BACKGROUND

There is growing pressure to reduce carbon dioxide emissions from industrial processes. A large hydrogen production plant may produce up to 900,000 metric tons of carbon dioxide per year, thus it may be considered a significant source of carbon dioxide.

In Europe, Canada, and California, carbon dioxide reduction regulations are being phased in gradually. This means that greenhouse gas (GHG) legislation remains a key consideration in projects in the 2012-2015 timeframe. The current understanding on this issue is that new plants will have to plan for carbon dioxide capture but may not be required to install and operate such systems at the project on-stream date. Therefore, industry desires a flexible carbon dioxide capture ready design that may be implemented when needed.

Industry desires to produce hydrogen by steam-hydrocarbon reforming while capturing carbon dioxide thereby decreasing or eliminating carbon dioxide emissions.

Industry desires to adjust the amount of carbon dioxide capture based on regulations and economics.

Industry desires an energy efficient large-scale hydrogen production process with decreased carbon dioxide emissions compared to conventional processes.

BRIEF SUMMARY

The present invention relates to a process for producing a hydrogen-containing product gas. The process comprises:

(a) introducing a process stream comprising steam and at least one hydrocarbon selected from the group consisting of methane, ethane, propane, butane, pentane, and hexane into a plurality of catalyst-containing reformer tubes in a reformer furnace and reacting the process stream inside the plurality of catalyst-containing reformer tubes at a first temperature ranging from 700° C. to 1000° C. and a first pressure ranging from 2 to 50 atmospheres to form a reformate stream comprising hydrogen, carbon monoxide, methane and steam and withdrawing the reformate stream from the plurality of catalyst-containing reformer tubes;

(b) reacting the reformate stream in the presence of a shift catalyst at a second temperature ranging from 190° C. to 500° C. and a second pressure ranging from 2 to 50 atmospheres to form a second process stream comprising carbon dioxide, hydrogen, carbon monoxide and methane;

(c) scrubbing the second process stream with a wash stream to form a carbon dioxide-depleted stream and a carbon dioxide-loaded wash stream;

(d) separating the carbon dioxide-depleted stream to form the hydrogen-containing product gas and a by-product gas comprising methane and carbon monoxide;

(e) introducing a portion of the by-product gas into the process stream at a location upstream of the plurality of catalyst-containing reformer tubes and/or into the reformate stream at a location upstream of a reforming catalyst in a secondary reforming reactor; and

(f) combusting a fuel gas comprising a portion of the hydrogen-containing product gas, optionally a portion of the by-product gas, and optionally a supplementary fuel in the reformer furnace external to the plurality of catalyst-containing reformer tubes to supply energy for reacting the process stream inside the plurality of catalyst-containing reformer tubes, and withdrawing a flue gas from the reformer furnace.

50% to 98% by volume of the by-product gas formed in step (d) may be introduced into the process stream in step (e).

The process may comprise reacting the process stream in the presence of a second reforming catalyst in an unfired reactor at a third temperature ranging from 425° C. to 600° C. and a third pressure ranging from 2 to 50 atmospheres to form carbon dioxide and hydrogen in the process stream prior to introducing the process stream into the plurality of catalyst containing reformer tubes. The portion of the by-product gas may be introduced into the process stream upstream of the unfired reactor. The process stream reacted in the unfired reactor may comprise a portion of the by-product gas.

The process may comprise:

introducing an oxygen-rich gas into the reformate stream after withdrawing the reformate stream from the plurality of catalyst-containing reformer tubes to partially oxidize the reformate stream; and

reacting the partially oxidized reformate stream in the presence of the reforming catalyst in the secondary reforming reactor under reaction conditions sufficient to form reaction products comprising carbon monoxide and hydrogen in the reformate stream before reacting the reformate stream in the presence of the shift catalyst.

The portion of the by-product gas may be introduced into the reformate stream at the location upstream of the secondary reforming reactor. The reformate stream may comprise at least a portion of the by-product gas.

The process may comprise:

introducing a feed gas comprising at least one hydrocarbon and optionally steam into the reformate stream after withdrawing the reformate stream from the plurality of catalyst-containing reformer tubes, the at least one hydrocarbon selected from the group consisting of methane, ethane, propane, butane, pentane, and hexane;

introducing an oxygen-rich gas into the reformate stream after withdrawing the reformate stream from the plurality of catalyst-containing reformer tubes to partially oxidize the reformate stream; and

reacting the partially oxidized reformate stream in the presence of the reforming catalyst in the secondary reforming reactor under reaction conditions sufficient to form reaction products comprising carbon monoxide and hydrogen in the reformate stream before reacting the reformate stream in the presence of the shift catalyst.

The process may further comprise reacting the second process stream in the presence of a second shift catalyst at a fourth temperature ranging from 190° C. to 300° C. and a fourth pressure ranging from 2 to 50 atmospheres to form carbon dioxide and hydrogen in the second process stream prior to the step of scrubbing the second process stream. The second shift catalyst may comprise copper.

The fuel gas may comprise 30 volume % to 98 volume % hydrogen-containing product gas and 2 volume % to 70 volume % by-product gas.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

FIG. **1** is a process flow diagram for a process for producing a hydrogen-containing product gas with reduced carbon dioxide emissions.

FIG. **2** is another process flow diagram for a process for producing a hydrogen-containing product gas with reduced carbon dioxide emissions.

FIG. **3** is another process flow diagram for a process for producing a hydrogen-containing product gas with reduced carbon dioxide emissions.

FIG. **4** is a process flow diagram for a prior art process for producing a hydrogen-containing product gas.

DETAILED DESCRIPTION

The articles "a" and "an" as used herein mean one or more when applied to any feature in embodiments of the present invention described in the specification and claims. The use of "a" and "an" does not limit the meaning to a single feature unless such a limit is specifically stated. The article "the" preceding singular or plural nouns or noun phrases denotes a particular specified feature or particular specified features and may have a singular or plural connotation depending upon the context in which it is used. The adjective "any" means one, some, or all indiscriminately of whatever quantity.

The phrase "at least a portion" means "a portion or all."

As used herein, "plurality" means at least two.

For the purposes of simplicity and clarity, detailed descriptions of well-known devices, circuits, and methods are omitted so as not to obscure the description of the present invention with unnecessary detail.

The present invention relates to a process for producing a hydrogen-containing product gas. The process is particularly useful for producing a hydrogen-containing product gas with reduced carbon dioxide emissions compared to conventional steam/hydrocarbon reforming processes.

With reference to FIGS. **1-3**, the process comprises introducing a process stream **10** comprising steam and at least one hydrocarbon selected from the group consisting of methane, ethane, propane, butane, pentane, and hexane into a plurality of catalyst-containing reformer tubes **104** in a reformer furnace **100** and reacting the at least one hydrocarbon and steam inside the plurality of catalyst-containing reformer tubes **104** at a temperature ranging from 700° C. to 1000° C. and a pressure ranging from 2 to 50 atmospheres to form hydrogen and carbon monoxide in the process stream **10** and withdrawing a reformate stream **12** from the plurality of catalyst-containing reformer tubes **104**.

As used herein, a reformate stream is any stream comprising hydrogen and carbon monoxide formed from the reforming reaction of a hydrocarbon and steam.

The process stream **10** may contain more than one hydrocarbon. The process stream may be initially formed from natural gas and steam, liquefied petroleum gas (LPG) and steam, naphtha and steam and/or other feedstocks known in the art. As described in more detail below, the process stream **10** may be processed in a prereformer prior to introducing the process stream **10** into the plurality of catalyst-containing reformer tubes **104**.

Reformer furnaces with a plurality of catalyst-containing reformer tubes, i.e. tubular reformers, are well known in the art. Suitable materials and methods of construction are known. Catalyst in the catalyst-containing reformer tubes may be any suitable catalyst known in the art, for example, a supported catalyst comprising nickel.

The reformate stream **12** withdrawn from the plurality of catalyst-containing reformer tubes **104** is cooled in a heat exchanger **30** which may be a boiler to produce steam **36** from a water-containing stream **34** by indirect heat transfer and thereby remove heat from the reformate stream **12**. Reformate stream **32** is withdrawn from the boiler **30**. Reformate stream **12** may be passed to the heat exchanger **30** to remove heat from the reformate stream **12** and improve the thermal efficiency of the process.

The reformate stream is passed to shift reactor **40**. The process further comprises reacting carbon monoxide and steam in the reformate stream **32** in the presence of a shift catalyst **44** at a temperature ranging from 190° C. to 500° C. and a pressure ranging from 2 to 50 atmospheres to form a second process stream **42** comprising carbon dioxide, hydrogen, carbon monoxide and methane.

Shift reactors and suitable shift catalysts are known in the art. The shift catalyst may be an iron-based high temperature shift catalyst, or a copper-based medium temperature shift catalyst, or a copper-based low temperature shift catalyst. Any suitable shift catalyst may be used. One skilled in the art can readily select a suitable shift catalyst.

The shift catalyst **44** may comprise iron oxide and the reaction temperature may be from 310° C. to 500° C. or 310° C. to 400° C.

The shift catalyst **44** may comprise copper and the reaction temperature may be from 200° C. to 400° C. or 200° C. to 350° C.

The process further comprises scrubbing the second process stream **42** with a wash stream **64** to form a carbon dioxide-depleted stream **62** and a carbon dioxide-loaded wash stream **66**. Scrubbing may be done in a so-called gas scrubber **60**. Carbon dioxide scrubbing is also known in the art as acid gas removal. The wash stream **64** may be any scrubbing fluid known in the art, for example N-methyl diethanolamine (aMDEA). Other scrubbing fluids associated with other scrubbing methods, for example, Rectisol®, Selexol®, Genosorb®, and sulfinol are known in the art.

The term "depleted" means having a lesser mole % concentration of the indicated component than the original stream from which it was formed. This means that carbon dioxide-depleted stream has a lesser mole % concentration of carbon dioxide than the second process stream which was introduced into the scrubber **60**. The wash stream, having an affinity for carbon dioxide will become "loaded" with carbon dioxide. Carbon dioxide will become absorbed or otherwise taken in by the wash stream **64**.

The carbon dioxide-depleted stream **62** contains only a small amount of carbon dioxide.

Water may also be removed from the second process stream **42** prior to the gas scrubber **60** and/or in the gas scrubber **60**.

The process further comprises separating the carbon dioxide-depleted stream **62** in a separator **70** to form the hydrogen-containing product gas **72** and a by-product gas **76** comprising methane and carbon monoxide. The step of separating the carbon dioxide-depleted stream may be done by pressure swing adsorption and/or temperature swing adsorption. The separator **70** may be a pressure swing adsorber and/or temperature swing adsorber. Construction and operation of pressure swing adsorbers and temperature swing adsorbers are known in the art. Suitable devices and operating conditions may be selected by one skilled in the art.

Simpler and less efficient pressure swing adsorbers and/or temperature swing adsorbers and their associated processes may be used since a portion of the hydrogen-containing product gas **72** may be blended with the by-product gas **76** for use as a fuel in the reformer furnace (described below).

More water may be removed from the carbon dioxide-depleted stream **62** prior to separating the carbon dioxide-depleted stream. Water removal is conventional and water may be removed by any suitable method and suitable water removal device known in the art.

With reference to FIGS. **1-3**, the process further comprises introducing a portion **78** of the by-product gas **76** into the process stream **10**, **14** at a location upstream of the plurality of catalyst-containing reformer tubes **104** and/or into the reformate stream **12** at a location upstream of a reforming catalyst in a secondary reforming reactor **20** (described later). The portion **78** of the by-product gas **76** may be introduced into the process stream at one or more locations in the process. The portion **78** of the by-product gas **76** may be introduced into the process stream **10**, **14** at a location upstream of the plurality of catalyst-containing reformer tubes **104**. The portion **78** of the by-product gas **76** may be introduced into the reformate stream **12** at a location upstream of a reforming catalyst

in a secondary reforming reactor **20**. The portion **78** of the by-product gas **76** may be introduced into the process stream **10**, **14** at a location upstream of the plurality of catalyst-containing reformer tubes **104** and introduced into the reformate stream **12** at a location upstream of a reforming catalyst in a secondary reforming reactor **20**.

The portion **78** of the by-product gas **76** may be a divided portion of the by-product stream **76** formed from the separation of the carbon dioxide-depleted stream **62** and thereby have the same composition as the by-product stream **76** formed from the separation of the carbon dioxide-depleted stream **62**. As used herein a "divided portion" of a stream is a portion having the same chemical composition as the stream from which it was taken.

By introducing the by-product gas back into the process stream for further processing, additional carbon in the stream may be converted to carbon dioxide and removed via the scrubbing step. Any by-product gas from the separator that is recycled back to the process feed stream reduces the CO_2 emitted from the overall hydrogen production process.

50% to 98% by volume of the by-product gas **76** formed by the separation of the carbon dioxide-depleted stream **62** in separator **70** may be introduced into the process stream **10**, **12**, and/or **14**. The amount of CO_2 emitted from the hydrogen production process can be effectively reduced by increasing the amount of by-product gas that is recycled back to process feed stream.

The process further comprises combusting a fuel gas **74** comprising a portion of the hydrogen-containing product gas **72**, optionally a portion **77** of the by-product gas **76**, and optionally a supplementary fuel **18** in the reformer furnace **100** external to the plurality of catalyst-containing reformer tubes **104** to supply energy for reacting methane and steam inside the plurality of catalyst-containing reformer tubes **104**. Flue gas **110** is withdrawn from the reformer furnace **100**, and because the fuel gas **74** comprises hydrogen in an amount greater than conventional reformer furnaces, the flue gas will contain a reduced amount of carbon dioxide compared to conventional reformer furnaces. The supplementary fuel **18** is often called a trim fuel and may be, for example, natural gas. The portion of the hydrogen-containing product gas **72** and the portion of the by-product gas **76** may be divided portions of the respective gases.

The amount of carbon dioxide emissions in the flue gas **110** can be adjusted by the amount of hydrogen-containing product gas **72**, the amount of by-product gas **76** and the amount of supplementary fuel **18** that are used as fuel.

For the case where most of the by-product gas **76** is recycled to the process stream and the fuel gas **74** consists essentially of the hydrogen-containing product gas **72**, the carbon dioxide emissions in the flue gas **110** will be substantially reduced. The fuel gas may comprise 90 volume % to about 98 volume % hydrogen-containing product gas **72**. For practical purposes, at least a portion of the by-product gas **76** may be used as fuel **74** to prevent the build up of inert gases (e.g. N_2 and Ar) in the process streams. Alternatively, and less desirably, a portion of the by-product gas **76** may be used in another process and/or disposed.

FIG. **2** and FIG. **3** show additional optional features, for example a so-called prereformer **80**, an oxygen secondary reformer **20**, and a second shift reactor **50**.

A prereformer is defined herein as any unfired vessel that converts hydrocarbon feedstock by reaction with steam over a catalyst with or without heating. A prereformer may be an adiabatic fixed bed reactor. A prereformer may be a tubular reactor. A prereformer generally employs a different type of catalyst than a primary reformer, for example a high activity, high nickel content catalyst. Temperatures in a prereformer may be in the range of about 400° C. to about 600° C. Heat to a prereformer may be provided from exhaust gases from a reformer or other source, but is characterized by the lack of direct heating by a combustion flame. A prereformer and a reformer may be physically connected.

As shown in FIG. **2** and FIG. **3**, prior to introducing the process stream **10** into the plurality of catalyst-containing reformer tubes **104**, the process may further comprise introducing the process stream **14** comprising steam and at least one hydrocarbon selected from the group consisting of methane, ethane, propane, butane, pentane and hexane into reactor **80** and reacting the at least one hydrocarbon and steam in the process stream **14** in the presence of a reforming catalyst **84** in an unfired reactor (prereformer) at a temperature ranging from 400° C. to 600° C. and a pressure ranging from 2 to 50 atmospheres prior to introducing the process stream **10** comprising steam and at least one hydrocarbon selected from the group consisting of methane, ethane, propane, butane, pentane, and hexane into the plurality of catalyst containing reformer tubes **104**.

As used herein, the "process stream" includes the stream comprising steam and at least one hydrocarbon upstream of the optional prereformer **80**, if present, to the exit from the plurality of catalyst-containing reformer tubes **104**, where it becomes the "reformate stream." In case the optional prereformer **80** is not present, the process stream includes the stream comprising steam and at least one hydrocarbon upstream of the inlet of the plurality of catalyst-containing reformer tubes **104** to the exit of the plurality of catalyst-containing reformer tubes.

The hydrocarbon composition may vary as process stream **10**, **14** is reacted. For example, the at least one hydrocarbon may initially include propane and butane and after reacting in a prereformer, the at least one hydrocarbon in the process stream may be methane.

Reforming catalyst **84** may be any suitable reforming catalyst known in the art for so-called "prereforming." Prereforming is a term used to describe reforming before the main reforming step, for example in a fired reformer. Catalysts for prereforming are commercially available. Since the articles "a" and "the" mean one or more, more than one prereformer and more than one reforming catalyst may be used.

Reforming catalyst **84** may comprise at least one metal selected from a group consisting of nickel, cobalt, platinum, palladium, rhodium, ruthenium, iridium and mixtures thereof.

Reforming catalysts suitable for prereforming are discussed in U.S. Pat. Nos. 4,105,591, 3,882,636, 3,988,425, GB 969,637, GB 1,150,066, and GB 1,155,843.

Reforming catalyst **84** may be in a wide variety of shapes or forms, for example cylindrical pellets, Raschig rings, multihole shaped catalyst, etc. or other form known in the art. The catalyst size may range from about 1 mm to about 15 mm in diameter. The length of the catalyst may range from about 3 mm to 10 mm. The ideal size for a given application depends on a number of factors including the catalyst shape and nickel loading, the operating temperature, pressure, and feed composition, and the allowable pressure drop. A catalyst with a multi-hole shape with a diameter in the range from 5 mm to 25 mm and a height to diameter ratio of 0.5 to 1.2 will be suitable for reforming catalyst **102**. One skilled in the art is able to select suitable catalyst with a suitable shape for reforming catalyst **84**.

Reforming catalyst **84** may also be structured packing catalyst where the catalyst is applied as a washcoat on a structured packing. Structured packing is known in the art. As used herein, the term "structured packing" means a flow guide having a plurality of substantially parallel passages. Substantially parallel means parallel within manufacturing tolerances. Davidson, U.S. Pat. No. 4,340,501 describes a structure in a reactor vessel where the fluid is intermittently but controllably brought into contact with the vessel walls.

As shown in FIG. **2** and FIG. **3**, a portion of by-product gas **76** may be recycled back to the reactor **80**. Process stream **14** may comprise a portion of the by-product gas **76**.

FIG. **2** and FIG. **3** also show an optional secondary reforming reactor **20** located in the process between the plurality of catalyst-containing tubes **104** and the shift reactor **40**. The process may further comprise introducing an oxygen-rich gas **26** into the reformate stream **12** after withdrawing the reformate stream **12** from the plurality of catalyst-containing reformer tubes **104** to partially oxidize the reformate stream, and reacting the partially oxidized reformate stream **12** in the presence of a reforming catalyst **24** in the secondary reforming reactor **20** under reaction conditions sufficient to form reaction products comprising carbon monoxide and hydrogen in the reformate stream **22**. The oxygen-rich gas **26** may be introduced into the reformate stream **12** before reactor **20** or may be introduced into the reformate stream **12** in reactor **20**, for example through a burner.

Secondary reforming reactors are well-known in the art and used widely for the production of ammonia and methanol. Secondary reforming reactors are refractory lined vessels with one or more burners and a reforming catalyst bed. Heat required for the reforming reaction is provided by partial oxidation (combustion) of a portion of the feed.

Effluent from the primary reformer is fed to the secondary reforming reactor where it is mixed with oxygen fed through a burner. Partial oxidation reactions occur in a combustion zone proximate or just below the burner. The partially oxidized mixture then passes through a catalyst bed where the mixture is substantially thermodynamically equilibrated over the reforming catalyst.

U.S. Pat. No. 3,479,298, incorporated herein by reference, discloses a secondary reformer for the production of a hydrogen-containing gas, and discloses that if oxygen is used instead of air, the process gas leaving the secondary reformer is a gas suitable for further treatment to yield methanol or high purity hydrogen.

Tindall et al., "Alternative technologies to steam-methane reforming," *Hydrocarbon Processing*, pp. 75-82, November, 1995, also disclose a oxygen secondary reformer for producing hydrogen.

As used herein, an oxygen-rich gas is an oxygen-containing gas having an oxygen concentration of 98 volume % to 100 volume %, for example industrial grade oxygen. Oxygen is added in an amount for incomplete combustion of any hydrocarbons in the reformate stream. The resulting stream **22** is rich in hydrogen and carbon monoxide.

The reforming catalyst **24** may be any conventional gas feed type of steam reforming catalyst suitable for promoting the reaction of methane and steam to produce hydrogen. Typical suitable reforming catalysts include nickel catalysts such as nickel and/or nickel oxide supported on a carrier such as alumina. The nickel catalyst generally contains 8 to 30 weight percent nickel calculated as NiO and may additionally contain other metal or metal compound promoters. Suitable catalysts may be readily selected by one skilled in the art.

Reaction conditions sufficient to form reaction products in the secondary reforming reactor **20** include a temperature ranging from 800° C. to 1200° C., or 900° C. to 1100° C., and a pressure ranging from 2 to 50 atmospheres.

As shown in FIG. **2** and in FIG. **3**, a portion **78** of the by-product gas **76** may be introduced into the process stream **10**, **14** at a location upstream of the plurality of catalyst-containing reformer tubes **104** and/or into the reformate stream **12** at a location upstream of the secondary reforming reactor **20**. The portion **78** of the by-product gas **76** may be introduced into one of the locations or subdivided and introduced into two or more locations. For example, the portion **78** of the by-product gas **76** may be introduced into the process stream **10** just upstream of the plurality of catalyst-containing reformer tubes **104**. Alternatively, the portion **78** of the by-product gas **76** may be divided with a first portion introduced into the process steam **10** at a location upstream of the plurality of the catalyst-containing reformer tubes and a second portion of the by-product gas introduced into the reformate stream **12** upstream of the secondary reforming reactor **20**. The reformate stream **12** may comprise at least a portion of the by-product gas **76**.

Generally, not all of the by-product gas **76** will be recycled to the process stream and/or the reformate stream. Another portion **77** of the by-product stream may be introduced in the fuel gas stream **74** as shown in FIGS. **1-3**. This other portion **77** may be required to purge the process of inert gases (e.g. N_2 and Ar).

As shown in FIG. **2** and FIG. **3**, the process may comprise introducing a feed gas **28** into the reformate stream **12** after withdrawing the reformate stream **12** from the plurality of catalyst-containing reformer tubes **104**. The feed gas **28** comprises at least one hydrocarbon and optionally steam. The at least one hydrocarbon is selected from the group consisting of methane, ethane, propane, butane, pentane, and hexane. Steam addition is optional in case a suitable amount of steam remains from the primary reformer. The process may further comprise introducing an oxygen-rich gas **26** into the reformate stream after withdrawing the reformate stream from the plurality of catalyst-containing reformer tubes to partially oxidize the reformate stream. The process may then comprise reacting the partially oxidized reformate stream in the presence of the reforming catalyst **24** in the secondary reforming reactor **20** under reaction conditions sufficient to form reaction products comprising carbon monoxide and hydrogen in the reformate stream **12**.

The feed gas **28** may be introduced into the reformate stream **12** before the resultant mixture is introduced into the secondary reforming reactor **20**. The feed gas **28** may be introduced into the reformate stream **12** in the secondary reactor **20**. Typically, the oxygen-rich gas will be introduced into the secondary reactor **20** separately from the feed gas **28** and the reformate stream **12**.

The hydrocarbon source for the feed gas **28** may be the same as the hydrocarbon source for the process stream **10**, **14**.

The benefit of providing a feed gas comprising at least one hydrocarbon and reacting the feed gas in the secondary reforming reactor **20** is that the size of the reformer furnace **100** and correspondingly, the plurality of catalyst-containing reformer tubes, will be smaller. One skilled in the art can suitably optimize the size of and amount of feedstock processed in the reformer furnace **100** and the secondary reforming reactor **20**. Another benefit is that fuel requirements in the primary reformer are reduced.

As shown in FIG. **2** and in FIG. **3**, the process may include a second shift reactor **50**. The second process stream **42** withdrawn from the shift reactor **40** may be further shifted in the second shift reactor **50**. The second process stream may be suitably cooled prior to being introduced into the second shift reactor **50**. The process may then further comprise reacting carbon monoxide and steam in the second process stream **42** in the presence of shift catalyst **54** at a temperature ranging from 190° C. to 300° C. and a pressure ranging from 2 to 50 atmospheres to form carbon dioxide and hydrogen in the second process stream **52**. Shift catalyst **54** may comprise copper. Suitable catalysts may be readily selected by one skilled in the art. This additional process step, if included, would be conducted prior to the step of scrubbing the second process stream **52**.

This sequence of two shift reaction steps may be a high temperature shift followed by a low temperature shift. The high temperature shift is conducted using an iron-based shift catalyst at a temperature ranging from 310° C. to 500° C. or 310° to 400° C. The low temperature shift is conducted using a shift catalyst comprising copper and optionally zinc oxide at a temperature ranging from 190° C. to 300° C.

As used herein, the "second process stream" includes the stream comprising carbon dioxide, hydrogen, carbon monoxide and methane from the exit of the upstream shift reactor to the exit of the scrubber where a portion becomes the "carbon dioxide-depleted stream."

EXAMPLES

The present invention will be better understood with reference to the following examples, which are intended to illustrate, but not to limit the scope of the invention; the invention being defined by the claims.

All of the following examples were simulated using Aspen Plus®. The results are normalized for an output of hydrogen product from the hydrogen production process of 100,000 Nm^3/h. The output of hydrogen product is the total hydrogen produced less any amount used for combustion in the reformer. The scrubbers **60** and **260** are assumed to be 100% effective in the removal of CO_2. Water is also removed in the scrubber.

The composition of the by-product gas **76**, **276** is based on a pressure swing adsorber. A prereformer was not used in any of the examples.

Natural gas was assumed to be 98 mole % CH_4 and 2 mole % N_2.

Example 1

FIG. **4** illustrates a process flow diagram for a prior art hydrogen production process. A high temperature shift reactor **240** is used. Fuel for the reformer is provided by the by-product gas **276** and natural gas trim fuel. No hydrogen is used as fuel and none of the by-product gas is recycled back to the process stream. Results are summarized in Table 1.

CO_2 emissions of 16,167 Nm^3/h were calculated for a hydrogen product output of 100,000 Nm^3/h. Flue gas CO_2 is about 40% of the CH_4 feed. The balance of 60% is removed in the scrubber **260**. For ease of comparison with other cases, the molar ratio of CO_2 emissions to the hydrogen product output (100 000 Nm^3/h) is shown in Table 1. The CO_2/H_2 molar ratio for this base case is 0.162.

TABLE 1

Stream	No Recycle
H_2-containing product gas used as fuel (Nm^3/h)	0
CO_2 in flue gas (Nm^3/h)	16 167
By-product gas recycled (Nm^3/h)	0
By-product gas used as fuel (Nm^3/h)	28 957
Reformer duty (kW)	106 658
CO_2/H_2	0.162
Mole fraction N_2 in recycle	0.027
CH_4 feed (Nm^3/h)	40 499

Example 2

Example 2 is based on the process flow diagram shown in FIG. **1**. Fuel to fire the reformer **100** is provided by by-product gas **76** and hydrogen-containing product gas **72**. The amount of by-product gas and hydrogen-containing gas depends on the amount of by-product gas recycled to the process stream. No natural gas trim fuel is used. A high temperature shift reactor **40** is used. Several cases are summarized in Table 2 representing various amounts of recycling of the by-product gas **76** back to the process stream **10** upstream of the plurality of catalyst-containing reformer tubes **104**.

Table 2 shows the effect of by-product recycle on the molar ratio of CO_2 emissions to the hydrogen product output. With 98% of the by-product gas recycled, the CO_2/H_2 molar ratio is reduced to 0.013 compared to 0.162 for Example 1.

For this case, small amounts of by-product gas recycle do not appear to improve the molar ratio of CO_2 emissions to the hydrogen product output very much. However, with higher levels of by-product gas recycle and using hydrogen as the trim fuel, the CO_2 emissions can be reduced by an order of magnitude.

With 98% by-product gas recycle, the N_2 content of the recycle gas is 34 mole %. This represents a large amount of N_2 circulating in the process loop, and the compression power for the system will be increased as a result. The reformer duty also increases with the amount of recycle flow. With additional capital, this stream may be heat exchanged to create steam which will be produced with low CO_2 emissions. This is in contrast to fired boilers, which generate substantial CO_2 emissions.

TABLE 2

Stream	No Recycle	50% by-product gas recycle	90% by-product gas recycle	98% by-product gas recycle
H_2-containing product gas used as fuel (Nm^3/h)	6 466	25 815	65 108	88 298
CO_2 in flue gas (Nm^3/h)	15 081	12 000	5 112	1 302
By-product gas recycled (Nm^3/h)	0	21 573	74 842	136 406
By-product gas used as fuel (Nm^3/h)	30 661	21 571	8 315	2 784
Reformer duty (kW)	113 451	126 056	158 178	182 204
CO_2/H_2	0.151	0.120	0.051	0.013
Mole fraction N_2 in recycle	0.027	0.039	0.109	0.343
CH_4 feed (Nm^3/h)	40 499	42 187	45 353	47 883

Example 3

Example 3 is based on the process flow diagram shown in FIG. **1** and is similar to example 2, except that a low temperature shift reactor is used along with the high temperature shift reactor. All of the trim fuel is provided by hydrogen-containing product gas.

Results are summarized in Table 3 for various amounts of recycling of the by-product gas back to the process stream upstream of the plurality of catalyst-containing reformer tubes **104**.

TABLE 3

Stream	No Recycle	50% by-product gas recycle	90% by-product gas recycle	98% by-product gas recycle
H_2-containing product gas used as fuel (Nm^3/h)	11 752	32 128	68 683	86 388
CO_2 in flue gas (Nm^3/h)	10 322	7 901	2 844	605
By-product gas recycled (Nm^3/h)	0	17 913	54 807	101 108
By-product gas used as fuel (Nm^3/h)	26 635	17 913	6 090	2 063
Reformer duty (kW)	114 489	128 316	157 495	175 840
CO_2/H_2	0.103	0.079	0.028	0.006
Mole fraction N_2 in recycle	0.031	0.048	0.148	0.455
CH_4 feed (Nm^3/h)	41 314	42 561	45 200	47 055

The results show that use of a low temperature shift reactor is effective for reducing the amount of CO_2 emissions. Compared to example 2, the CO_2 emissions are lower for each respective amount of by-product gas recycle.

Table 3 shows the effect of by-product recycle on the molar ratio of CO_2 emissions to the hydrogen product output. With 98% of the by-product gas recycled, the CO_2/H_2 molar ratio is reduced to 0.006, which is substantially lower than example 1 where the CO_2/H_2 molar ratio was 0.162.

In general, there is greater CO_2 recovery, less CO_2 emissions, lower reformer duty and smaller volumes of recycled gas compared to respective by-product gas recycle percentages in Examples 2 and 3.

TABLE 4

Stream	No Recycle	50% by-product gas recycle	90% by-product gas recycle	98% by-product gas recycle
H_2-containing product gas used as fuel (Nm^3/h)	23 200	31 441	39 960	47 078
CO_2 in flue gas (Nm^3/h)	1 524	832	176	32
By-product gas recycled (Nm^3/h)	0	10 921	28 101	72 796
By-product gas used as fuel (Nm^3/h)	19 557	10 922	3 123	1 485
Reformer duty (kW)	84 338	82 812	83 439	94 070
CO_2/H_2	0.015	0.008	0.002	0.0003
Mole fraction N_2 in recycle	0.043	0.078	0.274	0.597
Mole fraction Ar in recycle	0.007	0.013	0.048	0.106
O_2 requirement (Nm^3/h)	13 261	14 118	14 984	15 702
CH_4 feed (Nm^3/h)	42 166	42 366	42 838	44 518

In general, there is greater CO_2 recovery, less CO_2 emissions, lower reformer duty and smaller volumes of recycled gas compared to respective by-product gas recycle percentages in Example 2.

Example 4

Example 4 is based on the process flow diagram shown in FIG. **2** and is similar to Example 3, except that an oxygen secondary reformer is used. The oxygen for the oxygen secondary reformer **20** is assumed to by 99 vol. % O_2 and 1 vol. % Ar. All of the trim fuel is provided by hydrogen-containing product gas.

Results are summarized in Table 4 for various amounts of recycling of the by-product gas back to the process stream upstream of the plurality of catalyst-containing reformer tubes **104**.

Table 4 shows the effect of by-product recycle on the molar ratio of CO_2 emissions to the hydrogen product output. With 98% of the by-product gas recycled, the CO_2/H_2 molar ratio is reduced to 0.0003, which is substantially lower than example 1 where the CO_2/H_2 molar ratio was 0.162.

With the oxygen secondary reformer, the methane slip is very low and even without a recycle stream, the CO_2 emission is nearly as low as in Example 2 with 98% by-product gas recycle.

This configuration has low reformer duty and low methane feed requirements, but has an oxygen requirement.

In general, there is greater CO_2 recovery, less CO_2 emissions, lower reformer duty and smaller volumes of recycled gas compared to respective by-product gas recycle percentages in Examples 2 and 3.

Example 5

Example 5 is based on the process flow diagram shown in FIG. **3** and is similar to Example 4, except that the by-product gas is recycled to the oxygen secondary reformer instead recycling to the primary reformer **100**. The oxygen for the oxygen secondary reformer **20** is assumed to by 99 vol. % O_2 and 1 vol. % Ar. All of the trim fuel is provided by hydrogen-containing product gas.

Results are summarized in Table 5 for various amounts of recycling of the by-product gas back to the process stream downstream of the plurality of catalyst-containing reformer tubes **104** and upstream of the oxygen secondary reformer **20**.

Table 5 shows the effect of by-product recycle on the molar ratio of CO_2 emissions to the hydrogen product output. With 98% of the by-product gas **76** recycled, the CO_2/H_2 molar ratio is reduced to 0.0003, which is substantially lower than Example 1 where the CO_2/H_2 molar ratio was 0.162. The results are not much different than that of Example 4, except that the oxygen requirement is higher and the natural gas feed is higher. With proper integration of a heat exchanger, more steam may be generated. This steam will be produced with very low CO_2 emissions compared to a fired boiler.

With the oxygen secondary reformer, the methane slip is very low and even without a recycle stream, the CO_2 emission is nearly as low as in Example 2 with 98% by-product gas recycle.

In general, there is greater CO_2 recovery, less CO_2 emissions, lower reformer duty and smaller volumes of recycled gas compared to respective by-product gas recycle percentages in Examples 2 and 3.

TABLE 5

Stream	No Recycle	50% by-product gas recycle	90% by-product gas recycle	98% by-product gas recycle
H_2-containing product gas used as fuel (Nm^3/h)	23 200	32 779	42 082	46 471
CO_2 in flue gas (Nm^3/h)	1 524	838	173	27
By-product gas recycled (Nm^3/h)	0	11 031	28 611	76 310
By-product gas used as fuel (Nm^3/h)	19 557	11 032	3 179	1 557
Reformer duty (kW)	84 338	85 669	87 695	92 817
CO_2/H_2	0.015	0.008	0.002	0.0003
Mole fraction N_2 in recycle	0.043	0.078	0.276	0.593
Mole fraction Ar in recycle	0.007	0.013	0.05	0.127
O_2 requirement (Nm^3/h)	13 261	14 333	15 935	19 805
CH_4 feed (Nm^3/h)	42 166	42 832	43 845	46 406

Although the present invention has been described as to specific embodiments or examples, it is not limited thereto, but may be changed or modified into any of various other forms without departing from the scope of the invention as defined in the accompanying claims.

We claim:

1. A process for producing a hydrogen-containing product gas, comprising:

(a) introducing a process stream comprising steam and at least one hydrocarbon selected from the group consisting of methane, ethane, propane, butane, pentane, and hexane into a plurality of catalyst-containing reformer tubes in a reformer furnace and reacting the process stream inside the plurality of catalyst-containing reformer tubes at a first temperature ranging from 700° C. to 1000° C. and a first pressure ranging from 2 to 50 atmospheres to form a reformate stream comprising hydrogen, carbon monoxide, methane and steam and withdrawing the reformate stream from the plurality of catalyst-containing reformer tubes;

(b) reacting the reformate stream in the presence of a shift catalyst at a second temperature ranging from 190° C. to 500° C. and a second pressure ranging from 2 to 50 atmospheres to form a second process stream comprising carbon dioxide, hydrogen, carbon monoxide and methane;

(c) scrubbing the second process stream with a wash stream to form a carbon dioxide-depleted stream and a carbon dioxide-loaded wash stream;

(d) separating the carbon dioxide-depleted stream to form the hydrogen-containing product gas and a by-product gas comprising methane and carbon monoxide;

(e) introducing a portion of the by-product gas into the process stream at a location upstream of the plurality of catalyst-containing reformer tubes and/or into the reformate stream at a location upstream of a reforming catalyst in a secondary reforming reactor; and

(f) combusting a fuel gas comprising a portion of the hydrogen-containing product gas, optionally a portion of the by-product gas, and optionally a supplementary fuel in the reformer furnace external to the plurality of catalyst-containing reformer tubes to supply energy for reacting the process stream inside the plurality of catalyst-containing reformer tubes, and withdrawing a flue gas from the reformer furnace.

2. The process of claim **1** wherein 50% to 98% by volume of the by-product gas formed in step (d) is introduced into the process stream in step (e).

3. The process of claim **1** further comprising:

reacting the process stream in the presence of a second reforming catalyst in an unfired reactor at a third temperature ranging from 425° C. to 600° C. and a third pressure ranging from 2 to 50 atmospheres to form carbon dioxide and hydrogen in the process stream prior to introducing the process stream into the plurality of catalyst containing reformer tubes.

4. The process of claim **3** wherein the portion of the by-product gas is introduced into the process stream upstream of the unfired reactor.

5. The process of claim **1** further comprising:

introducing an oxygen-rich gas into the reformate stream after withdrawing the reformate stream from the plurality of catalyst-containing reformer tubes to partially oxidize the reformate stream; and

reacting the partially oxidized reformate stream in the presence of the reforming catalyst in the secondary reforming reactor under reaction conditions sufficient to form reaction products comprising carbon monoxide and hydrogen in the reformate stream before reacting the reformate stream in the presence of the shift catalyst.

6. The process of claim **5** wherein the portion of the by-product gas is introduced into the reformate stream at the location upstream of the secondary reforming reactor.

7. The process of claim **1** further comprising:

introducing a feed gas comprising at least one hydrocarbon and optionally steam into the reformate stream after withdrawing the reformate stream from the plurality of catalyst-containing reformer tubes, the at least one hydrocarbon selected from the group consisting of methane, ethane, propane, butane, pentane, and hexane;

introducing an oxygen-rich gas into the reformate stream after withdrawing the reformate stream from the plurality of catalyst-containing reformer tubes to partially oxidize the reformate stream; and

reacting the partially oxidized reformate stream in the presence of the reforming catalyst in the secondary reforming reactor under reaction conditions sufficient to form reaction products comprising carbon monoxide and hydrogen in the reformate stream before reacting the reformate stream in the presence of the shift catalyst.

8. The process of claim **1** wherein the shift catalyst comprises iron oxide and the second temperature ranges from 310° C. to 500° C.

9. The process of claim 1 wherein the shift catalyst comprises copper and the second temperature ranges from 200° C. to 400° C.

10. The process of claim 8 further comprising:

reacting the second process stream in the presence of a second shift catalyst at a fourth temperature ranging from 190° C. to 300° C. and a fourth pressure ranging from 2 to 50 atmospheres to form carbon dioxide and hydrogen in the second process stream prior to the step of scrubbing the second process stream.

11. The process of claim 10 wherein the second shift catalyst comprises copper.

12. The process of claim 1 wherein the fuel gas comprises 30 volume % to 98 volume % hydrogen-containing product gas and 2 volume % to 70 volume % by-product gas.

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(54) **PROCESS FOR PRODUCING AMMONIA SYNTHESIS GAS**

VERFAHREN ZUR HERSTELLUNG VON AMMONIAKSYNTHESEGAS

PROCÉDÉ DE PRODUCTION DE GAZ DE SYNTHÈSE D'AMMONIAC

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EP 2 817 260 B1

Description

Field of the invention

[0001] The invention relates to reforming of hydrocarbons for the preparation of a synthesis gas, also named syngas, for the production of ammonia.

Prior art

[0002] The synthesis of ammonia (NH_3) requires a synthesis gas comprising hydrogen (H_2) and nitrogen (N_2) in a suitable molar ratio (HN ratio) of about 3:1. The term ammonia syngas will be used with reference to a synthesis gas with the above composition.

[0003] It is known to produce said syngas from the reforming of a hydrocarbon source, for example containing methane.

[0004] Conventional reforming such as SMR (steam methane reforming) involves a primary reformer and a secondary reformer. A process for production of ammonia synthesis gas with a primary reformer and a secondary reformer is disclosed for example in EP-A-2 065 337.

[0005] According to the prior art, a hydrocarbon source such as natural gas is steam-reformed in a primary reformer at a temperature around 800 °C. The first gas product leaving the primary reformer is further reacted with air in a secondary reformer, obtaining a second gas product at around 1000°C. Said second gas product is then cooled for heat recovery and treated to remove carbon oxides and obtain a gas composition suitable for ammonia synthesis i.e. having a HN ratio close to 3:1. Treatment includes shift converters where CO is converted to carbon dioxide and hydrogen, carried out in a high-temperature shift reactor (HTS) at around 400-500 °C, and in a low-temperature shift reactor (LTS); a CO2 removal unit such as a washing column; a methanator reactor where the residual carbon oxides are catalytically converted to methane. The so obtained purified gas is then compressed in a syngas compressor to the synthesis pressure which is in the range 80 - 300 bar and typically around 150 bar. Due to inherent limitations of the catalyst loaded in the HTS reactor, the steam-to-carbon ratio (SC ratio) in the primary reformer must be greater than 2.7 and is typically equal to 3.0.

[0006] Some drawbacks of conventional SMR come from the primary reformer. The primary reformer is basically a bundle of externally heated catalytic tubes and introduces limitations in terms of maximum flow rate and pressure. A conventional primary reformer cannot operate at a pressure greater than 35-40 bar, in order to avoid excessive stress on the tubes; hence the duty of the main compressor is remarkable, with a difference of pressure over 100 bar and a pressure ratio greater than 5.

[0007] Another drawback of a conventional layout with HTS and LTS is that the high steam-to-carbon ratio means a higher flow rate in the reformer. This increases the duty and size of the steam reformer, due to the relevant flow rate of steam.

[0008] Hence the steam reformer of the front-end is substantially the bottleneck of the ammonia plant and imposes a maximum capacity around 3000 tons of ammonia per day.

[0009] Some variations to the above described conventional process are also known. Use of excess air can reduce the size of the steam reformer for a given capacity, but does not solve the problem of duty of the syngas compressor and increases complexity because and additional unit is required to remove the nitrogen in excess. A gas-heated reformer is another way to reduce size of the primary reformer, but increases cost and complexity.

[0010] A layout with no secondary reformer is also known. The effluent of the primary reformer is routed directly to the CO-shift section, and the purified syngas after shift and CO2 removal is mixed with nitrogen to reach the required HN ratio. Said nitrogen is produced in an air separation unit.

[0011] This layout is simple but absence of the secondary reformer may cause methane slip from the primary reformer. The necessary measures to avoid or at least reduce the methane slip include: steam-to-carbon ratio in the reformer close to 3.0; lower operating pressure in the reformer tubes, typically 25-30 bar, but a higher temperature (usually > 850 °C). Moreover, the duty of the steam reformer is high because the reformer has to produce all hydrogen for ammonia synthesis, in absence of a secondary reforming.

[0012] For the above reasons, a scheme with no secondary reformer has a large steam reformer, e.g. about 50% larger than conventional SMR, and maximum size of the ammonia plant is comparable.

[0013] The prior art also includes conversion of the hydrocarbon source in an autothermal reformer (ATR) or in a partial oxidation (POX) reactor. For example, US 4 725 380 discloses conversion of a hydrocarbon feedstock in an autothermal reformer.

[0014] The autothermal reformer is basically a catalytic converter where oxidation of the hydrocarbon source (usually natural gas) takes place and provides the heat for reforming. A POX reactor is a non-catalytic reactor which provides a partial oxidation of the hydrocarbon source.

[0015] An autothermal reformer or a POX reactor can operate at a higher pressure than a conventional tube reformer,

hence they reduce the duty of the main syngas compressor. However, the prior art layouts based, for example, on autothermal reforming are still quite complex. They usually comprise an ASU to furnish oxygen, a high-temperature shift, then CO2 removal, drying and nitrogen wash to remove inerts. The high-temperature shift forces a steam-to-carbon ratio in the ATR feed to around 3, which increases the size of the equipment in the ATR and HTS effluent cooling sections, and energy consumption. Moreover, due to high operating temperature of the HTS, a significant amount of CO (more than 4.0% v/v, dry) slips from the HTS converter and is lost as fuel gas, increasing the amount of natural gas consumed per ton of product, and the size of the front-end. Finally, the cryogenic purification is costly and energy intensive.

[0016] An improvement of these processes is highly desirable, to enable cost effective large ammonia production units which are also easy to operate.

Summary of the invention

[0017] The aim of the invention is to overcome the drawbacks of the prior art as above discussed.

[0018] To this purpose, the invention proposes a process for producing ammonia synthesis gas from a hydrocarbon source, comprising:

- conversion of said hydrocarbon source into a raw synthesis gas solely by means of a catalytic autothermal steam reforming or by means of a non-catalytic partial oxidation with steam, in ATR or POX reactor respectively and without a primary reforming stage;
- said steam reforming or said partial oxidation being carried out with an oxidant which is oxygen or oxygen-enriched air;
- a water-gas shift treatment of said raw synthesis gas, which consist of a medium-temperature shift at a temperature of 200 - 300 °C, thus obtaining a shifted synthesis gas;
- purification of said shifted synthesis gas, said purification including at least a step of pressure-swing adsorption to remove residual carbon oxides and methane from the synthesis gas, obtaining a purified synthesis gas (18), and
- optionally, addition of nitrogen (19) to said purified synthesis gas, thus obtaining ammonia synthesis gas with a desired hydrogen to nitrogen ratio,
- said conversion of the hydrocarbon source into raw synthesis gas being carried out in an autothermal steam reforming reactor or in a partial oxidation reactor, and the steam-to-carbon ratio in the feed of said reactor being lower than 2.

[0019] The conversion is carried out in an ATR or POX reactor according to the choice of autothermal steam reforming or partial oxidation. The invention uses no primary reformer or secondary reformer.

[0020] The effluent of the ATR or POX reactor, usually after cooling, is routed directly to a medium temperature shift (MTS) converter operating in the above range of 200 to 300 °C. According to the invention, the shift treatment consists of medium-temperature shift at the above defined medium temperature, without a low-temperature or high-temperature shift.

[0021] More preferably, the shift temperature is in the range 200 to 250 °C and even more preferably 230 to 250 °C.

[0022] Said MTS step can be adiabatic or isothermal. Isothermal MTS is preferred in order to improve the conversion of CO and to allow an optimal inlet temperature of the syngas in the MTS converter, as will be explained.

[0023] The invention allows the adoption of a low SC ratio in the feed of the reactor. When the reactor is an ATR, said SC ratio is preferably in the range 1.0 - 2.0. When the reactor is a POX reactor, said SC ratio is preferably in the range 0.5 - 1.0.

[0024] The ATR or POX reactor can be fired with oxygen or enriched air. Said oxygen or enriched air can be produced in an air separation unit (ASU). Said ASU can be of cryogenic type, or of pressure swing adsorption type (PSA), or of vacuum pressure swing adsorption type, or of membrane type.

[0025] In oxygen-fired embodiments, nitrogen needs be introduced in the synthesis gas to adjust the hydrogen-to-nitrogen ratio. Preferably, nitrogen is introduced downstream said step of pressure-swing adsorption, i.e. the effluent of the PSA unit is added with a nitrogen (N2) stream. Preferably said nitrogen stream is produced in the same ASU which produces the oxygen for the ATR or POX reactor, in oxygen-fired embodiments. Optionally, an additional stream of nitrogen can be used to regenerate the PSA unit, thus reducing the consumption of syngas. Said additional stream can be taken from the nitrogen stream leaving the ASU.

[0026] In enriched air-fired embodiments, nitrogen enters the ATR or POX reactor together with oxygen. Preferably the flow rate and/or enrichment (02 concentration) of the enriched air feed to the reactor is determined in such a way that the full amount of nitrogen is introduced with the enriched air feed. Hence, no further addition of nitrogen will be

required. Also in these embodiments, however, an additional stream of nitrogen could be used to regenerate the PSA unit.

[0027] The enriched air-fired embodiments provide that the feed of the PSA unit contains nitrogen. Preferably, the separation of carbon oxides in the PSA unit is limited to avoid a significant loss of nitrogen with said carbon oxides. As a consequence, a methanator is preferably provided downstream the PSA unit, to convert the residual CO and CO2 to methane.

[0028] Optionally, if pure CO2 product is required from the plant (e.g. for downstream urea production) the further purification of the shifted synthesis gas includes a CO2 removal, preferably prior to the step of pressure-swing adsorption. According to one embodiment, the shifted synthesis gas effluent after the medium-temperature shift treatment is directed to a CO2 removal step and the so obtained decarbonated synthesis gas is then directed to the step of purification with pressure-swing adsorption. In another embodiment, CO2 is removed from a fuel gas which is separated by said PSA step. The CO2 removal step can be based on a washing with an appropriate physical or chemical solvent.

[0029] A first advantage of the invention is the absence of a primary reformer. Hence, the related limits of pressure and flow rate are removed. The ATR or POX reactor can operate at a higher pressure thus providing a higher pressure at the suction side of the main syngas compressor. This means that size, cost and consumption of the compressor are reduced. In some embodiments, the syngas generation pressure can be as high as the ammonia synthesis pressure, so that the make-up compressor is no longer required.

[0030] It should be noted that the adoption of the primary reformer, in the prior art, is considered an advantage because it reduces the consumption of oxidant and energy, despite the need of a complex equipment, namely the primary reformer and usually a pre-reformer. The term of energy consumption refers generally to heat required for heating the process streams and/or to produce hot steam. Hence the prior art gives a strong incentive towards a "combined" layout with primary and secondary reforming. Contrary to this incentive, the applicant has found that the consumption of energy can be lower than expected, and that a solution without primary reforming, in combination with a low steam to carbon ratio and medium-temperature shift, can be attractive.

[0031] Moreover, a plant with no primary reformer according to the invention can be operated at low SC ratios even without a pre-reformer. A remarkable advantage of the invention is the opportunity to use a low SC ratio without the need of a pre-reformer; accordingly, the plant is much simpler and less expensive.

[0032] The medium-temperature shift, in fact, has the great advantage of operation with a lower SC ratio than a conventional HTS, due to different catalyst. Hence the ATR or POX reactor can operate with a lower SC ratio which means that flow rate vs. capacity is reduced. In other words, capacity for a given flow rate is increased or, in the same way, front-end equipment is smaller and less expensive than in the prior art, for a given capacity.

[0033] Apart from the above considerations, however, a low SC ratio was discouraged in the prior art due to the following reasons: risk of methane slip (unconverted methane from the reforming section); risk of carbon monoxide (CO) slip from the shift converter; formation of methanol as a byproduct of the shift reaction with copper-based catalysts, which methanol can damage the solution for CO2 removal. Carbon monoxide and methane contained in the product gas must be purged at the expense of energy and increase the volumetric flow rate (hence the size of equipments). In the prior art, they are usually combusted to recover energy, however this solution is feasible as long as the amount of CO and CH4 does not exceed the heat input required by the steam reformer, otherwise their combustion would be practically useless.

[0034] The applicant, however, has found that the above problems can be overcome with a process and plant according to the invention, because: purification via pressure-swing adsorption (PSA) is able to remove unconverted methane and CO and prevent from their accumulation in the synthesis loop; a PSA unit is not damaged by possible methanol contained in the gas, since methanol will be removed; the tail gas of the PSA unit can be entirely used as a fuel in the fired heater of the ammonia plant, to preheat the process feeds and superheat the steam, thereby containing the overall consumption of natural gas fuel. Hence, despite the low S/C ratio and unexpectedly, the heating value of the tail gas from the PSA is not more than the total fuel required by the process.

[0035] On the other hand, a low SC ratio (significantly lower than 3, and preferably lower than 2 according to some embodiments), has the following advantages. First, a low SC ratio reduces the amount of oxidant required by the partial oxidation step, thus compensating for the absence of a primary reformer and allowing a good conversion of methane into the synthesis gas; second, a low SC ratio reduces the residual heat in the synthesis gas leaving the shift section, which feature is synergistic with the choice of a PSA unit, since the PSA unit does not require a heat input for regeneration contrary to the conventional acid gas removal systems; third, a low SC ratio reduces the dew point of the gas; since the dew point is a function of the pressure (the higher the pressure, the higher the gas dew point), this allows for operation at a higher pressure, which is desirable for various reasons (e.g. smaller flow rate and equipment) without the risk of a damage to the shift catalyst by condensation of the syngas at the catalyst bed inlet.

[0036] For all the above reasons, the front-end of an ammonia plant, according to the invention, can be designed to reach a capacity much greater than in the prior art, for example 6.000 tons/day of ammonia or even more.

[0037] Another important advantage of the medium-temperature shift is that the inlet temperature of a MTS converter is sufficiently far from the dew point of the syngas, which is around 180 °C. Hence, the risk of condensation of syngas

and related damage of the catalyst is avoided. Isothermal MTS is preferred to keep a stable temperature in the MTS and further reduce this risk.

[0038] As already mentioned, a significant advantage of the PSA step is that it does not consume heat and can remove also methane (CH4) and argon, thereby reducing the concentration of inerts in the synthesis loop, and consequently reducing the size of synthesis equipment, including e.g. the ammonia converter and syngas compressor, and/or reducing the consumption of energy.

[0039] The embodiments with O2-enriched air firing the ATR or POX reactor have also the advantage of reducing size and duty of the ASU.

[0040] Basically, the invention encompasses the two options of using enriched air or substantially pure oxygen as the oxidant medium. If enriched air is used, introduction of further nitrogen (after purification) is possible; it is preferred, however, to provide a degree of enrichment such that the gas leaving the PSA unit has the desired hydrogen/nitrogen stoichiometric ratio for ammonia synthesis (around 3) without a further introduction of nitrogen, that is the enriched air contains all the required amount of nitrogen.

[0041] Preferably, the air is enriched to contain an amount not greater than 40% molar of oxygen (O_2), and more preferably said amount is in the range of 30% to 40% molar. The applicant has found that this degree is optimum for providing the required oxygen and, at the same time, a sufficient amount of nitrogen to reach the above mentioned stoichiometric ratio. Conventional systems with a higher degree (usually more than 50%) have the drawback that they require more oxygen (which is expensive to produce) and that they need additional nitrogen. It should be noted that not all air separation plants produce pure nitrogen in addition to oxygen. Hence the avoidance of a nitrogen feed for adjusting the stoichiometric ratio of the product gas is an advantage.

[0042] The use of enriched air, preferably with the amount of oxygen not greater than 40% molar as mentioned above, has also the advantage that a smaller and less expensive air separation plant (compared to oxygen-fired embodiments) is sufficient.

[0043] It can be noted that the present invention provides an efficient front-end for an ammonia plant featuring only four basic units, namely: an ASU for generation of oxygen or enriched air; ATR or POX reactor; MTS converter, PSA unit. In contrast, the prior art uses complex layouts with more units and/or with a conventional primary reformer and related drawbacks.

[0044] To summarize, the invention provides a simpler and less expensive layout as well as a larger single-train capacity, overcoming the bottlenecks of the prior art.

[0045] Another aspect of the invention is minimization of the excess of nitrogen, thanks to the use of pure oxygen or enriched air as the oxidant for the ATR or POX. In contrast, the use of air causes a large excess of nitrogen, increasing size and cost of the equipment especially from ATR (or POX) to the PSA unit. According to a preferred feature, excess of nitrogen, if any, is less than 50%.

[0046] The invention is now described with the help of the figures and referring to preferred embodiments.

Brief description of the figures

[0047]

Fig. 1 is a block diagram of a first embodiment of the invention.

Fig. 2 shows some option features of the embodiment of Fig. 1.

Fig. 3 is a block diagram of a second embodiment of the invention.

Fig. 4 shows some option features of the embodiment of Fig. 2.

Detailed description of a preferred embodiment

[0048] Fig. 1 shows a first embodiment with oxygen-fired reactor. A natural gas feed 10 is mixed with steam and is converted to synthesis gas by partial oxidation in oxygen-fired reactor 11 which is either an autothermal reformer or a partial oxidation reactor, according to different options.

[0049] The reactor 11 is fired with oxygen flow 12. Depending on the amount required, said oxygen flow 12 can be either produced in a pressure swing adsorption unit, or in a cryogenic air separation unit, or imported as such. In the figure, the oxygen flow 12 comes from an air separation unit (ASU) 13.

[0050] The reactor effluent 14, after cooling, is directly routed to a medium temperature shift (MTS) converter 15. Said MTS converter 15 operates at 200°C-250°C preferably. The effluent 16 of the MTS converter is routed to a pressure swing adsorption (PSA) unit 17 to remove the residual carbon oxides and methane, without the need of a CO2 washing

column.

[0051] The purified syngas 18 leaving the PSA unit 17 is added with a nitrogen stream 19 produced in the ASU 13. Optionally, a portion 20 of the available nitrogen stream (flow line 21) from said ASU 13 is used to regenerate the PSA unit 17. According to other (not shown) embodiments, said nitrogen stream 19 and/or stream 20 can be produced in a pressure swing adsorption unit or imported as such.

[0052] The PSA unit 17 produces also a fuel gas 22 containing some carbon oxides and methane.

[0053] The purified syngas, added with nitrogen and then having the required HN ratio, is then directed to ammonia synthesis section 30 where ammonia 31 is produced.

[0054] Upstream removal of CO2 is an optional feature, if pure CO2 is required as product (e.g. for urea production). This is shown in Fig. 2. Blocks 23 and 24 show optional CO2 removal units. In a first option, CO2 is removed from MTS converter effluent 16 before admission to PSA unit 17. Hence the PSA unit receives a decarbonated syngas 16' with a reduced content of CO2 or which is substantially CO2-free. In a second option, CO2 is removed from the fuel gas 22 and then a purified fuel gas 22' is obtained.

[0055] Fig. 3 shows an embodiment where the reactor 11 is fired with O2-enriched air. The ASU 13 now produces a stream of enriched air 28 which also contains nitrogen. Preferably the amount of said enriched air 28 is determined in such a way that the effluent 14 contains all the nitrogen required in the ammonia synthesis section 30, i.e. no addition of nitrogen is required. Said ASU 13 is preferably of cryogenic type, or of pressure swing adsorption type, or of vacuum pressure swing adsorption type, or of membrane type.

[0056] The effluent 18 of the PSA unit 17 is subject to methanation in a reactor 25, and the so purified gas 26 is directed to the ammonia synthesis section 30. Said reactor 25 convert catalytically the residual CO and CO2 to methane, thereby protecting the ammonia synthesis catalyst. Due to the presence of some methane in the ammonia synthesis gas, a purge stream must be taken from the loop to control the concentration of inerts therein.

[0057] The purge gas from the synthesis loop is preferably routed back to the frontend and mixed with the PSA feed, to recover H2 and N2 content of said purge gas.

[0058] Fig. 4 shows the optional CO2 removal units 23 and 24 for the embodiment of Fig. 3.

Example

[0059] The following table compares examples for a notional ammonia plant with 5'000 metric tons per day capacity. The table compares two cases:
(1) conventional layout with a primary reformer and a secondary reformer, high-temperature shift, low-temperature shift, CO2 removal (aMDEA wash) and methanation;
(2) Layout according to the invention.

		(1) Prior Art	(2)
Reformer radiant duty	Gcal/h	250	-
Total No. of tubes in the reformer	-	> 1'000	-
Flow to syngas compressor	m^3/h	25'000	16'700
Power of syngas compressor	MW	58	39

[0060] The example shows that the newly devised schemes require almost 30% less power for syngas compression than the prior art. This means that 30% larger capacity can be achieved with the same compression power. Moreover the invention does not require any steam reformer.

Claims

1. A process for producing ammonia synthesis gas from a hydrocarbon source, comprising the following steps:

   - conversion of said hydrocarbon source into a raw synthesis gas (14), wherein said conversion takes place solely by means of a catalytic autothermal steam reforming or by means of a non-catalytic partial oxidation with steam, without a step of primary reforming,
   - said autothermal steam reforming or said partial oxidation being carried out with an oxidant which is oxygen (12) or oxygen-enriched air (28);
   - a water-gas shift treatment of said raw synthesis gas (14), which consist of a medium-temperature shift (15)

at a temperature of 200 - 300 °C, thus obtaining a shifted synthesis gas (16);
- purification of said shifted synthesis gas (16), said purification including at least a step of pressure-swing adsorption (17) to remove residual carbon oxides and methane from the synthesis gas, obtaining a purified synthesis gas (18), and
- optionally, addition of nitrogen (19) to said purified synthesis gas (18), thus obtaining ammonia synthesis gas with a desired hydrogen to nitrogen ratio,
- said conversion of the hydrocarbon source into raw synthesis gas being carried in an autothermal steam reforming reactor (11) or in a partial oxidation reactor, and the steam-to-carbon ratio in the feed (10) of said reactor (11) being lower than 2.

2. A process according to claim 1, said temperature of the shift treatment being in the range 200 to 250 °C and preferably 230 to 250 °C.

3. A process according to claim 1 or 2, said conversion of the hydrocarbon source into raw synthesis gas being carried out by means of autothermal steam reforming in ATR reactor (11), and the steam-to-carbon ratio in the feed (10) of said reactor (11) being in the range 1.0 to lower than 2.0.

4. A process according to claim 1 or 2, said conversion of the hydrocarbon source into raw synthesis gas being carried out by means of partial oxidation in a POX reactor, and the steam-to-carbon ratio in the feed (10) of said reactor (11) being in the range 0.5 - 1.0.

5. A process according to any of the previous claims, where:

- said steam reforming or partial oxidation is carried out with oxygen (12) produced by an air separation unit (13), and said air separation unit (13) also produces a nitrogen stream (21), and
- at least a portion (19) of said nitrogen stream (21) is added to said purified synthesis gas (18), after pressure-swing adsorption (17), thus obtaining ammonia synthesis gas with a desired hydrogen to nitrogen ratio.

6. A process according to any of claims 1 to 4, where:

- said steam reforming or partial oxidation is carried out with oxygen-enriched air (28) produced by an air separation unit (13), and
- the amount of said enriched air feed (28) is determined in such a way to contain the full amount of nitrogen which is needed in the ammonia synthesis gas, so that the raw synthesis gas (14) contains the required nitrogen and no further nitrogen is added to the synthesis gas.

7. A process according to claim 6, where the oxygen contained in the enriched air (28) is not greater than 40% molar, and preferably is in the range 30% to 40% molar.

8. A process according to claim 6 or 7 where the purified synthesis gas (18), after pressure-swing adsorption (17), is subject to methanation (25).

9. A process according to claim 6, 7 or 8 in which the synthesis loop purge is mixed with the syngas feed to PSA unit.

10. A process according to any of the preceding claims, where said purification of shifted synthesis gas (16), comprises only said step of pressure-swing adsorption (17), so that the purified synthesis gas after said step of pressure-swing adsorption (17) and optionally after addition of nitrogen (19) constitutes the ammonia synthesis gas suitable for reaction in an ammonia synthesis section (30).

11. A process according to any of the previous claims, where said medium-temperature shift is isothermal.

12. A process according to any of the preceding claims, where said purification of shifted synthesis gas (16), comprises a step of CO2 removal (23) prior to said step of pressure-swing adsorption (17).

13. A process according to any of the preceding claims, said hydrocarbon source being natural gas.

Patentansprüche

1. Verfahren zur Herstellung von Ammoniaksynthesegas aus einer Kohlenwasserstoffquelle, umfassend die folgenden Schritte:

   - Umwandlung der genannten Kohlenwasserstoffquelle in ein Rohsynthesegas (14), wobei die genannte Umwandlung ausschließlich mittels einer katalytischen autothermen Dampfreformierung oder mittels einer nicht katalytischen Partialoxidation mit Dampf ohne einen Schritt der Primärreformierung erfolgt,
   - wobei die autotherme Dampfreformierung oder die partielle Oxidation mit einem Oxidationsmittel durchgeführt wird, das Sauerstoff ist (12) oder mit Sauerstoff angereicherte Luft (28) ist;
   - eine Wasser-Gas-Konvertierung-Behandlung des rohen Synthesegases (14), die aus einer Mitteltemperaturkonvertierung (15) bei einer Temperatur von 200-300 ° C besteht, wodurch ein konvertiertes Synthesegas (16) erhalten wird;
   - Reinigung des konvertierten Synthesegases (16), wobei die Reinigung mindestens einen Schritt der Druckwechseladsorption (17) einschließt, um restliche Kohlenoxide und Methan aus dem Synthesegas zu entfernen, wodurch ein gereinigtes Synthesegas (18) erhalten wird, und
   - gegebenenfalls Zugabe von Stickstoff (19) zu dem gereinigten Synthesegas (18), wodurch Ammoniaksynthesegas mit einem gewünschten Wasserstoff-Stickstoff-Verhältnis erhalten wird.
   - wobei die Umwandlung der Kohlenwasserstoffquelle in Rohsynthesegas in einem autothermen Dampfreformierungsreaktor (11) oder in einem Teiloxidationsreaktor durchgeführt wird und das Verhältnis von Dampf zu Kohlenstoff in der Zufuhr (10) des Reaktors (11) niedriger ist als 2.

2. Verfahren nach Anspruch 1, wobei die Temperatur der Konvertierungs-Behandlung im Bereich von 200 bis 250 ° C und vorzugsweise von 230 bis 250 ° C liegt.

3. Verfahren gemäß Anspruch 1 oder 2, wobei die Umwandlung der Kohlenwasserstoffquelle in Rohsynthesegas mittels autothermer Dampfreformierung im ATR-Reaktor (11) durchgeführt wird und das Verhältnis von Dampf zu Kohlenstoff in der Zufuhr (10) des Reaktors (11) im Bereich von 1,0 bis weniger als 2,0 liegt.

4. Verfahren gemäß Anspruch 1 oder 2, wobei die Umwandlung der Kohlenwasserstoffquelle in Rohsynthesegas mittels partieller Oxidation in einem POX-Reaktor und das Verhältnis von Dampf zu Kohlenstoff in der Zufuhr (10) des Reaktors (11) im Bereich von 0,5-1,0 liegen.

5. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei:

   - die Dampfreformierung oder partielle Oxidation mit Sauerstoff (12) durchgeführt wird, welches durch eine Luftzerlegungseinheit (13) erzeugt wird, und wobei die Luftzerlegungseinheit (13) auch einen Stickstoffstrom (21) erzeugt, und
   - mindestens ein Teil (19) des Stickstoffstroms (21) zu dem gereinigten Synthesegas (18) nach der Druckwechseladsorption (17) zugegeben wird, wodurch Ammoniaksynthesegas mit dem gewünschten Wasserstoff-Stickstoff-Verhältnis erhalten wird.

6. Verfahren gemäß einem der Ansprüche 1 bis 4, wobei:

   - die Reformierung oder partielle Oxidation wird mit sauerstoffangereicherter Luft (28) durchgeführt wird, welches von einer Lufttrenneinheit (13) erzeugt wird, und
   - die Menge der sauerstoffangereicherter Luft Zufuhr (28) so bestimmt wird, dass es die volle Menge an Stickstoff enthält, die in dem Ammoniaksynthesegas benötigt wird, so dass das rohe Synthesegas (14) den erforderlichen Stickstoff erhält und keinen weiteren Stickstoff zu dem Synthesegas hinzugefügt wird.

7. Verfahren gemäß Anspruch 6, wobei der Sauerstoff in der angereicherten Luft (28) nicht mehr als 40% molar ist und vorzugsweise im molaren Bereich von 30% bis 40% liegt.

8. Verfahren gemäß Anspruch 6 oder 7, bei dem das gereinigte Synthesegas (18) nach der Druckwechseladsorption (17) einer Methanisierung unterzogen (25) wird.

9. Verfahren gemäß Anspruch 6, 7 oder 8, bei dem die Synthesekreisspülung mit der Syngaszufuhr zur PSA-Einheit gemischt wird.

10. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei die Reinigung des konvertierten Synthesegases (16) nur den Schritt der Druckwechseladsorption (17) umfasst, so dass das gereinigte Synthesegas nach dem Schritt der Druckwechseladsorption (17) und gegebenenfalls nach Zugabe von Stickstoff (19) das für die Reaktion in einem Ammoniaksyntheseabschnitt (30) geeignete Ammoniaksynthesegas darstellt.

11. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei die Konvertierung bei mittlerer Temperatur isotherm ist.

12. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei die Reinigung von konvertiertem Synthesegas (16) einen Schritt der CO_2-Entfernung (23) vor dem Schritt der Druckwechseladsorption (17) umfasst.

13. Verfahren gemäß einem der vorhergehenden Ansprüche, wobei die Kohlenwasserstoffquelle Erdgas ist.

Revendications

1. Un procédé de production de gaz de synthèse d'ammoniac à partir d'une source d'hydrocarbures, comprenant les étapes suivantes :

    - conversion de ladite source d'hydrocarbures en un gaz de synthèse brut (14), ladite conversion s'effectuant uniquement au moyen d'un reformage catalytique à la vapeur autothermique ou au moyen d'une oxydation partielle non catalytique à la vapeur, sans étape de reformage primaire,
    - ledit reformage à la vapeur autothermique ou ladite oxydation partielle étant effectué avec un oxydant qui est de l'oxygène (12) ou de l'air enrichi en oxygène(28) ;
    - un traitement par passage eau-gaz dudit gaz de synthèse brut (14), qui consiste en un passage d'une température moyenne (15) à une température de 200 à 300°C, obtenant ainsi un gaz de synthèse modifié (16) ;
    - purification dudit gaz de synthèse modifié (16), ladite purification comprenant au moins une étape d'adsorption modulée en pression (17) pour éliminer du gaz de synthèse les oxydes de carbone et le méthane résiduels, obtenant un gaz de synthèse purifié (18), et
    - optionnellement, addition d'azote (19) audit gaz de synthèse purifié (18), obtenant ainsi du gaz de synthèse d'ammoniac avec un rapport hydrogène sur azote souhaité,
    - ladite conversion de la source d'hydrocarbures en gaz de synthèse brut étant effectuée dans un réacteur autothermique (11) de reformage à la vapeur ou dans un réacteur d'oxydation partielle, et le rapport vapeur / carbone dans la charge (10) dudit réacteur (11) étant inférieur à 2.

2. Un procédé selon la revendication 1, ladite température du traitement de passage étant comprise entre 200 et 250°C et de préférence entre 230 et 250°C.

3. Un procédé selon la revendication 1 ou la revendication 2, dans lequel la transformation de la source d'hydrocarbures en gaz de synthèse brut est effectuée par reformage à la vapeur autothermique dans le réacteur ATR (11) et le rapport vapeur / carbone dans la charge (10) dudit réacteur (11) étant compris dans l'intervalle allant de 1,0 à moins de 2,0.

4. Un procédé selon la revendication 1 ou la revendication 2, ladite conversion de la source d'hydrocarbures en gaz de synthèse brut étant réalisée par oxydation partielle dans un réacteur POX, et le rapport vapeur / carbone dans la charge (10) dudit réacteur (11) étant dans l'intervalle allant de 0,5 à 1,0.

5. Un procédé selon l'une quelconque des revendications précédentes, dans lequel :

    - ledit reformage à la vapeur ou ladite oxydation partielle est effectué(e) avec de l'oxygène (12) produit par une unité de séparation d'air (13), et ladite unité de séparation d'air (13) produit également un courant d'azote (21), et
    - au moins une partie (19) dudit courant d'azote (21) est ajoutée audit gaz de synthèse purifié (18), après adsorption modulée en pression (17), obtenant ainsi un gaz de synthèse d'ammoniac avec un rapport hydrogène / azote souhaité.

6. Un procédé selon l'une quelconque des revendications 1 à 4, dans lequel :

    - ledit reformage à la vapeur ou ladite oxydation partielle est réalisé(e) avec de l'air enrichi en oxygène (28)

produit par une unité de séparation d'air (13), et
- la quantité de ladite alimentation en air enrichi (28) est déterminée de manière à contenir la quantité totale d'azote qui est nécessaire dans le gaz de synthèse d'ammoniac, de sorte que le gaz de synthèse brut (14) contient l'azote requis et qu'il n'y ait plus d'azote ajouté au gaz de synthèse.

7. Un procédé selon la revendication 6, dans lequel l'oxygène contenu dans l'air enrichi (28) n'est pas supérieur à 40% molaire, et de préférence est compris dans l'intervalle allant de 30% à 40% molaire.

8. Un procédé selon la revendication 6 ou la revendication 7, dans lequel le gaz de synthèse purifié (18), après adsorption modulée en pression (17), est soumis à une méthanation (25).

9. Un procédé selon l'une des revendications 6, 7 ou 8, dans lequel la purge de boucle de synthèse est mélangée avec l'alimentation en gaz de synthèse à l'unité PSA.

10. Un procédé selon l'une quelconque des revendications précédentes, dans lequel ladite purification du gaz de synthèse modifié (16) comprend seulement ladite étape d'adsorption modulée en pression (17), de sorte que le gaz de synthèse purifié après ladite étape d'adsorption modulée en pression (17) et optionnellement après addition d'azote (19) constitue le gaz de synthèse d'ammoniac approprié pour la réaction dans une section de synthèse d'ammoniac (30).

11. Un procédé selon l'une quelconque des revendications précédentes, dans lequel ledit changement de température moyenne est isotherme.

12. Un procédé selon l'un quelconque des revendications précédentes, dans lequel ladite purification du gaz de synthèse modifié (16) comprend une étape (23) d'élimination du CO_2 avant ladite étape d'adsorption modulée en pression (17).

13. Un procédé selon l'une quelconque des revendications précédentes, ladite source d'hydrocarbures étant du gaz naturel.

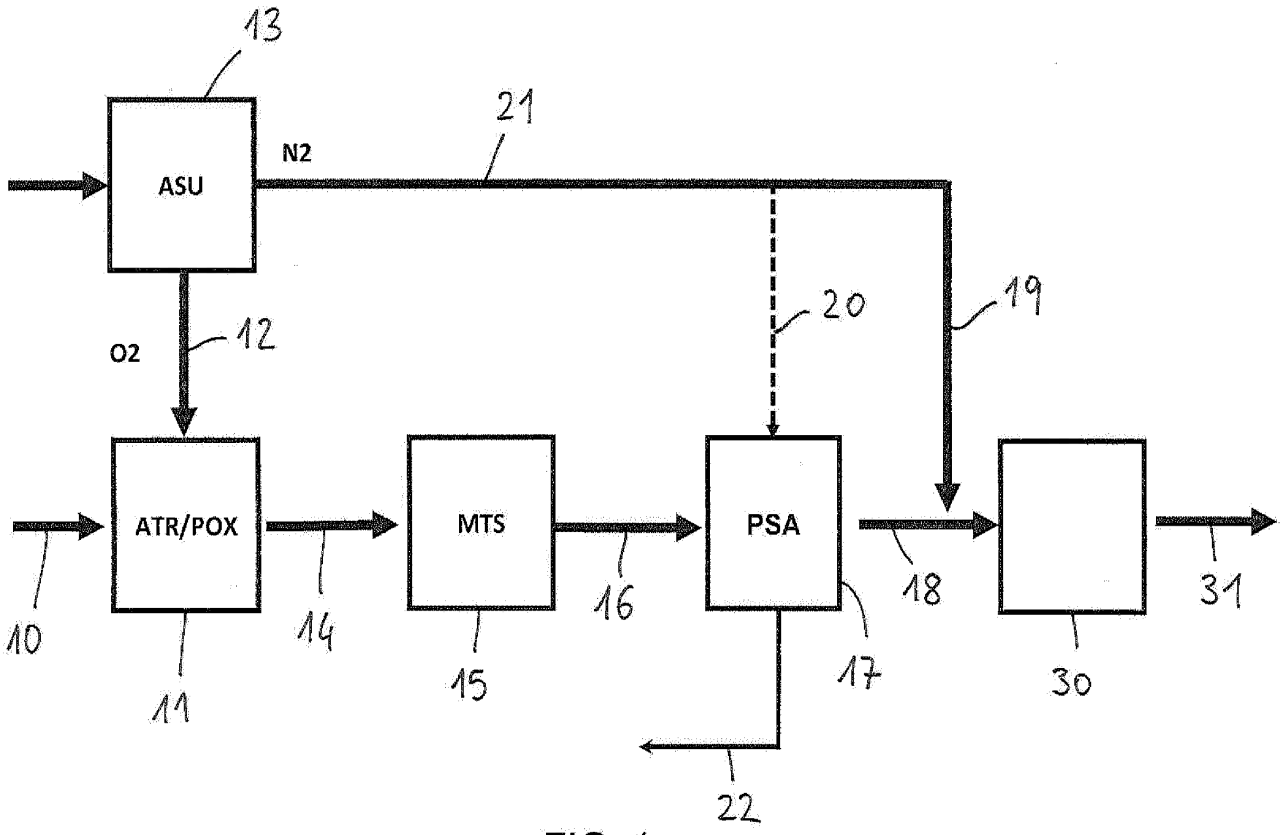


FIG. 1

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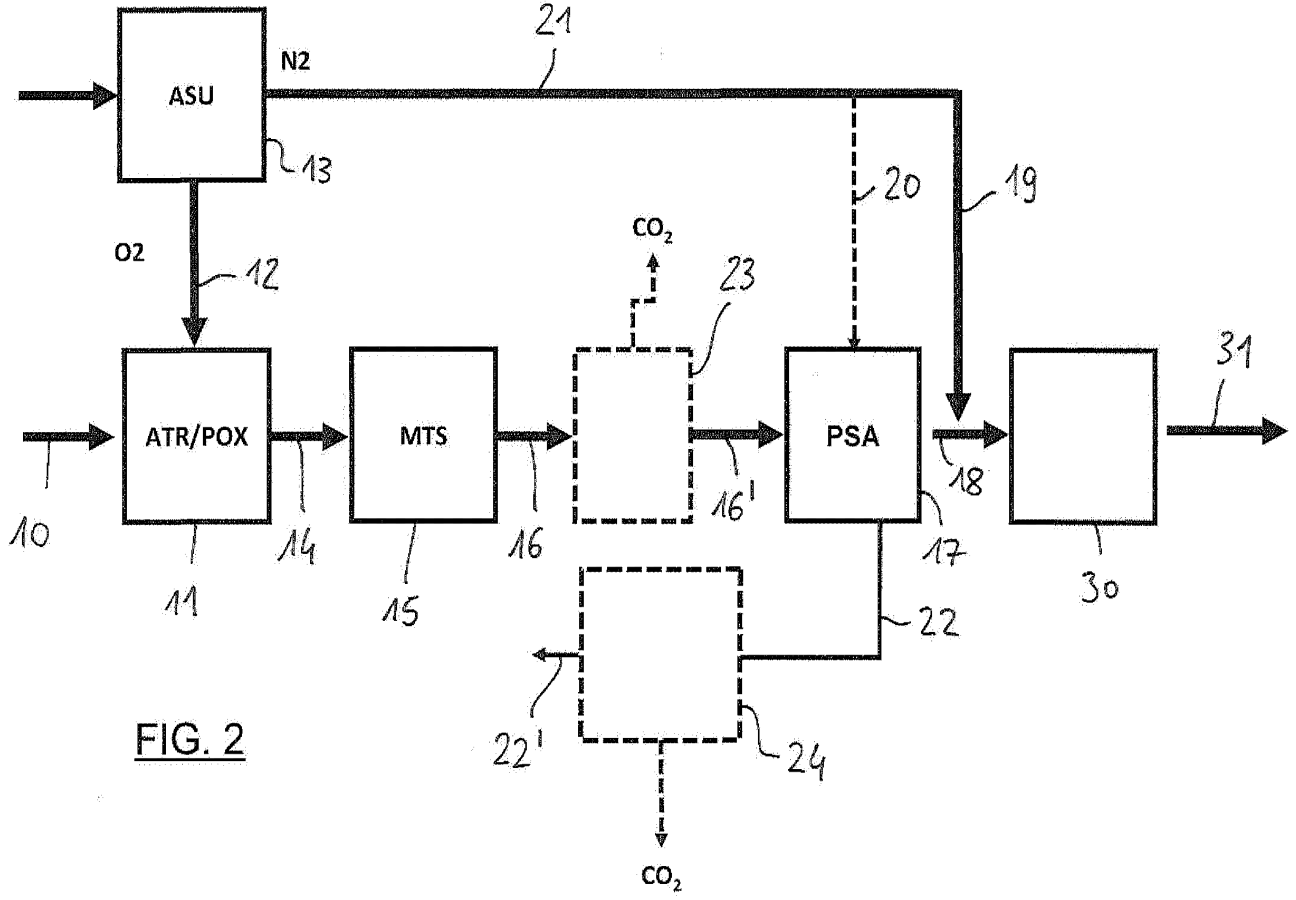

ASU
N2
21
13
20
19
O2
12
CO_2
23
ATR/POX
MTS
PSA
31
10
11
14
15
16
16'
17
18
30
22
22'
24
CO_2

FIG. 2

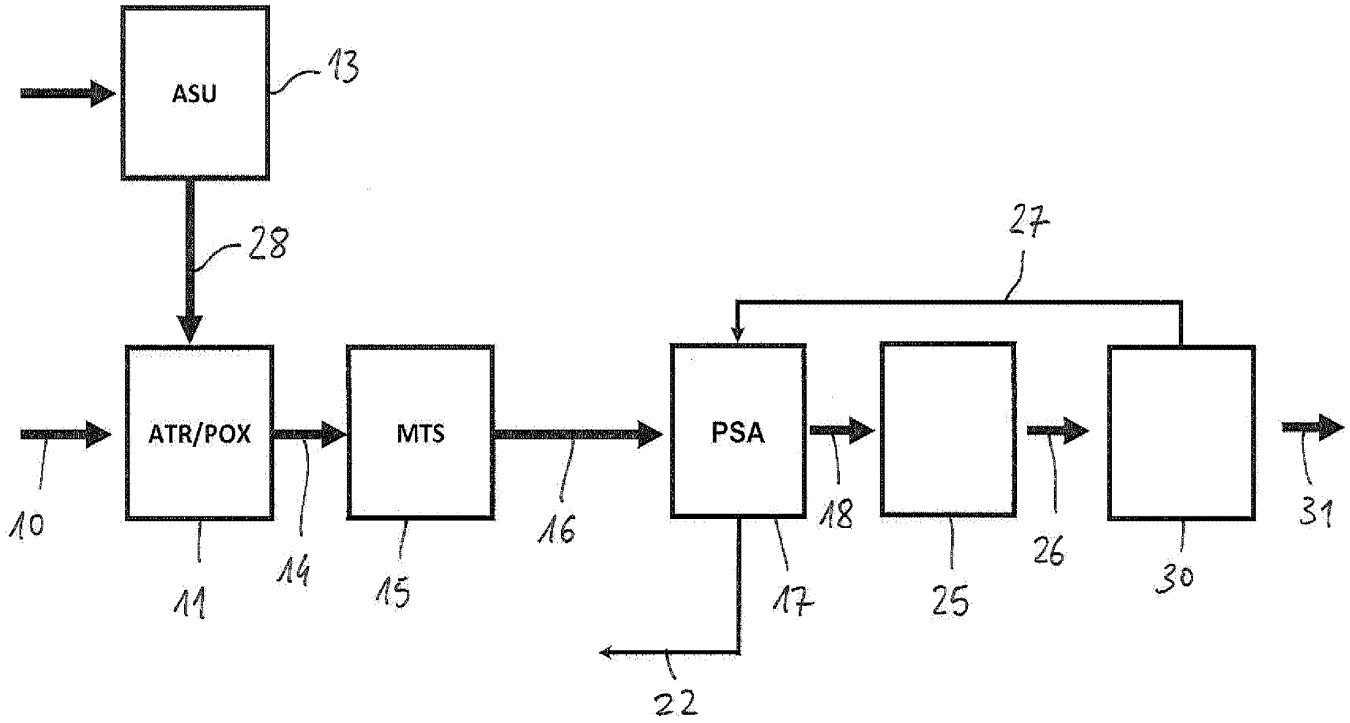


FIG. 3

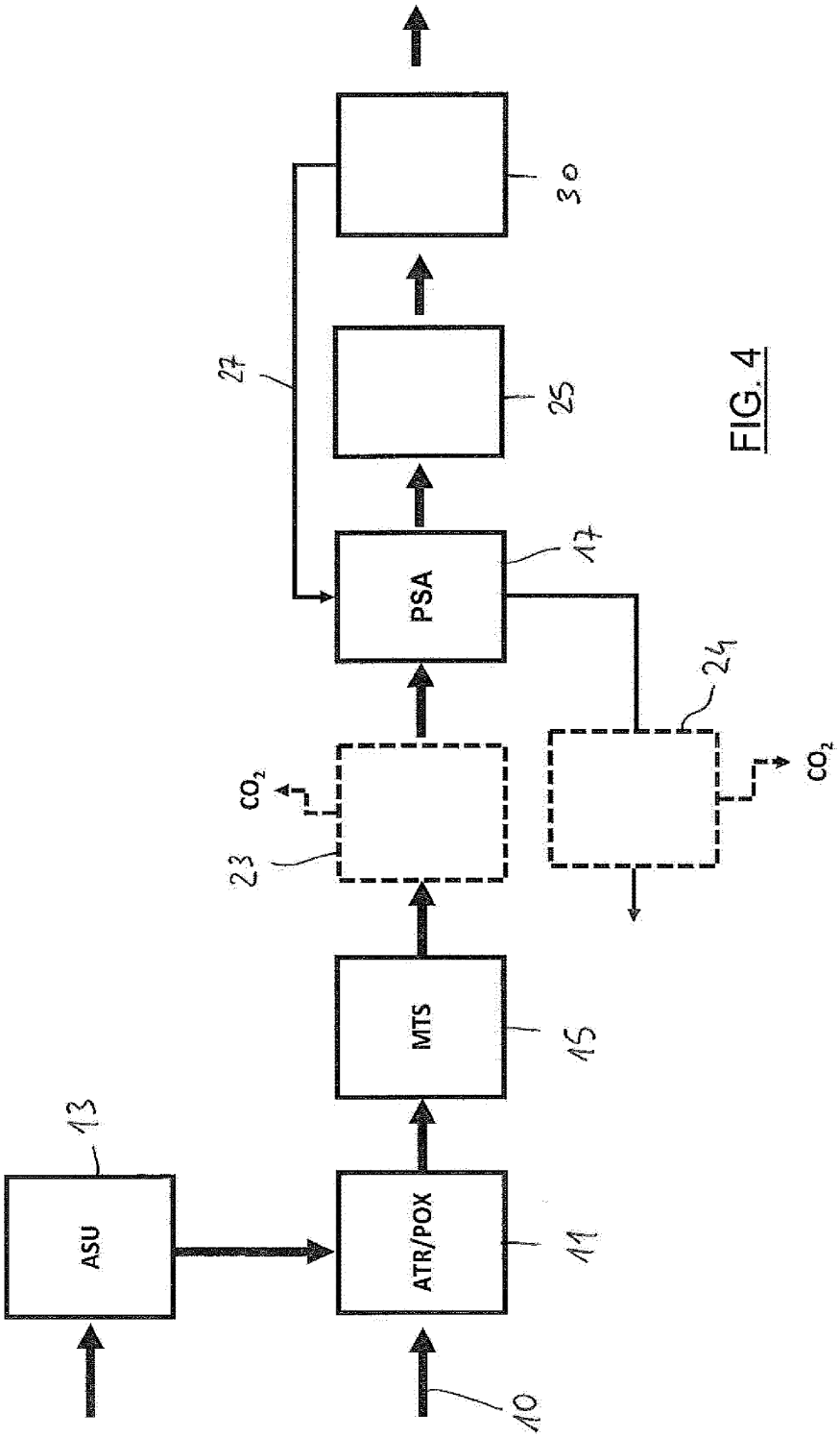


FIG. 4

REFERENCES CITED IN THE DESCRIPTION

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Hydrogen, 3. Purification

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ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY

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1. Introduction

In many cases it is necessary to purify technical grade hydrogen by using a variety of processes. These must be chosen in accordance with the final use of the hydrogen to give an economically satisfactory result. This article gives an overview of the technically important purification steps. They are classified according to the physical and chemical operations involved in the separation processes.

Frequently in industrial-scale plants combinations of the various processes are used. In addition, several alternative processes may be available and may be used depending on the economic situation. In → Hydrogen, 2. Production and → Hydrogen, 5. Handling some examples of typical combinations of various gas production and purification processes are given.

2. Low-Temperature Processes

The large temperature difference between the boiling point of hydrogen and that of the most frequent impurities is the basis of the low-temperature process (LT process) for the purification of hydrogen. Table 1 shows important properties of hydrogen and the most frequent impurities present in the hydrogen to be treated. The impurities are condensed or sublimated. Low-temperature rectification processes are used, if the impurities are also to be separated from one another. The use of *scrubbing* and *adsorption processes* at low temperatures leads to both high purities and high yields.

An overview of the basic physical processes which are used for the liquefaction of gases as well as the most important parts of the plants, equipment and machines is given in [1] and [2]. Properties of two- and multicomponent mixtures with hydrogen, which are the basis for the calculation of the separation processes given here, can be seen in → Hydrogen, 1. Properties and Occurence, Chap. 2.).

Such property data are available in computer data banks of engineering companies. Some data otherwise available is given in [3, 4].

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Table 1. Boiling points at atmospheric pressure, triple point and critical data of hydrogen and some important components which can be present in raw hydrogen streams

Component	Boiling point at 101.3 kPa		Triple point data		Critical data	
	Temperature, K	°C	Temperature, K	Pressure, kPa	Temperature, K	Pressure, kPa
He	4.23	−268.9	2.17[b]	5.1	5.3	230
H_2[a]	20.4	−252.8	13.9	7.0	33.3	1 320
Ne	27.1	−246.1	24.6	43.3	44.5	2 760
Ar	87.3	−185.9	83.8	68.8	150.7	4 870
N_2	77.3	−195.9	63.2	12.6	126.1	3 390
O_2	90.2	−183.0	54.4	0.2	154.3	5 040
CO	81.6	−191.5	68.1	15.4	133.0	3 500
NO	121.2	−151.9	109.9	2.3	179.2	6 590
H_2O	373.2	100.0	273.2	0.6	647.4	22 140
H_2S	212.9	− 60.3	187.6	23.2	373.6	9 020
SO_2	263.2	− 10.0	197.8	1.7	430.4	7 870
CO_2	194.7[c]	− 78.5	216.6	18.0	304.2	7 390
NH_3	239.8	− 33.4	195.4	6.1	405.6	11 300
CH_4	111.7	−161.5	90.7	11.7	190.7	4 620
C_2H_6	184.6	− 88.6	89.9	<0.1	305.3	4 890
C_2H_4	169.5	−103.7	104.0	0.1	282.0	6 280
C_3H_8	231.1	− 42.1	85.4	<0.1	370.0	4 260
C_3H_6	225.5	− 47.7	88.0	<0.1	365.3	4 570

[a] In more detail in → Hydrogen, 1. Properties and Occurence, Section 2.1.
[b] Upper λ point.
[c] Sublimation

2.1. Condensation Processes

Simple condensation processes are used, if the difference between the boiling point of hydrogen and the condensing phase, usually hydrocarbons, is sufficiently high. Hydrogen is frequently separated from refinery and dealkylation off-gases, as well as ammonia and methanol synthesis purge gases by the condensation process.

The gas from which hydrogen is to be recovered, usually contains components which are solid at the temperature of the final condensation step. Therefore, a *prepurification* stage is usually required to prevent blockage of heat exchangers, knock-out drums, and piping in the low-temperature section of the plant.

Prepurification and drying remove in particular impurities with a high boiling point such as water, carbon dioxide, and hydrocarbons such as benzene and toluene. These processes (often carried out in stages) are *scrubbing* (e.g., glycol scrubbing for water removal), *adsorption* (e.g., on activated carbon or molecular sieve beds), or *condensation* and *sublimation* of the impurities on reversible regenerator beds or reversing heat exchangers (Revex).

The residual gas mixtures, usually hydrogen – methane, hydrogen – carbon monoxide, or hydrogen – nitrogen mixtures, are cooled down below the condensation temperature. The lower the temperature chosen, the purer is the hydrogen product. In the case of the mixture hydrogen – methane the temperature in the condensator can be lowered below the solidification point of pure methane by the addition of ethane or propane and the hydrogen purity can thereby be increased.

The hydrogen yield depends on the solubility of the hydrogen in the condensate and on the amount of condensate. The yield of hydrogen increases, if the condensate is depressurized in a series of stages and the hydrogen-rich depressurization gas is recycled to the first stage of the compressor. Figure 1 shows the most important ways of generating refrigeration for low-temperature processes in industrial plants.

If amount and pressure of the impurities, such as methane, carbon monoxide or nitrogen, are large enough (> 3 – 5 vol %), the refrigeration requirements of the plant can be covered by *depressurizing the condensate* in a throttle (Joule – Thomson effect) (Fig. 1 A). Hydrogen is then recovered at high pressure. If the nitrogen or methane content is too low or variable, so that

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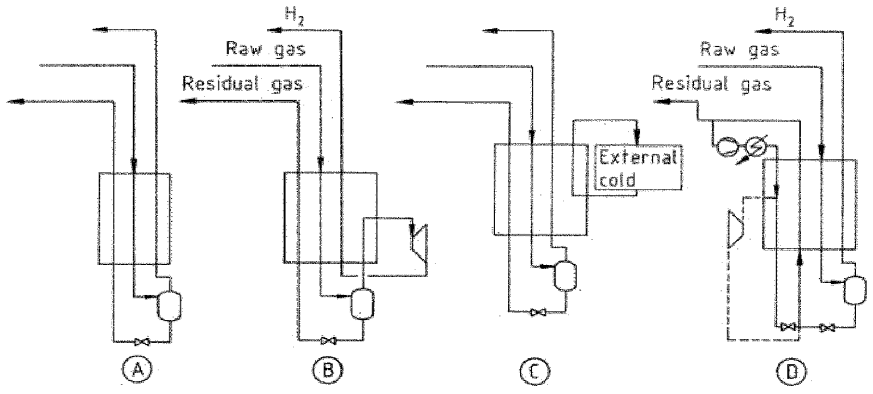


Figure 1. Principle ways of producing refrigeration for low-temperature hydrogen purification
A) Joule – Thomson expansion of residual gas; B) Hydrogen expansion in a turbine; C) Cold from external refrigeration sources (NH_3, freon, ethylene, etc.); D) Refrigeration cycle with residual gas

the refrigeration requirements cannot be covered reliably, then hydrogen itself can be expanded, e.g., by producing work in a turbine (Fig. 1 B).

If hydrogen, however, is required under high pressure, *external* refrigeration must be used. This can be done by a conventional external refrigeration plant using ammonia or freon as refrigerant (Fig. 1 C), or using other agents that are suitable for the required temperature level of condensation, in this case, e.g., nitrogen, carbon monoxide or methane (Fig. 1 D). The latter possibility requires the most sophisticated equipment. However, it leads to the greatest plant flexibility with regard to throughput and concentration of the impurities, because the refrigeration load is controlled directly by means of the external refrigeration cycle.

Some examples of processes using condensation alone are:

1. Refinery-gas purification plants, in which refrigeration is by a methane cycle or by decompressing the condensate (Fig. 1 A) with partial depressurization of the product [5].
2. Purification of the off-gas of the toluene dealkylation. Here a two-stage condensation is used for the recovery of pure hydrogen, a C_2, and a methane fraction. The refrigeration is supplied by an ammonia or freon cycle if necessary [6].
3. Recovery of hydrogen from the purge gas of ammonia plants. Here, a one-stage condensation process is sufficient. This process is particularly economic, when argon is recovered as an additional product by fractionation. A nitrogen cycle is used as refrigerant [7, 8].

Further common variations of the condensation process are as follows:

1. Staged decompression of the condensate and recycle of the decompressed gas to increase the hydrogen yield.
2. Partial condensation to fractionate the condensate and, eventually, to avoid the precipitation of solids. In this case the refrigeration can be supplied at a higher temperature, thus saving energy, by using refrigeration cycles which are optimized for the various condensation temperatures (see Fig. 1).

2.2. Condensation and Rectification

In large-scale plants higher yields and greater product purity are obtained by adding a rectification stage to the condensation step. This is also an advantage, if the impurities must be separated from one another. For the refrigeration many tailored variations exist.

Ethylene Plants. Pure hydrogen is recovered as a byproduct after low-temperature separation of ethane and ethylene from the methane – hydrogen fraction. The demethanizer plays an important part in the economics of the plant because the refrigeration required is at the lowest

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temperature of the process (→ Ethylene, Section 5.3.2.2.0.7.).

Coal Liquefaction. Hydrogen is recovered from the off-gas of the Fischer – Tropsch synthesis (operated on a large scale in South Africa by SASOL) by means of low-temperature condensation and rectification processes.

Figure 2 shows the LT separation of the purification unit of the SASOL II plant. In this unit 8675 mol/s (700 000 m^3 [STP]/h) crude gas is separated into 7 fractions, 5 of them in a LT plant. The hydrogen fraction is ca. 3700 mol/s (300 000 m^3 [STP]/h) of 80 % pure H_2 [9]. The crude gas, freed from carbon dioxide, is cooled down close to the hydrate point (i.e., the temperature at which precipitation of solid gas hydrates occurs) [10]. The water condensate is removed and separated into a water and a C_{3+} fraction. The gas phase is dried in an adsorber and cooled down to −35 °C. The condensate produced in this stage is fed to the rectification column g and separated into a C_2 and a C_{3+} fraction. In the following condensation stage a C_2 fraction is recovered by cooling down to ca. −95 °C, in the final stage at −150 °C liquid methane is produced. Methane, the C_2 fraction and the C_3 product are separated in two columns. The gaseous phase in the final knock-out drum e_5, is ca. 80 % pure hydrogen.

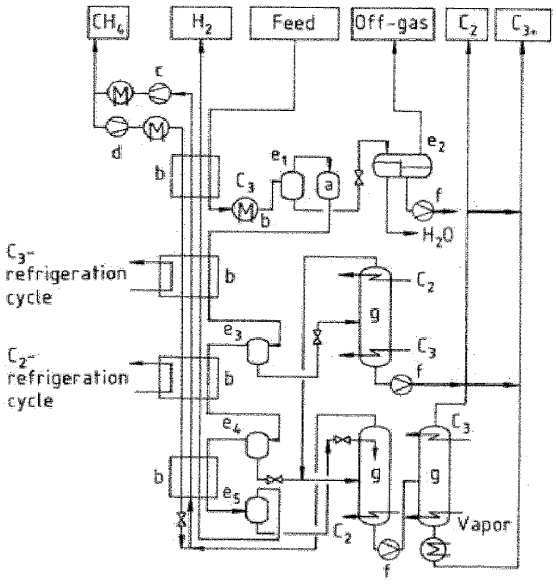


Figure 2. Production of H_2 and hydrocarbon fractions from Fischer – Tropsch synthesis off-gas by staged condensation. Separation of the hydrocarbon fractions by low-temperature rectification [9]
a) Adsorber for drying and elimination of traces of long-chain hydrocarbons; b) Heat exchanger; c) Compressor; d) CH_4 recycle compressor; e_1 – e_5) Knock-out drums; f) Pump; g) Column

This purity is suitable for the Fischer – Tropsch synthesis for which the main portion of the hydrogen-rich gas is required. A smaller part of the gas is used for hydrogenation purposes and is purified to 99.5 % using a pressure-swing adsorption process (see Section 3.3).

The refrigeration for the LT plant is supplied by an ethylene-propylene cascade and a methane cycle (see Figs. 1 C and 2, compressor d). The refrigeration must compensate for losses to the surroundings, in the heat exchanger and in the liquid product.

The refrigeration is supplied in 7 stages (including methane cycle) between + 9 °C and − 150 °C. The ethylene-propylene cycle has a power requirement of ca. 23 MW.

Low-temperature processes have been proposed for purification of the flash gas which is recovered on the decompression of the coal oil in plants for coal liquefaction by means of hydrogenation. Compared to other alternatives such as scrubbing at low temperature or diffusion separators [11], this concept has shown to be superior with regard to yield, energy requirements, economics and feasibility.

Hydrogen – Carbon Monoxide Recovery. Figure 3 shows a low-temperature process, which simultaneously delivers hydrogen and carbon monoxide of high purity from converted gases and gases from partial oxidation. After leaving a carbon dioxide scrubber, the converted and non-converted crude gas is (1) freed from traces of carbon dioxide and water in an adsorber, (2) cooled in two heat exchangers and in the sump of the carbon monoxide column down to the condensation temperature of carbon monoxide, i.e., ca. 80 K.

Energy and refrigeration is produced by expanding hydrogen in a turbine, thereby expanding down to the inlet pressure of a PSA plant in which hydrogen of 99.9 % end purity can be recovered. The carbon monoxide content in the hydrogen is <0.5 ppm. Liquid carbon monoxide

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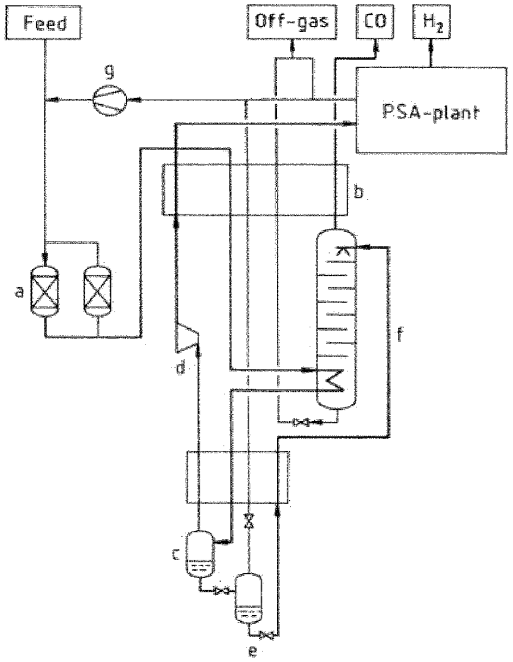


Figure 3. H_2 production from synthesis gas by low-temperature condensation and pressure-swing adsorption and production of pure carbon monoxide by rectification (German Linde)
a) Preadsorber; b) Heat exchanger; c) Condensation of CO and CH_4; d) Expansion turbine; e) Joule – Thomson expansion for H_2 recycle; f) CO/CH_4 rectification; g) Compression of expanded gas and PSA gas

is decompressed stagewise, whereby the major part of the refrigeration requirements of the plant is covered. After warming, the carbon monoxide is fed into a rectification column and purified to about 99 %, the maximum hydrogen impurity thereby being 0.5 %. A plant corresponding to Fig. 3 for a gas throughput of 833 mol/s (67 250 m^3 [STP]/h) synthesis gas has been constructed in two trains. The purge gas of the PSA plant can be recycled to obtain a higher yield of hydrogen and carbon monoxide [12].

Hydrogen – Nitrogen Rectification. Whereas in low-temperature hydrogen purification processes the rectification is employed principally to purify the byproducts, large-scale industrial processes also exist in which hydrogen itself is directly involved in the rectification. In the Braun purifier (part of an Ammonia synthesis process, using steam reforming of light hydrocarbons) (→ Ammonia) [13] ammonia synthesis gas is produced by condensing excess nitrogen from the raw gas which contains hydrogen, carbon monoxide, methane and nitrogen. Figure 4 shows the rectification of the hydrogen-nitrogen mixture. The refrigeration is provided by the decompression under production of energy in turbine (b) and by the Joule – Thomson decompression of the remaining gas in a throttle. A similar process for the production of ammonia synthesis gas from nitrogen rich blast-furnace gas or pit gases has been described [14].

Ammonia Purge Gas Separation. A low temperature process for ammonia plant purge gas purification features especially high yields in ammonia recovery and in recovery of hydrogen as a product and for recycle. The application of this process is especially advantageous if the low temperatures occurring in the initial condensation step are utilized in further stages to recover other valuable components such as noble gases and methane [15, 16]. Figure 5

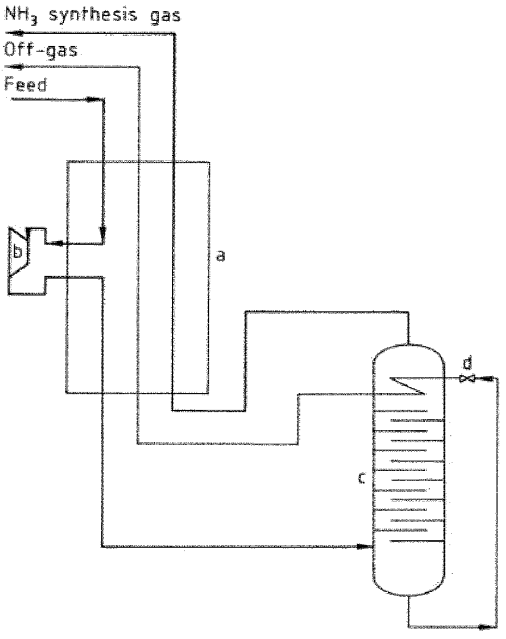


Figure 4. Rectification of an H_2/N_2 mixture and production of NH_3 synthesis gas (molar ratio $H_2 : N_2 = 3 : 1$) in the Braun purifier [13]
a) Heat exchanger; b) Expansion turbine; c) Rectification column; d) Joule – Thomson expansion

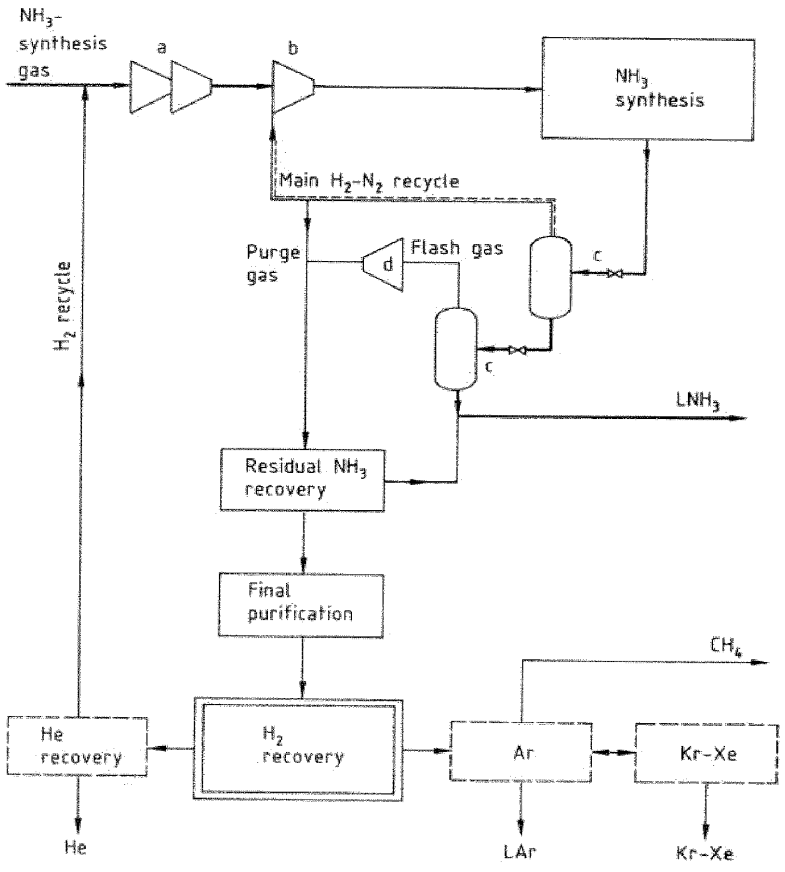


Figure 5. Integration of the low-temperature process into an ammonia plant [18]
a) Compressor; b) Recycle compressor; c) NH_3 condensate separator; d) Expansion turbine

shows the integration of the low-temperature process into the ammonia plant. Several plants have been built for the recovery of liquid argon. If only hydrogen is to be recycled, adsorption is a competing process (see Chap. 12). Combinations of both processes have also been proposed [12, 17].

2.3. Low-Temperature Absorption Processes

Absorption processes can yield greater purities than the condensation processes. Absorption processes are operated at higher temperature and thus with lower refrigeration requirements. The low-temperature processes described in this section are physical absorption processes, in which the impurities are condensed and either completely or partially utilized as scrubbing agent (for absorption processes with other scrubbing agents see Chap. 5).

Nitrogen Wash. A high-purity hydrogen – nitrogen mixture for ammonia synthesis is obtained by using a liquid nitrogen scrubber (→ Ammonia) [19]. This scrubber can not only reduce the catalyst poison carbon monoxide down to a few ppm but the inert gases such as methane and argon can also be removed. The methanation step can thus be avoided.

For modern ammonia processes, in which the synthesis gas is produced at high pressure, the nitrogen scrubber is particularly interesting (see → Hydrogen, 2. Production, Section 1.2.) At low temperatures around 80 K the system hydro-

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gen – nitrogen is still in the subcritical range, although pure nitrogen under these conditions is already supercritical. The necessary refrigeration for the nitrogen scrubber is produced by decompression of the nitrogen into the hydrogen stream.

Methane Scrubber. For the recovery of pure hydrogen from hydrogen – carbon monoxide mixtures (e.g., from synthesis gas) the use of a methane scrubber is frequently an alternative to the condensation of carbon monoxide. Methane scrubbers attain much higher hydrogen purities, especially with regard to the carbon monoxide content, than would be possible with the carbon monoxide condensation process. Simultaneously, pure carbon monoxide can be produced. Figure 6 shows the most important process stages of a methane scrubber [20].

Crude gas between 1.5 and 4.5 MPa is dried in adsorber (a) and cooled down to ca. 90 K in a heat exchanger (b). The carbon monoxide remaining in the gas phase after condensation is removed down to a few ppm in the scrubber (c) with subcooled liquid methane. The liquid phase from the knock-out drum (d) and from the column bottom after decompression and partial evaporation is fed into the carbon monoxide – methane separation column (e). Here the sump product is pure methane, which is used for scrubbing, whereas a carbon monoxide fraction is obtained as the head product. A carbon monoxide cycle provides the heating and the reflux for the separation column as well as the cooling for the scrubbing column. By decompressing a fraction of the carbon monoxide cycle and generating energy the refrigeration for the heat exchanger is obtained.

In a similar fashion, however without a carbon monoxide – methane separation column, methane scrubbers are used for the purification of refinery off-gas or for the production of pure hydrogen from the purge gas of hydrogenation plants (coal hydrogenation, heavy oil hydrogenation). Similarly, as shown in Figure 6, methane scrubbers combined with adsorption processes can be used for the recovery of pure hydrogen, oxo-synthesis gas and a methane-rich heating gas fraction [16].

Other Scrubbing Agents. Absorption processes at low temperatures are not confined to the aforementioned scrubbing agents. Higher hydrocarbons such as ethylene or propane have also been used. Hydrogen itself can also be used as a scrubbing agent if the product desired is helium. Processes of this kind have been proposed and plants built for the recovery of helium and neon from air separation units and from ammonia purge gas streams [21]. In both cases the noble gases are already preconcentrated by several orders of magnitude compared to their natural abundance.

3. Adsorption Processes

3.1. Principles

Because of the only slight interaction of hydrogen with the usual adsorbing agents in technically important pressure and temperature ranges,

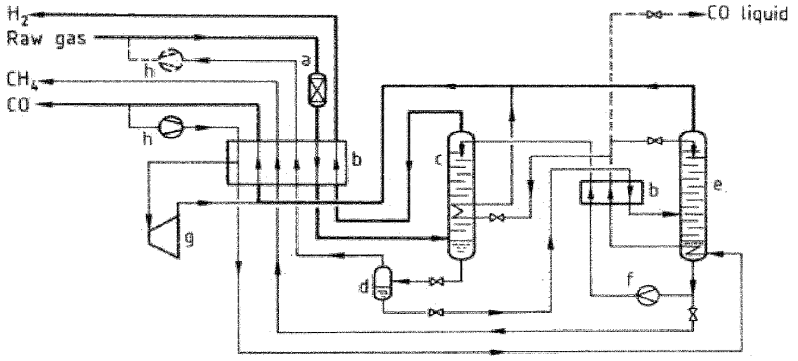


Figure 6. Plant for the recovery of hydrogen and carbon monoxide from H_2/CO-rich gases using a CH_4 scrubbing process
a) Adsorber for removal of H_2O and CO_2; b) Heat exchanger; c) Scrubbing column for CO with subcooled liquid methane; d) Knock-out drum; e) Separation of loaded wash methane to liquid lean methane (bottom) and pure carbon monoxide (top); f) Pump; g) Expansion turbine; h) Compressor

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Table 2. Adsorbents for the purification of raw hydrogen

Type	Main adsorption duty
Aluminum oxides	water
Silica gel	water, CO_2, C_{4+}
Activated carbon	CO_2, CH_4, C_{2+}, N_2
Molecular sieve (zeolite)	CH_4, CO, N_2
Carbon molecular sieve	O_2

adsorption processes are particularly suitable not only for the separation of hydrogen from other gases but also for the separation of impurity traces from hydrogen. For the principles of adsorption see → Adsorption [22–24].

The adsorbents for hydrogen purification are chosen according to the impurities to be removed. The most common adsorbents are given in Table 2. The gas mixtures are separated by various effects. *Steric effects* prevail if the adsorbent has a uniform and narrow micropore distribution, as is found particularly with the zeolites. *Equilibrium effects* result from different adsorption forces of the gases on the solids, and *kinetic effects* are caused by the different diffusion mobilities of the gases into the pores of the adsorbing agents.

Although each of these effects is present to a various degree in the adsorbent-gas combinations given in Table 2, the strength of the adsorption forces of the various impurities in the raw hydrogen mixtures can be used to put them in the order shown in Table 3. The sequence shown there may change slightly depending on adsorption agent, partial pressure of the impurity and total gas pressure of the system.

The static equilibrium loading capacity of the adsorbent for a particular component is depicted in the form of an *adsorption isotherm* (loading capacity depending on partial pressure at constant temperature). Adsorption isotherms have typical values for the adsorbents and the components in question and must be determined experimentally. For a number of typical components and some adsorbents these values have been compiled in handbooks and in specification sheets of the various producers.

Figure 7 shows the principal adsorption isotherms of various gases present during hydrogen purification on carbon molecular sieve (active charcoal obtained from coal). There is a characteristic affinity between each particular gas and the solid.

Adsorption is an exothermic process. Desorption, subsequently, is endothermic. In *thermally regenerated adsorbers* the energy necessary for the desorption is obtained by indirect heating of the bed or by using hot purge gas. In *pressure-swing adsorption* the desorption energy is obtained from the energy stored in the adsorption bed (thereby causing a temperature drop) if the pressure or the partial pressure of the components to be desorbed is decreased.

Table 3. Adsorption forces for various components in hydrogen purification

Component	Adsorption forces
Hydrogen	weak
Helium	
Oxygen	
Argon	
Nitrogen	
Carbon monoxide	
Methane	
Carbon dioxide	
Ethane	
Ethylene	
Propane	
Isobutane	
Propylene	
Hydrogen sulfide	
Mercaptans	
Benzene	
Toluene	
Ethylbenzene	
Styrene	
Water	strong

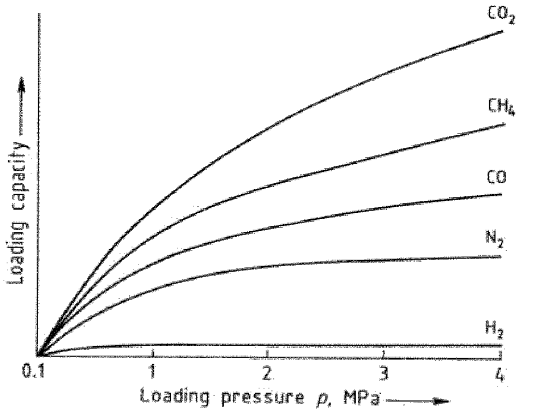


Figure 7. Principle form of equilibrium isotherms of mixtures of hydrogen with nitrogen, carbon monoxide, and methane [25]
Adsorbent material: carbon molecular sieves (activated carbon obtained from coal)

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Hydrogen purification takes place in adsorption vessels with fixed beds of adsorbents. Other types, such as trickle beds, adsorption columns with solid circulation, moving beds, or adsorption in ebullating beds, are not used for hydrogen purification on a technical scale.

3.2. Thermally Regenerated Adsorbers

Thermally regenerated adsorbers are used to remove traces of impurities from hydrogen streams or for selective removal of certain substances which disturb ensuing process steps. The process is often designated as temperature-swing adsorption (TSA).

The adsorbers are usually switched alternately. While one adsorber is in the adsorption stage, the other is regenerated or is held in readiness. Switching usually takes place in a defined sequence, whereby the time for the adsorption step must be chosen shorter than the time calculated for the breakthrough of the impurities. Typical cycle times for these processes are in the range of some hours up to several days.

The process is illustrated in Figures 8 and 9 for the adsorption of carbon dioxide in a hydrogen-rich synthesis gas on a molecular sieve (5 A). As shown in Figure 9, the adsorber becomes loaded to give a local concentration distribution which is indicated by curve a. The maximum adsorbed amount of carbon dioxide in the zone of the equilibrium concentration EZ is given by the equilibrium isotherm for 25 °C at point a in Figure 8.

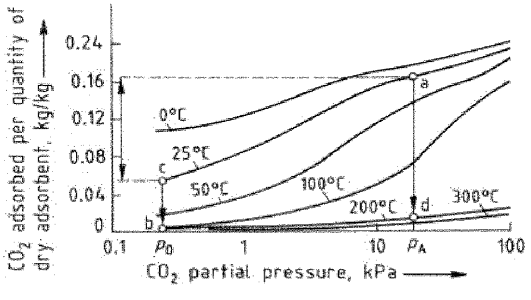


Figure 8. Adsorption and regeneration of CO_2 and molecular sieve 5 A, pellets
a) Adsorption loading; b) Desorption loading after decomposition and heating up; c) Theoretical desorption loading after decompression; d) Desorption loading after heating up without decompression
p_A = adsorption pressure; p_D = desorption pressure

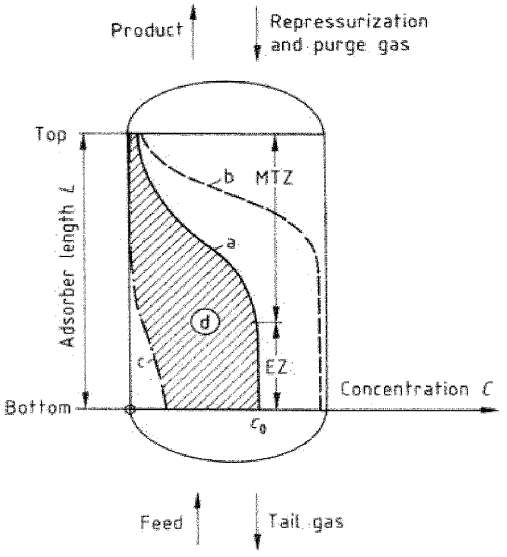


Figure 9. Concentration profiles in an adsorber (MTZ = mass transfer zone; EZ = equilibrium loading zone)
a) End of adsorption; b) End of cocurrent expansion; c) End of regeneration (residual loading); d) Useful cyclic capacity

In most cases regeneration is initiated by depressurizing. This procedure causes a desorption along the 25 °C isotherm to point c. However, because the depressurization is not isothermal, a cooling effect occurs, so that besides the kinetics of the desorption the adsorption conditions at the lower resulting temperature must also be considered. For a so-called cocurrent depressurization the distribution of the concentration in the adsorber is given by curve b of Fig. 9. The equilibrium along the isotherm is attained very slowly. The desorption energy requirements caused by the depressurization lead to a strong cooling of the adsorbent, which in the presence of water vapor can lead to formation of a liquid phase and thus to an irreversible damage of the adsorbent.

The main desorption takes place after the pressure has been lowered (point c in Fig. 8) mainly by increasing the temperature, in this case to 200 °C (point b or, if no previous depressurization took place, point d). The required heat is provided either indirectly by means of inserted heat exchanger coils or by direct heating with a purge gas at higher temperature. After regenera-

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tion, the adsorber is cooled to normal operating temperature and pressurized back to normal adsorption pressure.

Applications. Before low-temperature purification and separation can be carried out (see Chap. 11), gas components, which would at low temperatures form solid deposits in the heat exchangers and knock-out drums, must be removed. In synthesis gases from partial oxidation and steam reforming these are in particular water and carbon dioxide, whereas in refinery gases these are usually higher hydrocarbons. In dealkylation and coke oven gases benzene, toluene, and other aromatics must be removed, whereas in sulfur-containing raw gases hydrogen sulfide and carbonyl sulfide are the disturbing components.

If these impurities are present in higher concentrations, the major portion may first be removed by condensation (water and hydrocarbons) and/or scrubbing (CO_2, H_2S and COS). Final purification is then by TSA. A process description of the removal of water and carbon dioxide from a water-rich synthesis gas by TSA is given elsewhere (→ Gas Production, Section 5.5.2.).

Further applications for TSA in hydrogen purification processes are:

1. Removal of water and ammonia from ammonia purge gases before low-temperature separation.
2. Purification of hydrogen from electrolysis plants. The main impurities are water and oxygen. The latter is converted by means of catalytic oxidation (see Chap. 13) to water and then removed by condensation and TSA. Hydrogen from the chlor-alkali electrolysis contains also traces of mercury. This can be removed by TSA on a special molecular sieve [26].
3. Removal of various impurities from pure hydrogen before liquefaction. Here the adsorption is carried out at liquid nitrogen temperature. The regeneration is done with pure hydrogen from the recycle gas at ambient temperature (see → Hydrogen, 4. Liquefaction).

3.3. Pressure-Swing Adsorption (PSA)

Adsorption Mechanisms. Contrary to adsorption with thermal regeneration, pressure-swing adsorption operates at almost constant temperature using partial-pressure differences. However, the small temperature gradients occurring with ad- and desorption contribute considerably to the mechanism of the process. The components to be removed are adsorbed at high system pressure and high partial pressure and are desorbed at low system pressure in accordance with the appropriate equilibrium isotherms of the various impurities (see Fig. 7).

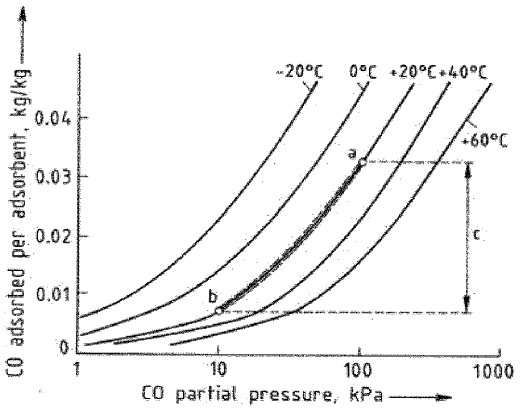


Figure 10. Adsorption isotherms for CO on molecular sieve a) Adsorption; b) Desorption; c) Adsorption capacity

Figure 10 shows, for the example of a hydrogen – carbon monoxide mixture, how carbon monoxide, which is easily adsorbed, reaches the equilibrium loading, a, on the molecular sieve, while pure hydrogen exits the adsorber. When the adsorber capacity is exhausted, the adsorbent must be regenerated. The carbon monoxide loading on the absorbent is reduced by depressurization and hydrogen purging. The difference c is the *available working capacity* of the adsorbent. However, as in the case of TSA, the *actual working capacity* of the total adsorbent is influenced by the presence of mass transfer zones (MTZ) (see Fig. 9). The length of a MTZ is basically determined by (1) the concentration of the component to be removed in the raw gas, (2) by the required product purity, and (3) by kinetic effects.

The PSA Process. Like the TSA process, the PSA process is cyclic, however, contrary to temperature swings, pressure changes can be carried out more rapidly and allow a shorter adsorption time. Typical cycle times are in the range of 3 to 10 min. Thus, removal of impurities

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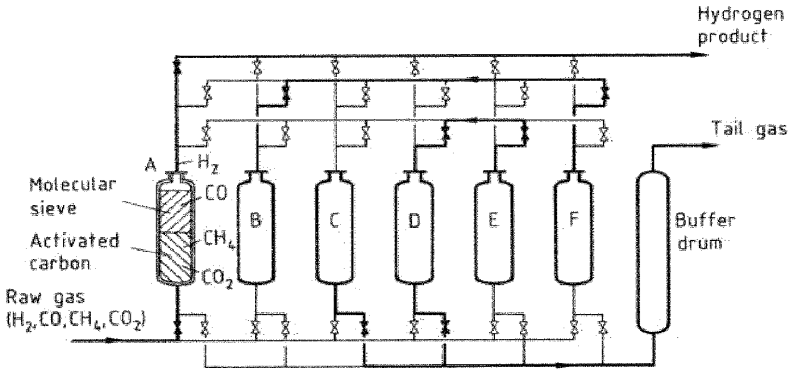


Figure 11. Six-bed PSA unit. Main flows for adsorption, repressurization, counterflow expansion (dump), counterflow purge, etc. for H_2 production by adsorber A. After termination of this adsorption step, next on-stream adsorber is B, etc.

Adsorber	A	B	C	D	E	F
Function	Adsorption	Repressurization	Dump	Purge	Depressurization	Depressurization
Start pressure, (MPa)	2.8	1.6	0.4	0.2	0.8	2.8
Final pressure, (MPa)	2.8	2.2	0.2	0.2	0.4	2.2

present in high concentrations can be accomplished using moderately sized adsorber vessels. The essential steps carried out in a PSA unit are shown in Figure 11 [27]. Each adsorber is performing a different task, depending on which phase of the complete PSA cycle is regarded. The chronological sequence of all steps constitutes the cycle of one adsorber:

1. Adsorption at the pressure of the raw gas (highest system pressure), hydrogen production (adsorber A);
2. Cocurrent depressurization, provision of gas for pressure equalization and purging (adsorbers F and E);
3. Countercurrent depressurization, production of part of the tail gas (adsorber C);
4. Countercurrent purging (lowest system pressure), production of another part of the tail gas (adsorber D);
5. Countercurrent repressurization (adsorber B).

Figure 12 [28] shows the different process stages with respect to the equilibrium loading on the adsorbent. The possibility of continuing the decompression stage into vacuum is also shown. This latter mode of operation is indicated for the enrichment and recovery of the adsorbed component. However, production of concentrated byproducts during the production of pure hydrogen is usually carried out by low-temperature processes and not by the adsorption process.

The mode of operation of a PSA can be summarized as follows:

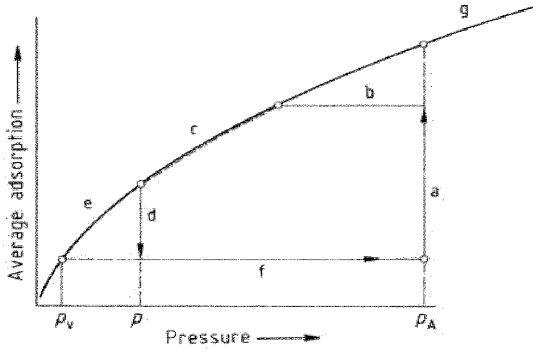


Figure 12. Theoretical pattern of the status of PSA adsorbers in respect to loading during one adsorption cycle [28]
a) Adsorption; b) Cocurrent depressurization; c) Countercurrent depressurization; d) Purge; e) Depressurization to vacuum; f) Repressurization; g) Equilibrium adsorption isothermal
p_A = adsorption pressure, p = purge gas pressure; p_v = final vacuum obtained

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1. Pure hydrogen is produced continuously at adsorption pressure.
2. Tail gas is produced continuously, the pressure, composition, and amount of which fluctuate periodically. These fluctuations are smoothed out by buffer vessels.
3. The efficiency of a PSA is defined by the amount of pure hydrogen produced in relation to the total hydrogen amount present in the crude gas. Depending on the crude gas composition and the degree of technical sophistication utilized, the PSA efficiency ranges between 70 and 90 %.

Technical PSA Plants. The simplest PSA system requires three adsorbers to enable continuous operation. Hydrogen yields of > 80 % can only be attained in systems with more than 4 adsorbers.

Since the size of the adsorber is usually limited because of manufacturing or transport considerations, larger quantities of crude gas can only be treated if several adsorbers are used in the adsorption phase simultaneously (multi-bed process) [29, 30]. With such schemes PSA plants using 3 to 12 adsorbers can process amounts of crude gas ranging from 100 to more than 100 000 m^3 (STP)/h.

The maximum attainable hydrogen yield is influenced by a number of factors, the most important are:

1. *Composition of the crude gas.* For the economical operation of a plant the hydrogen content of the crude gas should be at least 50 %. The maximum hydrogen content is 95 – 99 %. Depending on the total amount of gas, TSA plants may be more suitable for such high-purity raw gases.The concentration and nature of impurities with respect to their ad- and desorption behavior determines basically the size of the adsorber which in turn results in higher or lower loss of hydrogen.
2. *Pressure ratio feed gas: purge gas.* This influences the size of the adsorber and the extent of the effort necessary for regeneration. At high pressure ratios the yields can be increased by using several pressure equalization steps (plants with more than 4 adsorbers).
3. *Purity requirements and nature of impurities.* The hydrogen purity in the PSA plants is usually >99.9 %. Higher purities with respect to those compounds which are poorly adsorbed, such as the inert gases nitrogen, argon, etc., are attainable at the expense of the yield. In spite of this, purities of 99.9999 %, i.e., hydrogen with <1 ppm impurities, can be realized on an industrial scale.
4. *Temperature of the feed gas.* High temperatures (>40 °C) result in a lower capacity of the plant, or in a poorer yield. Lower temperatures are therefore favored. Care must be taken, however, to avoid condensation of certain impurities in the regeneration step. For example, liquid or freezing water can damage the adsorbent.

Important developments in the design of large PSA plants were first possible after the introduction of microprocessor control systems. The main problems facing the control system are caused by the speed and the precision required by the short-time cycles. For this reason, modern plants are controlled by microprocessors using a 1-s sequence achieving "real time" control. Beyond this, it is now possible, not only to control the sequence and valves, but also to have a real process control system. This allows a high degree of flexibility for the changing of various process parameters and the indication of disturbances. In particular, the automatic initiation of disturbance strategies in the case of process, pressure and valve failures, e.g., shut-down of an upset adsorber without interrupting hydrogen production, is possible. Very high requirements are placed on the vessels and valves with up to 50 000 cycles (i.e., valve closures) per year. The operational practice has shown, however, that these plants are very reliable, so that they have become standard.

In the past years purification of hydrogen by means of PSA has increased more than any other gas purification process. Figure 13 gives an impression of the breakthrough of this new technology. As can be seen from the number of plants corresponding to the plant capacity, not only the number of plants per year put on stream has increased, but also the amount of hydrogen purified per plant. Plants > 100 000 m^3 (STP)/h inlet gas are not uncommon nowadays.

Applications [27]. *Gas Purification in Steam-Reforming Plants* (see → Hydrogen, 2. Production, Section 1.3.). Other gas purification

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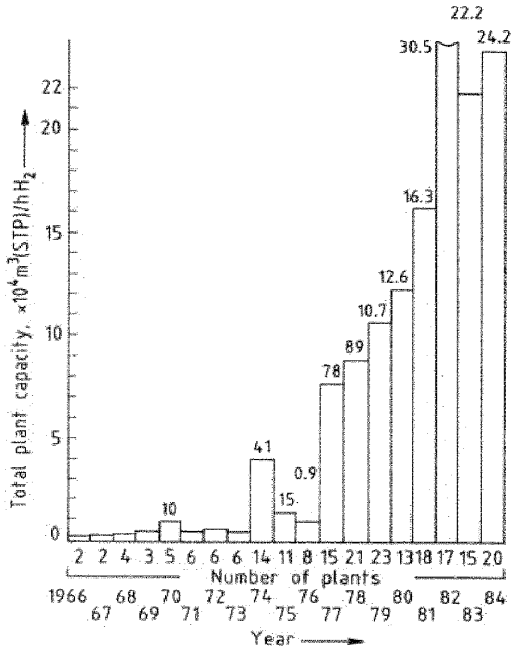


Figure 13. Worldwide capacity of H_2 gas purification plants with pressure-swing adsorption technology (put into operation from 1966 to 1984)

processes have been more or less completely replaced in this area [31]. For the production of hydrogen and carbon monoxide by steam reforming, PSA in combination with a low-temperature plant can also be economically used. The amount of gas handled by the plants built ranges from 500 – 87 000 m^3 (STP)/h of product gas. These plants use the tail gas produced to fire the reformer. Specially designed control loops and buffer systems lead to a very homogeneous tail-gas flow which is discharged with only small fluctuation in composition and flow, so that a reliable operation of the burners is possible.

Refinery Gases (see → Hydrogen, 2. Production, Section 1.4.). Because of the increasing demand for hydrogen for hydrogenation in refineries the PSA process is used there for hydrogen recovery and production. Refinery gases have a hydrogen content of 60 – 80 % the remainder being higher boiling hydrocarbons (C_6 – C_{10}). These are adsorbed well, but are difficult to desorb which can cause damage to the adsorbent. By choice of suitable adsorbents these difficulties can be avoided. Plants with feed gas capacities up to 100 000 m^3 (STP)/h have already been built. Figure 14 shows the hydrogen purification section in a large refinery in Kuwait.

Coke Oven Gas (see Section → Hydrogen, 2. Production, Section 1.1.). Coke oven gas purification places the highest demands on the adsorption technology because of the inlet gas composition. Special preadsorbers have been used to remove impurities such as tar, naphthalene and

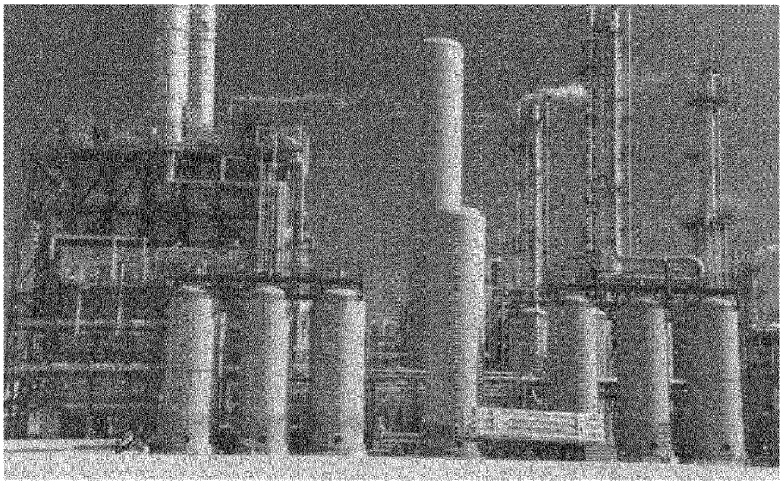


Figure 14. Production of hydrogen from refinery off-gas. Plant with 12 adsorbers and 2 buffer drums (in the center) for flow and composition equalization
Plant capacity: 100 000 m^3 (STP)/h refinery gas; H_2 content: 80 %; product purity: >99 %; recovery rate: 89.5 %. Erected by German Linde in Kuwait in 1986

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higher sulfur compounds, which have a poor desorption capacity.

Hydrogen-Rich Gases from Various Synthesis Processes. Apart from numerous small plants which operate for example with ammonia or methanol plant purge gas, the coal gasification at SASOL is to be mentioned. 160 000 m^3 (STP)/h of off-gas from the coal gasification, respectively the Fischer – Tropsch synthesis is purified in five PSA plants.

4. Catalytic Gas Purification

Four distinct cases for the use of catalytic processes for gas purification can be distinguished:

1. A component of the crude gas is to be catalytically converted to hydrogen, i.e., a secondary hydrogen production process.
2. Impurities in the crude hydrogen are to be catalytically converted into a form which allows them to be more easily removed from the gas by other purification processes (condensation, adsorption).
3. Gas components, which even in traces could be detrimental to the use of the hydrogen, are converted into harmless components with only minor changes in the gas purity.
4. Adsorption processes, in which certain impurities are chemically bound to the adsorbent so strongly that a regeneration during normal operation does not take place.

4.1. Carbon Monoxide Removal

Hydrogen from synthesis gas may contain up to 50 % carbon monoxide (partial oxidation). Carbon monoxide can be recovered for CO production by a methane scrubber (see Section 2.3) and used for synthesis, or it can be reacted with water to produce hydrogen and carbon dioxide (water – gas reaction, shift conversion):

$$CO+H_2O \rightarrow H_2+CO_2$$

The reaction is exothermal. Because of the equilibrium conditions the carbon monoxide conversion is incomplete in adiabatic reactors. For increased carbon monoxide conversion a greater amount of water ($c_{H2O}/c_{CO} > 3$) is necessary. At high carbon monoxide concentration a series of adiabatic reactors with intercooling is used. Isothermal reactors have also been suggested [32]. Depending on the type of catalyst used, three types of conversion may be identified.

Conversion of Sulfur-Containing Gas. Crude gas from partial oxidation or coal gasification, which contains at least 50 ppm hydrogen sulfide, can be converted on metals of group 6, 8, 9, or 10 of the periodic table (exceptions: Cr and Fe) or on mixtures of these metals. The carrier is aluminum oxide, sometimes alkaline compounds are present as a promoter. The metals are totally or partially sulfided, the sulfided form being the most active form. The usual catalysts contain cobalt, molybdenum, and nickel as active components. They can be used at 10 MPa and 250 – 550 °C.

An industrial process with these catalysts was described in → Hydrogen, 2. Production, Section 1.2. A detailed description of the kinetics of crude-gas conversion is found in [33], patents in [34].

High-Temperature Shift (HT Conversion). For essentially sulfur-free gases, e.g., the product gas of the steam reformer or the secondary reformer, the well-known carrier-free conversion catalysts on iron oxide – chromium oxide basis can be used, e.g., 74 % Fe_2O_3, 10 % Cr_2O_3, 0.2 % MgO (rest: volatile components). Sulfur up to several hundred ppm can be tolerated although the activity then drops; catalyst poisons are phosphorus, silicon and unsaturated hydrocarbons in the presence of NO_x.

The shift reaction runs almost to equilibrium at space velocities between 3000 and 10 000 m^3 (STP) h^{-1} m^{-3} and pressures up to 7 MPa. The reaction temperatures are in the range 300 – 530 °C [35].

In steam reforming plants usually only one HT conversion stage is installed. To decrease the carbon monoxide concentration further, low-temperature conversion catalysts are used. If the purified synthesis gas in coal gasification plants is to be converted, a series of adiabatic reactors can be used. The last stage of this cascade usually consists of a low-temperature conversion.

Low-Temperature (LT) Conversion. The catalysts for LT conversion are supplied in their oxidized form, the major component of the un-

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reduced catalyst is CuO, usually in a mixture with ZnO. Other components may be Cr_2O_3 and Fe_2O_3 (stabilizers) and Al_2O_3 (carrier) [33, 36]. The temperature range used is 190 – 260 °C; the lower temperature is limited by the dew point of the gas, the upper temperature because of the sensitivity of the copper catalyst to thermal deactivation.

These catalysts are extreme sensitive to sulfur, contents of 0.1 ppm leading to their deactivation, so that a suitably large reactor volume must be used to ensure that any slow deactivation of the catalyst will not cause any premature shutdown of the unit. Very often guard beds are placed before the actual catalyst [37]. For more details on the use of HT and LT shift conversion in steam reforming plants see → Hydrogen, 2. Production, Section 1.3. and → Gas Production.

The thermal stability of copper catalysts can be raised considerably if they are used in a silica-supported form. These supported catalysts are prepared by precipitation from a homogeneous solution and are found to be very active for the water – gas shift reaction [38]. The catalyst can be reduced at a temperature of 450 °C and can be operated between 275 and 400 °C with initial carbon monoxide concentrations up to 10 %. A $Fe_2O_3 - Cr_2O_3$ catalyst has been prepared in a similar way and also shows improved activity at lower temperature, at the same time the resistance to traces of sulfur and chlorine compounds [39] still being preserved.

Because of considerations of equilibrium, reaction temperature and efficiency of the catalyst, the shift reaction can remove carbon monoxide only down to a remaining concentration of ca. 0.2 – 0.5 vol % in the dry gas. For refinery gases, however, purities <0.1 %, for hydrogenation of fats and oils <10 ppm (mL/m^3) and for ammonia synthesis <1 ppm (mL/m^3) are required (see → Hydrogen, 6. Uses). For these and other purposes a further purification stage is necessary. In many cases this is the methanation step.

4.2. Methanation

Here, methanation is described as a process for the removal of traces of carbon monoxide or carbon dioxide. For the conversion of large carbon monoxide concentrations to yield substitute natural gas see → Gas Production, Section 5.3.4.

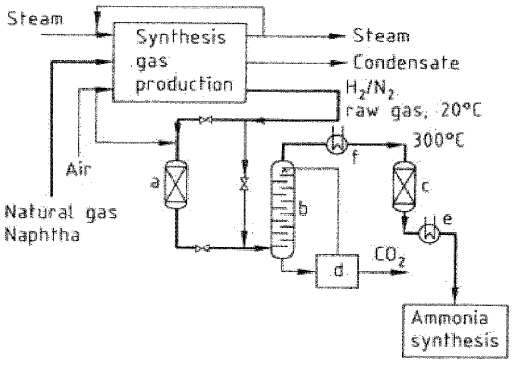


Figure 15. Removal of CO and CO_2 from ammonia synthesis gas ($3H_2 + N_2$) by selective oxidation (SELECTOXO), CO_2 scrubbing, and methanation
a) Selective oxidation; b) CO_2 scrubber; c) Methanation; d) Regeneration of the scrubbing agent; e) Gas cooling; f) Gas heating

Especially for ammonia plants the carbon monoxide concentration in the gas must be decreased (see also Fig. 15). This is done by using the reaction

$$CO + 3\,H_2 \rightarrow CH_4 + H_2O$$

The methanation converts carbon monoxide, which is a poison for the ammonia synthesis catalyst, to the inert gas methane. However, losses in hydrogen content (3 mol H_2 per mole of converted carbon monoxide) must be accepted. The design of methanation reactions is described [40].

Under typical methanation conditions (high hydrogen partial pressure, low methane and water content) the equilibrium is shifted far to the methane side, so the resulting carbon monoxide concentrations are usually below the detection limit. Nickel oxide, sometimes together with chromium oxide, is used as a catalyst. However, it must be reduced before the start-up. Aluminum oxide or diatomaceous earth is used as carrier. The metallic content of the catalyst is very high (30 – 60 %) compared to the nickel catalyst used for steam reforming.

The following undesired side reactions may occur:

$$CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O$$

$$2\,CO \rightarrow C + CO_2$$

$$Ni + 4\,CO \rightarrow Ni(CO)_4$$

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4.3. Selective Oxidation

The disadvantage of hydrogen losses and increased inert content in the aforementioned methanation process can be avoided, if carbon monoxide is oxidized to carbon dioxide, because the latter can be readily removed from hydrogen. However, as a side reaction oxidation of hydrogen, which is present in much greater concentration, may occur:

$$2\,CO + O_2 \rightarrow 2\,CO_2$$

$$2\,H_2 + O_2 \rightarrow 2\,H_2O$$

In spite of this, selective oxidation of carbon monoxide can be achieved on a special noble metal catalyst [41–43]. The incorporation of this process stage into the synthesis gas production for ammonia is shown in Figure 15.

The selective oxidation is placed behind the last shift reactor after removal of excess water by condensation. Air, which is taken from the compressed air for the secondary reformer, is used as oxidizing agent. Oxidation takes place at 50 – 70 °C in an adiabatic bed reactor. The temperature increase resulting from the heat of reaction amounts to 10 K per 0.1 mol % carbon monoxide. The carbon monoxide content can be reduced to ca. 100 ppm (mL/m^3) by this method. If the gas is to be used for ammonia synthesis, an additional methanation stage must still be incorporated for final clean-up.

4.4. Catalytic Removal of Sulfur Compounds

Sulfur compounds are catalyst poisons for hydrogen production and the various syntheses using hydrogen. Desulfurization is achieved in two stages: (1) hydrogenation and (2) hydrogen sulfide removal. Depending on the feed gas, these stages may be carried out separately or simultaneously. In the first step, organic sulfur compounds and carbonyl sulfide are hydrogenated to hydrogen sulfide

$$RCH_2SH + H_2 \rightarrow H_2S + RCH_3$$

$$COS + H_2 \rightarrow H_2S + CO$$

a cobalt – molybdenum contact is normally used as hydrogenation catalyst. If the gas contains a great amount of carbon monoxide, e.g., coke oven gases, the cobalt – molybdenum catalyst must be sulfided in order to avoid methanation of carbon monoxide (see Section 4.2).

Hydrogenation of sulfur compounds is favored by high hydrogen partial pressure and temperatures around 350 °C. After the hydrogenation of the sulfur compounds, the hydrogen sulfide formed can be removed by chemical or physical scrubbing (see Chap. 14), if its concentration is > 1 %

For lower concentrations, hydrogen sulfide is absorbed on zinc oxide.

$$ZnO + H_2S \rightarrow ZnS + H_2O$$

Zinc oxide is available in the form of spheres, tablets or extrusions. The average sulfur pick-up until hydrogen sulfide breaks through the bed is ca. 25 % of the stoichiometric amount. The reaction temperatures are 100 – 350 °C (max. 400 °C). Organic sulfur compounds and carbonyl sulfide are partially cracked and absorbed in the zinc oxide bed, so that for natural gases with a low sulfur content the hydrogenation may not be necessary. The final purity after a zinc oxide bed is <1 ppm (mL/m^3) sulfur. The zinc oxide cannot be regenerated in situ but must be replaced.

Other materials used for desulfurization are, e.g., iron hydroxide (a byproduct of aluminum production), iron ore, and other purification agents containing iron oxide or iron hydroxide activated with alkaline compounds [44]. These absorption agents are mainly used for purification of coke oven gas before it is used as town gas. The achievable purity is <2 mg sulfur/m^3 (STP) (ca. 10 ppm [mL/m^3] S as H_2S). Iron- or copper-activated carbon can also be used. The regeneration of these agents with superheated steam is, however, only partially possible.

Chemisorption:

$$2\,Fe(OH)_3 + 3\,H_2S \rightarrow Fe_2S_3 + 6\,H_2O$$

Regeneration:

$$Fe_2S_3 + 3\,H_2O + 3/2\,O_2 \rightarrow 2\,Fe(OH)_3 + 3\,S$$

4.5. Removal of Oxygen

Hydrogen from coke oven gas and from an electrolysis (contrary to the hydrogen produced from other reducing processes) very often con-

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tains oxygen in concentrations up to 1 %. This oxygen is removed in *deoxo* reactors.

$$2\,H_2+O_2 \rightarrow 2\,H_2O$$

Small levels of platinum and palladium on typical carriers such as α-Al_2O_3, active charcoal, or aluminosilicates provide highly active catalysts for the conversion (e.g., 0.3 % palladium on alumina). The catalyst is active even at ambient temperature, although usually higher temperatures are used.

Because of the strongly exothermic reaction a heat exchanger is installed after the deoxo reactor. The reaction product water is removed by adsorption. An example for the use of this process with prepurified coke oven gas is given in Figure Hydrogen, 2. Production, Figure 3.

Another method for oxygen removal is the use of catalytically active non-noble metals, usually copper or nickel, on carriers, e.g., silicon dioxide. These contacts operate at higher temperatures (300 °C) and are less sensitive to impurities such as hydrogen sulfide than are the noble metal catalysts. Both catalytic processes for oxygen removal are very selective, yielding purities of 1 ppm (mL/m^3) oxygen.

4.6. Removal of Nitrogen Oxides

In gases from coke ovens and coal gasification plants, in particular from entrained-bed gasifiers, traces of nitrogen oxides are present. These must be removed before gas separation in a cryogenic process is possible. Principally, nitrogen oxides can be removed from hydrogen streams by either oxidation or reduction. In the *reduction process* the nitrogen oxides are hydrogenated on sulfided cobalt – molybdenum catalysts, and water and nitrogen are produced. The reaction can be accelerated if small amounts of ammonia are present in the gas. Water and ammonia are removed in downstream scrubbers. The nitrogen produced can usually be neglected for the hydrogen purity.

Oxidative removal of NO takes place with ozone or, particularly selective, with ClO_2. The NO_2 produced is removed by use of scrubbers with alkaline-reducing agents (reduction to nitrogen). Final purities of ca. 0.01 ppm (mL/m^3) NO can be attained.

5. Scrubbing Processes

Scrubbing processes are used to purify large quantities of hydrogen. The compounds to be removed are absorbed in the scrubbing liquid. Since this can be done by utilizing either their different solubility in the scrubbing agent or by reaction with the scrubbing agent, the scrubbing processes are subdivided into physical and chemical processes.

5.1. Principles

For a detailed description of the physical and chemical principles of gas scrubbing see → Absorption, 1. Fundamentals and [45–47].

For selection, design and economics of a physical absorption process the most important factor is the solubility coefficient of a component given as λ (m^3 [STP] $bar^{-1}\,t^{-1}$) or λ' (kmol $bar^{-1}\,t^{-1}$) [3]. The capacity of an absorbent can be represented by the solubility curve as a function of pressure and temperature. These are shown in Figure 16 for carbon dioxide.

For physical absorption the capacity at first follows Henry's law (i.e., a linear relationship, curves a, f, g, h), while for chemical absorbents typically a curve, which approaches a saturation value (curves b, c, d, e) is found. Apart from solely physical or solely chemical scrubbing, combined process can be used. Here the scrubbing stages

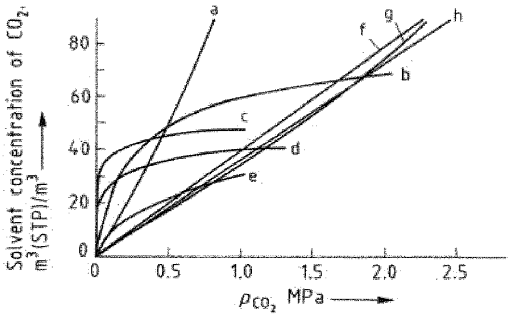


Figure 16. Absorption equilibria of carbon dioxide in various solvents [47]
a) Methanol, −15 °C; b) MDEA (methyl diethanolamine), 75 °C, 3.5 molar; c) MEA (monoethanolamine) 75 °C, 3 molar; d) Hot potassium carbonate, 110 °C; e) TEA (triethanolamine), 75 °C, 2.5 molar; f) NMP (*N*-methylpyrrolidone), 20 °C; g) Propylenecarbonate, 25 °C; h) Selexol (polyethyleneglycol dimethyl ethers)

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may be separate and operated in series (e.g., crude and fine scrubbing) or a mixture of a physical and a chemical scrubbing agent may be used.

Chemical scrubbing is only suitable for acid gas components such as CO_2, H_2S, COS, and HCN. Physical scrubbing, on the other hand, can also be used for other components such as benzene, and higher hydrocarbons.

The raw gases for hydrogen production, depending on their source, contain several impurities in various concentrations; apart from that, they are at various pressures. For the choice of the optimum scrubbing process, the following factors are important:

1. Type, amount and partial pressure of the component to be removed;
2. Type, amount and total pressure of the gas to be purified;
3. Required final purity, utilization or subsequent process steps for the product gas and the impurities removed;
4. Consumption figures

Physical scrubbing is preferred for large gas quantities at high pressure with high concentrations of impurities to be removed; *chemical scrubbing* is particularly suitable when the absolute amount of the component to be removed is small. It can be used both at atmospheric and at higher pressure. With chemical scrubbing it must also be certain that there is no component in the raw gas, that can react irreversibly with the scrubbing agent. Carbonyl sulfide, for example reacts with MEA (monoethanolamine) to form stable salts. Here the absorbent cannot be regenerated by heat alone, and this leads to a loss of scrubbing agent.

Figure 17 shows how the choice of a suitable scrubbing process can be made for certain limiting parameters (e.g., partial pressure of the substance to be removed in the inlet and the exit gas). An overview of the processes used at present to remove acidic components from gases (synthesis and natural gas), is given in [49].

The most important processes used for purification in hydrogen production are:

1. Carbon dioxide removal from converted steam reformer gases for the production of hydrogen or ammonia synthesis gas. Here the hot potash scrubbers and modifications thereof, often combined with an amine wash, are used (see → Absorption, 1. Fundamentals). In recent times activated MDEA (methyl diethanolamine) wash processes and certain mixed amine processes have been found to

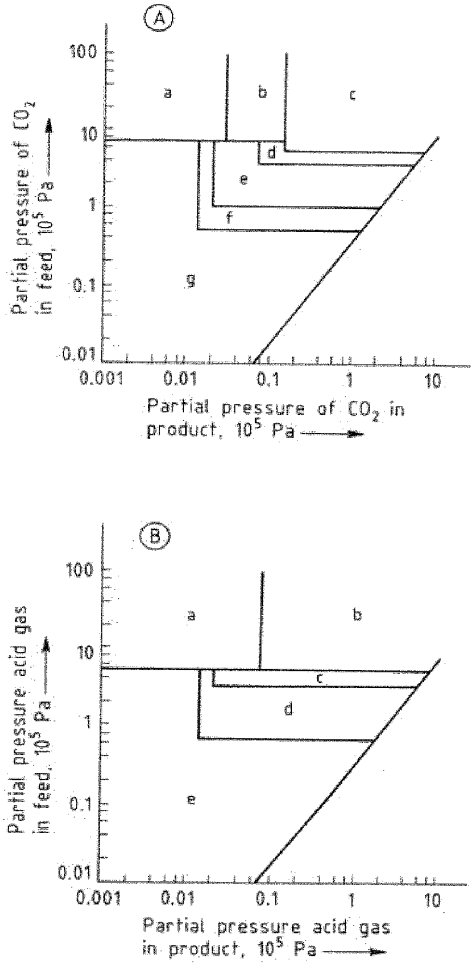


Figure 17. Examples for the selection of a suitable scrubbing process for CO_2 or CO_2 – H_2S removal with respect to partial pressures in feedgas and product gas, [48]
A) Selection of solvent for CO_2-removal, no H_2S; a) Physical solvent plus amine; b) Physical solvent, physical solvent plus amine or activated hot potassium carbonate; c) Physical solvents, d) Physical solvents or activated hot potassium carbonate; e) Activated hot potassium carbonate or concentrated amine; f) Activated hot potassium carbonate or amine; g) Amine
B) Selection of solvent for simultaneous removal of H_2S and CO_2; a) High loading amines (DEA), Selexol, Rectisol; b) Physical solvents; c) Physical solvents or diglycolamine; d) Activated hot potassium carbonate, Sulfinol, amines; e) Amines, Sulfinol

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have some economic advantages, however, there still is a tendency to use physical scrubbing processes (Selexol, Sepasolv, etc.) for crude gas purification.

2. For the simultaneous and separate removal of carbon dioxide and hydrogen sulfide from converted or unconverted raw gas from partial oxidation of heavy oil or coal, the Rectisol process has been successful and is used almost exclusively for coal gasification plants.

5.2. Physical Scrubbing (Rectisol Process)

The Rectisol process (→ Gas Production) (jointly developed by Linde and Lurgi) is a physical scrubbing process with methanol as the preferred scrubbing agent. Newer variations use other organic solvents or solvent mixtures (e.g., Rectisol II, [51]). Since the absorption capability of organic solvents increases at lower temperatures and since, in addition, losses of scrubbing agent are smaller, Rectisol processes are usually operated at 200 – 260 K. The solubility of various gases in methanol is given in [3] and [51].

Depending on the process chosen, carbon dioxide and hydrogen sulfide can be recovered together or separately. Usually the simpler plants have a common scrubbing stage. Proper configuration of the main scrubbing and the purification section allows a very high attainable purity (20 – 50 ppm [mL/m^3] CO_2). For special purposes (e.g., methanol synthesis gas), a certain amount of CO_2 can be left in the gas and the fine scrubbing can be used only for the sulfur containing compounds. The disadvantage of the simple process is that a tail gas is obtained which, apart from carbon dioxide, also contains a certain amount of sulfur compounds and other traces (HCN, CO). Such a gas must, therefore, be treated by special processes.

For the production of a sulfur-free carbon dioxide fraction and a hydrogen sulfide fraction suitable for the Claus process, selective Rectisol scrubbing processes are used (→ Gas Production). Figure 18 shows a simplified process scheme with process description. Rectisol is very flexible with respect to the attainable purity of the product gas, the pressure range and any possible process variations. In addition, there are no corrosion problems. For ammonia synthesis gas the Rectisol process can be combined advantageously with a low-temperature liquid nitrogen wash (see Section 2). Other physical gas scrubbing processes are summarized in Table 4.

5.3. Chemical Scrubbing Processes

An example of chemical scrubbing in hydrogen production is the combination Benfield – DEA scrubber (so-called High-Pure Benfield). For the SASOL II and III plants carbon dioxide is re-

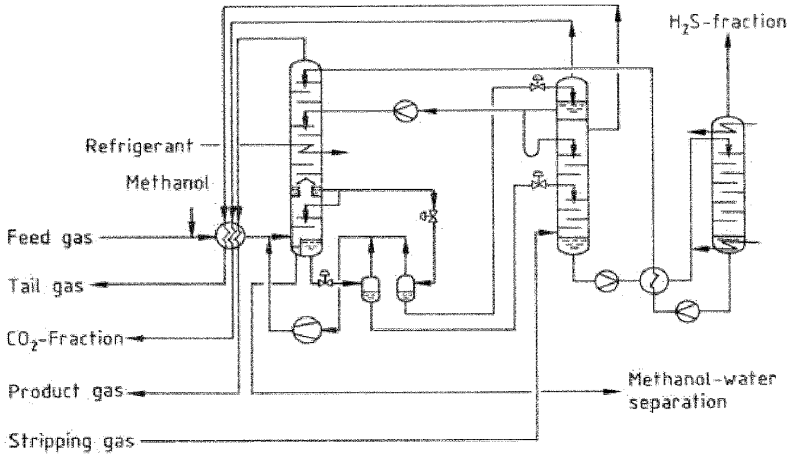


Figure 18. Selective Rectisol scrubbing process for production of a sulfur-free carbon dioxide fraction and a hydrogen sulfide fraction suitable as Claus plant feed [52]

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Table 4. Physical gas-scrubbing processes

Name	Solvent	Temperature, °C	Licensor
Fluor-Solvent	propylene carbonate	ambient	Fluor
Purisol	*N*-methyl pyrrolidone	ambient	Lurgi
Selexol	polyethyleneglycol dimethylether	0 – 40	Norton
Sepasolv	polyethyleneglycol diisopropylether	0 – 40	BASF

moved from the recycle gas of the Fischer – Tropsch synthesis, which in total amounts to 7×10^5 m^3 (STP). After the ensuing low-temperature separation, a gas with 80 % hydrogen is obtained which is fed either to the Synthol synthesis or to a PSA plant. A process scheme is shown in Figure 19.

High-Pure Benfield Process. Both scrubbers contain an absorption and a regeneration tower, the latter operating at almost atmospheric pressure. The temperature ranges between 70 and 108 °C in (a) and between 50 and 60 °C in (f). The absorbents are regenerated by indirect heating with steam. The final cooling of the regenerated absorbents takes place in air coolers, the cooling of the purified gas in water coolers. The hot potash scrubber (first stage) lowers the carbon dioxide level below 0.8 vol %, the final DEA scrubber below 80 ppm (mL/m^3). The relatively small carbon dioxide amount from the DEA

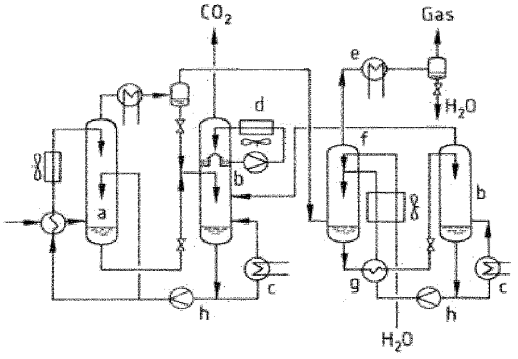


Figure 19. Flowsheet of a combined Benfield – DEA scrubber (High Pure Benfield) for CO_2 removal from Fischer – Tropsch synthesis recycle gas (SASOL II and III) [53]
a) Absorption column; b) Regeneration column; c) Steam generator; d) Air cooler; e) Water cooler; f) DEA scrubber; g) Heat exchanger; h) Pump

Table 5. Industrially important chemical scrubbing processes

Classification	Scrubbing agent	Additives	Trade name, licensor
Amine washes	MEA		
	MEA	not specified	Aminguard (UCC)
	DEA		
	HDEA		Linde
	MDEA		
	DGA		Fluor
	DIPA		Adip
	activated		Shell
	MDEA,	various	BASF
	t-amines	various	UCARSOL (UCC)
Physical – chemical washes	sulfolane, DIPA		Sulfinol (Shell)
	methanol, amine		Amisol (Lurgi)
Hot potash washes	K_2CO_3– H_2O	vanadium, DEA	Benfield
		amineborate	Catacarb
		borax	Lurgi
		arsenate	Giammarco
Caustic scrubber	NaOH – H_2O	only used for fuel purification, no regeneration	

regeneration column (b_2) is fed to the hot potash regeneration column (b_1) and there, together with the main amount of carbon dioxide, vented into the atmosphere or recovered and used for other purposes.

Table 5 lists some other chemical scrubbers.

Oxidative scrubbing processes are sometimes used to remove hydrogen sulfide, e.g., for the purification of coke oven gas or other gases from hydrogen purification plants. Hydrogen sulfide is absorbed and oxidized in the scrubbing agent to form elemental sulfur (→ Gas Production). Such processes are:

Stretford process (British Gas Corp.)
Locat process (ARI)
Sulfolin process (Linde)

An overview of the literature on hydrogen sulfide removal from coke oven gas, low-Btu gas, rest gases and natural gas is given in [54], on newer oxidative scrubbing processes in [55]. The scrubbing processes described, however, are unable to remove the so-called "inert components" (noble gases, nitrogen, carbon monoxide, methane). In general, further purification steps on the basis of adsorption and catalysis (see Chap. 4) as well as low-temperature processes including

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cryogenic scrubbing with liquid methane (see Chap. 2) are necessary.

6. Permeation Processes

For purification of hydrogen and for separation of hydrogen from gas mixtures processes based on the principle of diffusion and permeation through membranes are also suitable. The physical fundamentals of diffusion processes are given in [56] together with a detailed description of diffusion separation methods in [57].

The driving force for gas transport through membranes is the partial pressure of the gases. The permeating flux Q_i (per unit area of surface and time) is given by Equation (57):

$$Q_i = \frac{P_i}{d} \cdot (p_{i2} - p_{i1}) \quad (57)$$

where P_i, the permeation coefficient, is the product of solubility and diffusion coefficients of a gas i, p_{i2} and p_{i1} are partial pressures on the high- and the low-pressure sides of the membrane and d is the membrane thickness.

To separate various components it is essential to have different permeation coefficients. The separation capability of the membrane is defined by the selectivity α; this is the ratio of the permeation coefficients of the two gases i and j

$$\alpha = P_i/P_j$$

The fact that the permeation coefficient of hydrogen is much higher than that of other gases is utilized to separate hydrogen by diffusion through metal or polymer membranes.

6.1. Metal Membrane Techniques

Hydrogen diffuses well and with a high specific permeation rate through membranes consisting of palladium, palladium – silver or palladium – rare earths. Silver – palladium alloys with 23 wt% silver are most suitable. The diffusion rate of hydrogen is highest at a composition close to the maximum solubility of silver in palladium (i.e., ca. 23 wt%); furthermore, material distortion by $\alpha - \beta$ phase transition in the palladium-hydrogen system is substantially decreased. Optimum operating conditions, i.e., maximum hydrogen throughput and high durability are found at 350 °C and 2 MPa hydrogen pressure. Unsaturated hydrocarbons, halogens and sulfur compounds can lead to rupture of the membrane. The hydrogen suffers a great pressure drop after permeation through the membrane, however, it is particularly pure (impurities and moisture <0.5 ppm [mL/m^3]). Palladium membrane diffusion is discussed in [58].

Portable small-sized hydrogen generators or containerized medium-sized units (the latter are constructed from modular units) can be used for the final purification of hydrogen or for separation from raw gas mixtures, e.g., from methanol or ammonia reforming (see → Hydrogen, 2. Production, Chap. 5.). Main parts of a module are the diffusion elements which consist of a number of silver – palladium tubes contained within a cylindrical cell.

Figure 20 shows the cell performance data of commercial pure-hydrogen plants on the basis of diffusion. The raw hydrogen must be fed to the unit at 2.1 MPa, the operating temperature is 300 °C and the average specific energy consumption amounts to ca. 100 W per cubic meter of hydrogen [59]. The process is considered suitable for small- to medium-scale plants. Metal membrane processes have not been adopted for industrial-scale hydrogen purification.

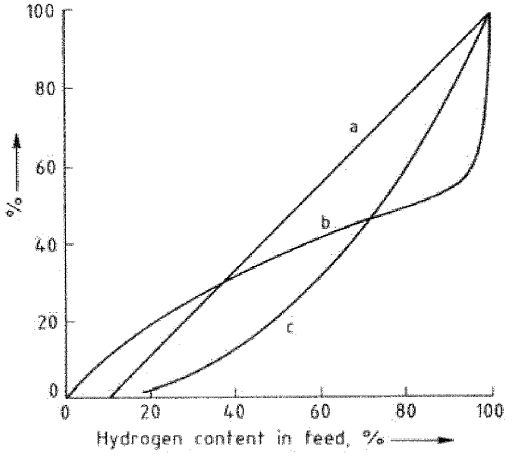


Figure 20. Operating data of hydrogen diffusion cells with Pd-Ag membranes
a) Yields (%, related to input hydrogen amount); b) Hydrogen content in off-gas (vol%); c) Cell output) (% of nominal capacity)

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6.2. Polymer Membrane Processes

New developments in the area of polymer membrane materials also allow their utilization in gas separation technology. The main criteria for suitable separation membranes are high permeation rates together with high selectivity, pressure-resistant membrane structures and chemical as well as thermal stability. State-of-the-art membranes have asymmetric composite layer structures on a woven material support or a composite hollow-fiber membrane structure. The membrane separation stage is built as module; for gas separation module constructions with high packing densities are used, namely spiral-wound modules ($> 900\ m^2/m^3$) and hollowfiber modules ($9000\ m^2/m^3$). An overview is given in [60–62]. From the process point of view various module arrangements such as cascades or membrane columns [63] may be used.

Asymmetric composite membranes based on cellulose acetate or polysulfones have a particularly high specific permeability for hydrogen, as do aromatic polyimide membranes; they are used for the industrial scale separation of hydrogen.

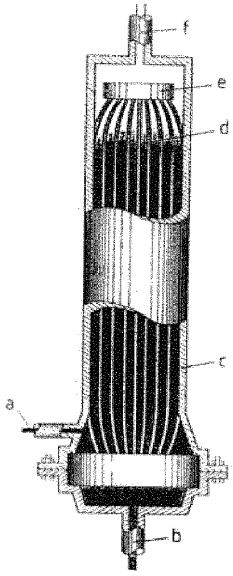


Figure 21. The Prism separator module of Permea
a) Feed stream of mixed gases; b) Permeate gas outlet; c) ASME-coded carbon steel shell; d) Hollow fiber membranes; e) Fiber bundle plug; f) Nonpermeate gas outlet

The product of Permea, a Monsanto company, is leading in this field. The Perma Prism process [64] uses asymmetrical hollow-fiber membranes of polysulfone with an active siloxane layer (300 – 500 μm outer diameter, 100 – 250 μm inner diameter, effective siloxane separating layer 0.1 μm). Several 10 000 of hollow fibers are connected together in a module, as shown in Figure 21. The fiber bundle is sealed at one end (top) and enclosed in an epoxide mantle at the other end. The modules are installed vertically and have a diameter of 100 or 200 mm and a maximum length of 3 or 6 m. The feed gas, which should be freed of disturbing components (NH_3,

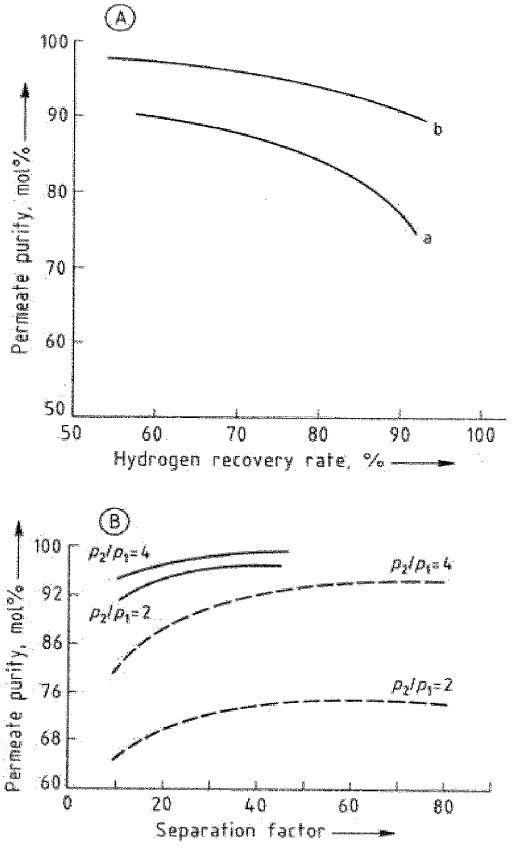


Figure 22. A) Obtainable hydrogen purity vs. hydrogen recovery rate
a) Partial pressure difference 3.52 MPa, H_2 in feed 63 vol %; b) Partial pressure difference 3.52 MPa, H_2 in feed 86 vol %
B) Permeate purity with two feeds at different pressure ratios [60] ------- 40 % H_2, 60 % C_1; —— 70 % H_2, 30 % C_1
p_1 = permeate pressure, p_2 = feed gas pressure

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Table 6. Hydrogen containing gases membrane modules can handle

Source of feedgas	Components		Pressure, MPa	Product composition, % H_2	Pretreatment, remarks
	% H_2	others			
Ammonia synthesis purge gas	60	N_2, CH_4, Ar, NH_3	13.0	H_2, 85	water wash, NH_3– conc. <200 ppm (mL/m^3)
Methanol synthesis purge gas	58	CO, CO_2, N_2, CH_4, CH_3OH, H_2O	5.0	H_2, CO_2, 80	water wash, CH_3OH conc. <100 ppm (mL/m^3)
Catalytic reformer off-gas	70 – 80	CH_4, alkanes, aromatics	3.0 – 5.0	H_2, 95	oil separation by refrigeration or oil scrubber, C_2– C_6 <80 % satur. aromatics <50 ppm (mL/m^3)
Catalytic cracker purge gas	10 – 30	N_2, O_2, CH_4, CO,	0.7 – 1.4	H_2, 60 – 80	compression, water wash
Catalytic cracker purge gas	10 – 30	N_2, O_2, CH_4, CO, CO_2, H_2S, alkenes, higher and lower olefins, aromatics	0.7 – 1.4	H_2, 60 – 80	compression, water wash
Hydrocracker purge gas	75	CH_4, H_2S, H_2O, NH_4, alkenes, aromatics	7.0 – 11.0	H_2, 95	aromatics <50 ppm (mL/m^3)
Hydrotreater purge gas	60	CH_4, H_2O, alkenes, aromatics	35 – 50	H_2, 97	feed <30 mol % H_2, uneconomic, aromatics <50 ppm (mL/m^3)
Toluene hydrodealkylation		CH_4, H_2O, alkenes, aromatics	30	H_2	oil separation by refrigeration or scrubber, aromatics <50 ppm, (mL/m^3)
Steam – methane reformer gas		CH_4, CO, CO_2, H_2O	30 – 80	H_2, H_2/CO_2	
Oxo-synthesis gas	70	CO	variable	H_2/CO 1 : 1	H_2/CO adjustment

H_2S, CH_3OH) by a suitable scrubbing system, is fed into the module near the base. The permeate is removed from the base of the module while the remaining gas is removed from the top. The fibers can be operated with a pressure of up to 15 MPa, whereby the pressure difference may amount to 7 MPa. The operating temperature can be up to 100 °C.

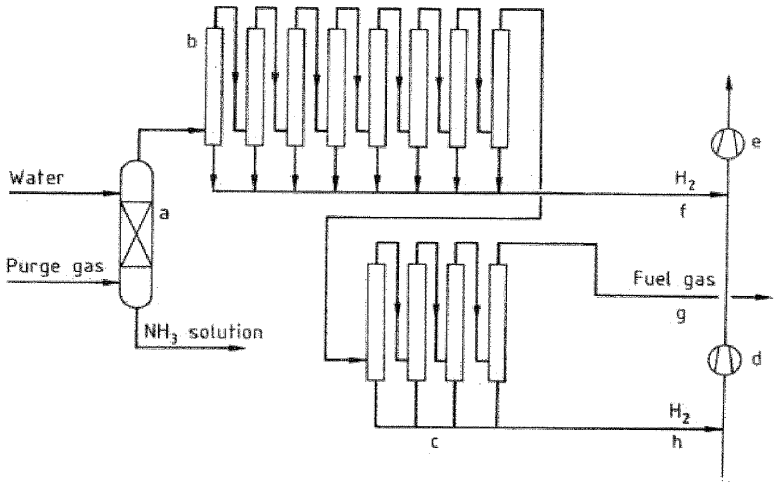


Figure 23. Flowsheet of a hydrogen recovery unit with Prism separator modules in an ammonia plant
a) Water scrubber; b) First bank Prism separators; c) Second bank Prism separators; d) Syngas compressor first stage (2.4 MPa suction pressure); e) Syngas compressor second stage (6.8 MPa suction pressure); f) H_2 recycle to second stage suction syngas compressor; g) Fuel gas to NO_x abatement or primary reformer; h) H_2 recycle to first stage suction syngas compressor

The stability of the membranes towards impurities is given in % of the corresponding saturation value at 20 °C:

Hydrogen sulfide	up to 10 % of the saturation value
Ammonia	up to 2 % of the saturation value
Water	up to 100 % of the saturation value
Hydrocarbons ($C_2 - C_6$)	up to 80 % of the saturation value

The degree of purity and the hydrogen recovery rate are determined by the partial pressure difference between the inside and the outside of the hollow fiber, the remaining gas components (i.e., their permeation coefficient) and their partial pressure.

Figure 22 A shows the rate of hydrogen recovery and the obtainable purity as a function of various hydrogen contents in the raw gas. Plots for two feeds (70 % and 40 % H_2) in Figure 22 B show that the ratio of total pressures dramatically affects permeate purity, whereas the effect of further increase in membrane selectivity leads to a plateau above a selectivity factor of 40.

Hollow-fiber separators were adopted quickly for commercial applications, more than 160 membrane separation systems have been installed for hydrogen recovery since 1979. Preferred applications are hydrogen recovery from purge gases of ammonia or methanol synthesis loops or from other hydrogen containing gases in the refinery or gas industries. Table 6 gives a survey. Figure 23 shows the process scheme of a plant for hydrogen recovery from the purge gas of a 545 t/d ammonia plant. 3000 m^3 (STP)/h gas is led through two rows of modules (containing 8 and 4 modules, respectively) at various pressure levels, 90 % of the hydrogen thereby being recovered. This system is especially useful, because a part of the hydrogen can be led back to the synthesis stage at 7 MPa. In a 1000 t/d ammonia plant the recovered hydrogen leads to an additional ammonia production of 40 t/d (ca. 5 %) [65]. However, other valuable components of the gas, such as argon, cannot be recovered in a pure form.

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(54) **IMPROVED AMMONIA PLANT CONFIGURATION AND METHODS**

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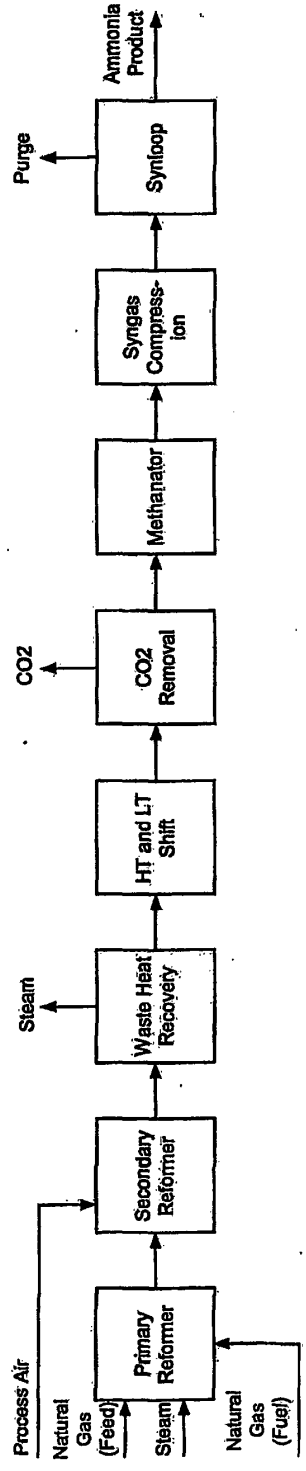
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(57) **ABSTRACT**

A synthesis plant **(200)** includes a separation system upstream of a synthesis loop that removes excess nitrogen and other gaseous compounds from a feed gas having a ratio of hydrogen to nitrogen of less than 3:1, thereby producing a syngas with a ratio of hydrogen to nitrogen at about 3:1. Particularly preferred separation systems include a coldbox **(270)** with a refrigerant other than air, or a pressure swing absorption system.



Prior Art
Figure 1

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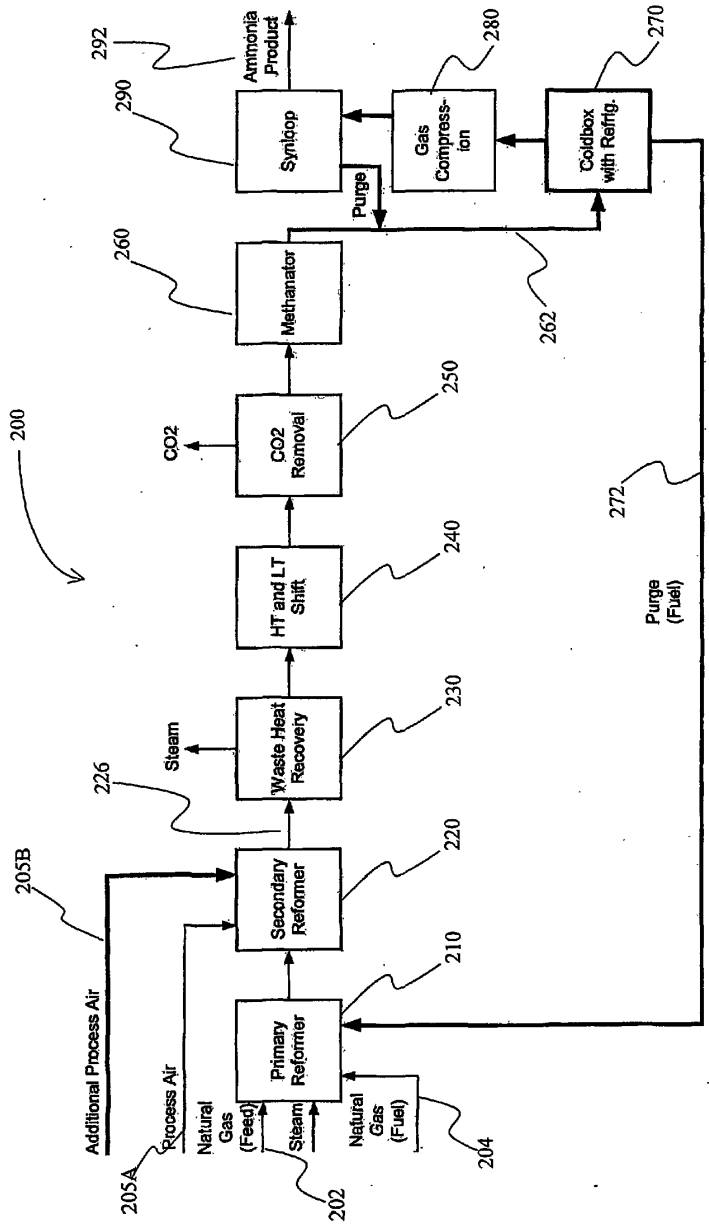


Figure 2

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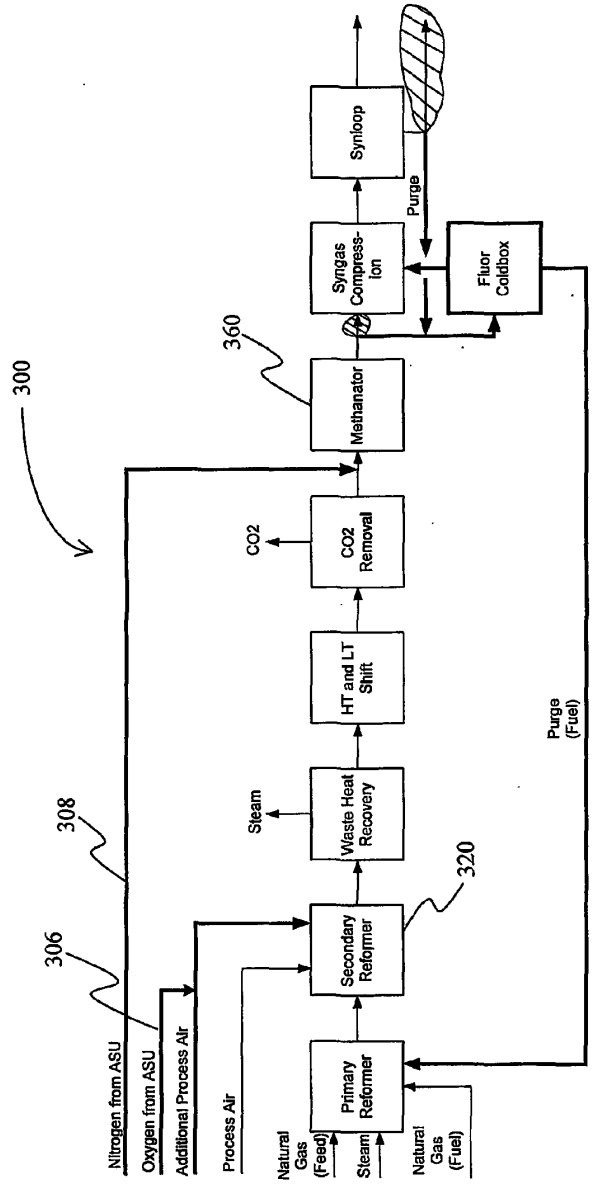


Figure 3

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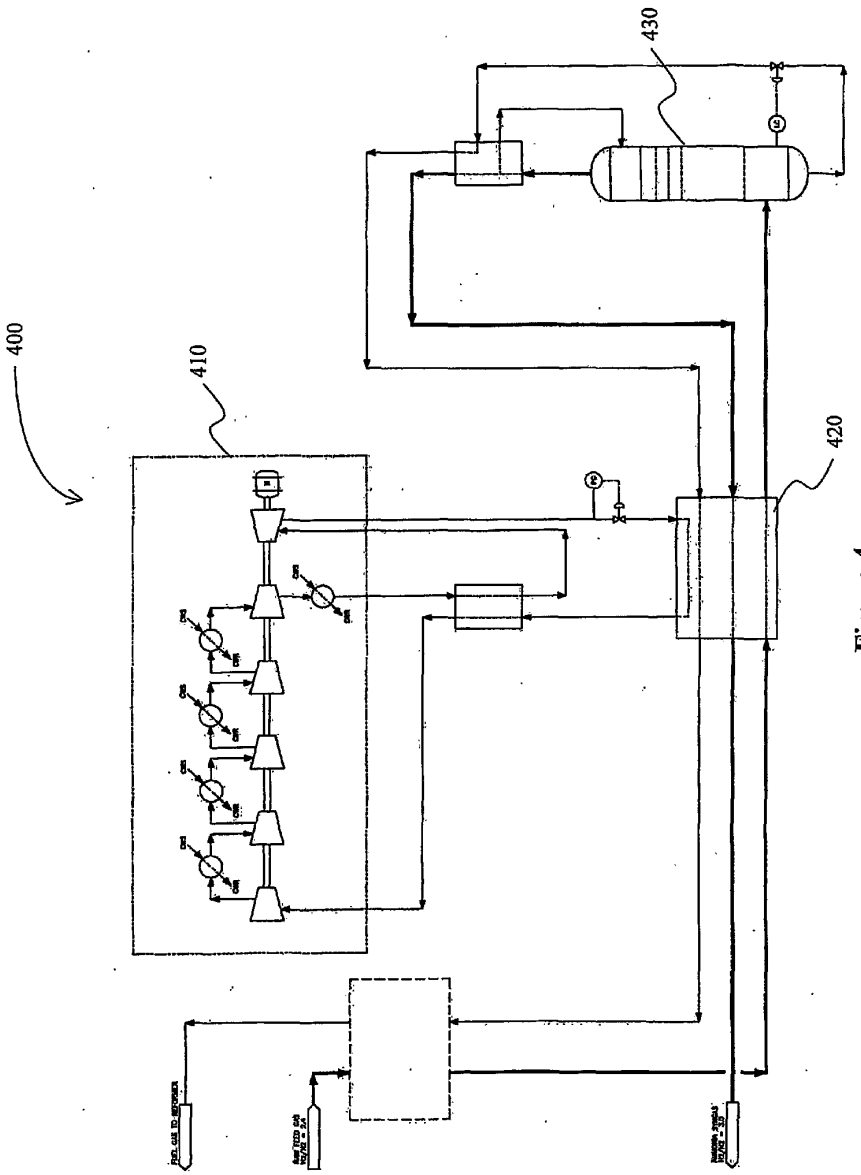


Figure 4

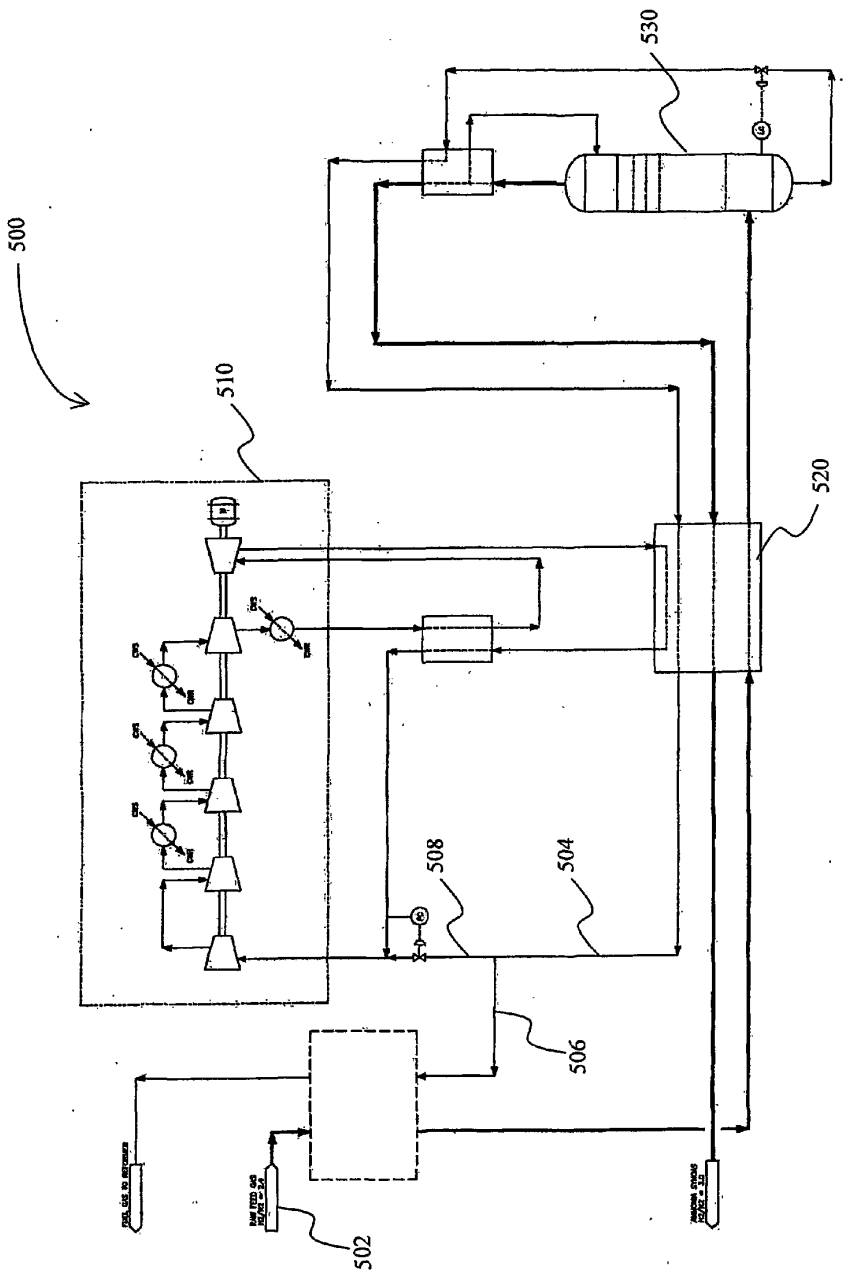


Figure 5

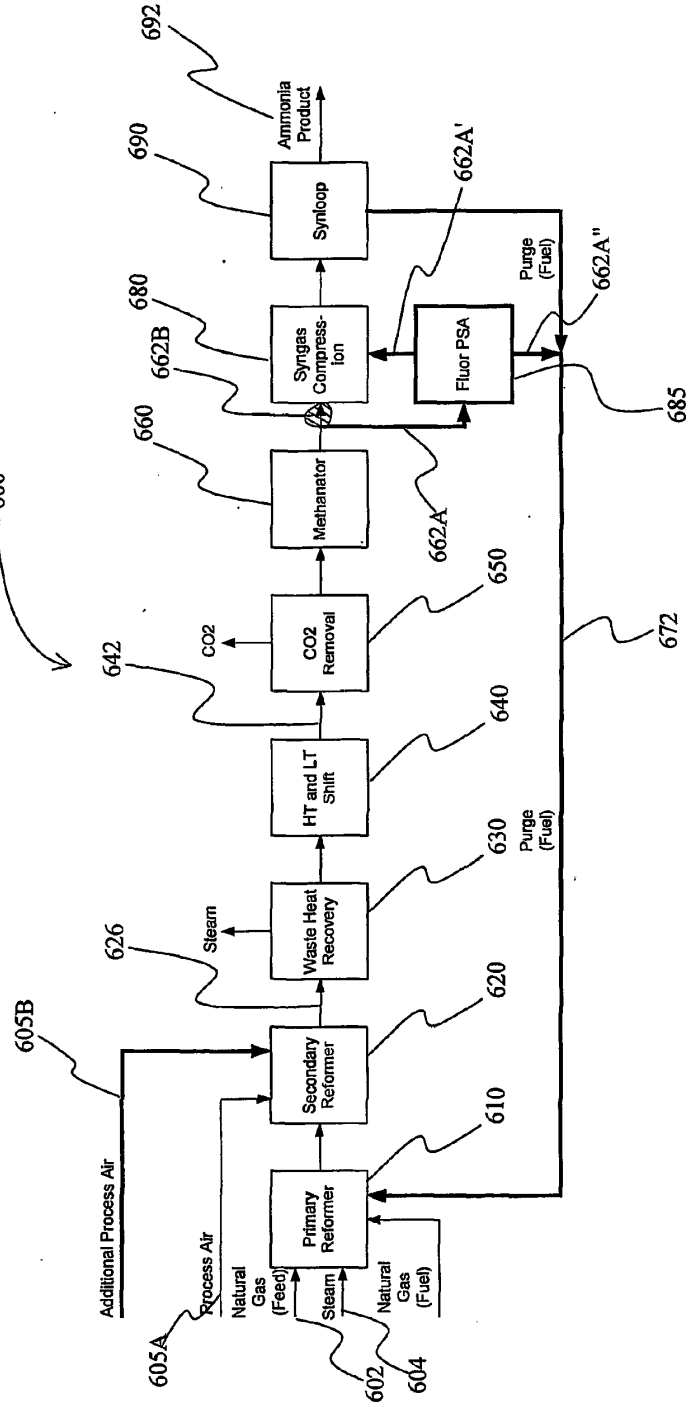


Figure 6

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IMPROVED AMMONIA PLANT CONFIGURATION AND METHODS

[0001] This application claims priority to U.S. provisional patent application with the serial No. 60/302,055, which was filed on Jun. 28, 2001 and is incorporated by reference herein.

BACKGROUND OF THE INVENTION

[0002] The relatively high price of natural gas has recently resulted in the closure of a few inefficient ammonia plants in the US. To make matters worse, natural gas prices are expected to remain high in the foreseeable future. Thus, for ammonia plants to become and remain profitable, it will be imperative to increase revenue and reduce operating costs. Viewed from another perspective, plants will have to find ways to increase production and reduce their energy consumption per ton of ammonia produced.

[0003] In a typical prior art plant configuration as depicted in Prior art **FIG. 1**, natural gas is processed through primary and secondary reformers, and the reformed gas stream is then subjected to a shift conversion after excess heat has been recovered from the reformed gas stream. In a further step, acid gas (here: carbon dioxide) is removed, and residual carbon monoxide (CO) and carbon dioxide (CO_2) are almost completely eliminated in a methanator. The resulting gas stream is then passed into the synthesis loop for production of ammonia, wherein the nitrogen is typically provided from process air that is fed into the secondary reformer.

[0004] Production capacity can be increased by removing excess nitrogen from the syngas stream by combination of gas expansion, autorefrigeration, and cryogenic separation as for example described in U.S. Pat. No. 3,442,613 to Grotz. While Grotz's configuration is relatively effective in some ammonia production plants, retrofitting of existing plants is relatively problematic since the expansion step requires considerable increase in front-end pressure in a ammonia synthesis plant (and thereby typically necessitating retrofits/rebuilds to accommodate for the increased pressure).

[0005] To circumvent at least some of the problems associated with retrofitting existing ammonia synthesis production plants, Bhakta describes in U.S. Pat. No. 5,935,544 a configuration in which a purifier process has been applied to a low methane content syngas with moderate N_2 excess, wherein an external refrigeration step produces a syngas with sufficiently low inert content to significantly increase synthesis capacity or decrease in synthesis loop pressure. Although Bhakta's configuration overcomes in many cases the need for retrofitting existing plants, Bhakta's configuration is typically limited to relatively narrow process parameters in order to provide satisfactory improvements in synthesis capacity.

[0006] Although there are various configurations and processes for improvements of ammonia synthesis are known in the art, all or almost all of them suffer from one or more disadvantages. Therefore, there is still a need to provide improved methods and configurations for improved of ammonia synthesis.

BRIEF DESCRIPTION OF THE DRAWING

[0007] **FIG. 1** is a prior art schematic of a known configuration for an ammonia plant.

[0008] **FIG. 2** is an exemplary configuration of one contemplated ammonia plant that includes a coldbox.

[0009] **FIG. 3** is an exemplary configuration of another contemplated ammonia plant that includes a coldbox.

[0010] **FIG. 4** is an exemplary detail of a coldbox using nitrogen as a refrigerant in an ammonia plant.

[0011] **FIG. 5** is an exemplary detail of a coldbox using tail gas as a refrigerant in an ammonia plant.

[0012] **FIG. 6** is an exemplary configuration of yet another contemplated ammonia plant that includes a pressure swing absorption unit.

SUMMARY OF THE INVENTION

[0013] The present invention is generally directed towards configurations and methods of a plant, and especially a synthesis plant, in which excess nitrogen and other gases components are removed from a gas stream using a separator upstream from a synthesis loop.

[0014] In one particularly preferred aspect of the inventive subject matter, contemplated plants include an ammonia synthesis loop that receives an ammonia synthesis make-up gas having a molar ratio of hydrogen to nitrogen of about 3.0 that is cooled in a refrigeration circuit using a refrigerant other than air (and optionally fuel gas), and wherein a separation unit separates a feed gas having a molar ratio of hydrogen to nitrogen of less than 2.5 into a fuel gas and the ammonia synthesis make-up gas.

[0015] Preferred refrigerants include the fuel gas (which may be combusted in a reformer after the fuel gas cooling the ammonia synthesis make-up gas) and refrigerants that are substantially devoid of a component that forms an explosive or reactive mixture with the ammonia synthesis make-up gas (e.g., a gas comprising at least 98 vol % nitrogen). It is also contemplated that suitable refrigerants may be at least partially, and more preferably entirely recycled within the plant. The term "refrigerant other than air" refers to any gaseous (at 20° C.) refrigerant that has a composition other than the average composition of air (i.e., N_2 about 78%, O_2 about 21%, Argon about 0.9%, CO_2 about 0.03%, wherein the term about refers to absolute deviations of no more than 10%). Consequently, contemplated refrigerants especially include processed air from which at least one component (e.g., oxygen) has been at least partially removed, or to which at least one component (e.g., nitrogen) has been added, and partially (to at least 70% purity) or highly (to at least 95% purity) purified gases.

[0016] It is further contemplated that the refrigeration circuit may functionally cooperate with a plant configuration as an upgrade that increases an ammonia production of the plant configuration in an amount of between about 0.1% to 25%, and in yet further aspects of the inventive subject matter, the ammonia synthesis make-up gas is produced from natural gas via a primary and secondary reformers, wherein an air separation unit provides an oxygen rich stream to the secondary reformer, and wherein the air

separation unit further provides a nitrogen rich stream to the ammonia synthesis make-up gas at a position upstream of the separation unit.

[0017] In another particularly preferred aspect of the inventive subject matter, contemplated plants may include a pressure swing absorption unit that receives a first portion of a feed gas having a molar ratio of hydrogen to nitrogen of less than 2.9 and produces a hydrogen product gas a fuel gas, and may still further include a synthesis loop that receives an ammonia synthesis make-up gas that is formed from at least the hydrogen product gas and a second portion of the feed gas.

[0018] Especially preferred feed gas is produced in such configurations from a natural gas via a primary and secondary reformer, and wherein additional process air is provided to the secondary reformer, and suitable plants may advantageously further include a methanator and/or an acid gas removal unit upstream of the pressure swing absorption unit. In yet further contemplated aspects, the synthesis loop produces a purge gas, and at least one of the purge gas and the fuel gas are combusted in the primary reformer. The ammonia synthesis make-up gas preferably has a molar ratio of hydrogen to nitrogen of about 3:1, and at least a portion of nitrogen, argon, and methane contained in the feed gas is removed from the feed gas in the pressure swing absorption unit via the fuel gas. While contemplated configurations may be operated as new plants, it is especially contemplated that the pressure swing absorption unit may functionally cooperate with a plant configuration as an upgrade that increases an ammonia production of the plant configuration in an amount of between about 0.1% to 25%.

[0019] Various objects, features, aspects and advantages of the present invention will become more apparent from the following detailed description of preferred embodiments of the invention, along with the accompanying drawings in which like numerals represent like components.

DETAILED DESCRIPTION

[0020] The majority of ammonia plants operating today use a stoichiometric amount of process air in the secondary reformer in order to maintain a hydrogen to nitrogen molar ratio of 3 to 1 in the methanator effluent gas, which is typically the make-up gas to the ammonia synthesis loop.

[0021] The inventors have discovered that a separation system, and most preferably a coldbox or pressure swing absorption (PSA) system can advantageously be integrated in an ammonia production plant (e.g., installed downstream of a methanator to process the methanator effluent gas before it enters the ammonia synthesis loop), thereby increasing the production capacity and/or reducing the energy requirements. Thus, excess air and/or nitrogen can be introduced to the front-end of the syngas production process to improve capacity in contemplated configurations, while maintaining the stoichiometric ratio of hydrogen to nitrogen at about 3:1. The term "a molar ratio of hydrogen to nitrogen of about 3.0" as used herein refers to molar ratios of between 2.95 to 3.05, and more preferably between 2.97 to 3.03, and most preferably between 2.99 to 3.01. Moreover, it should be appreciated that contemplated configurations may be operated using relatively wide process parameters while improving productivity and/or reducing energy requirements.

[0022] One exemplary configuration of contemplated ammonia synthesis plants including a coldbox is depicted in **FIG. 2**. In particular, it is contemplated that installation of a coldbox allows addition of significant quantities of excess air, typically at least 5%, more typically at least 15%, and most typically between at least 20 to 25 percent and even more excess process air (i.e. more than the stoichiometric amount) in the secondary reformer. Consequently, significantly more methane and other hydrocarbons can be reformed in the secondary reformer, thereby increasing the plant's net syngas production without raising the primary reformer heat load.

[0023] In the exemplary configuration of **FIG. 2**, plant **200** includes primary and secondary reformers **210** and **220**, respectively, in which the natural gas feed **202** is converted using steam **204**, stoichiometric amounts of process air **205**A, additional process air **205**B, and appropriate catalysts/reaction conditions to produce reformer effluent **226** predominantly comprising carbon monoxide, hydrogen, and nitrogen. The term "stoichiometric amounts of process air" refers to the quantity of process air that will provide a molar ratio of hydrogen to nitrogen of about 3.0 after shift conversion and optionally after the methanator in the syngas.

[0024] Heat from the reforming process is recovered in a waste heat recovery unit **230**, and the reformer effluent is shift converted in one or more downstream shift converters (e.g., high and low temperature shift converters) **240** to produce converter effluent **242**, predominantly comprising hydrogen, nitrogen, and carbon dioxide. A subsequent acid gas removal unit (here: carbon dioxide removal unit) **250** removes significant quantities of carbon dioxide, and a methanator **260** downstream of the acid gas removal unit converts residual carbon monoxide and carbon dioxide to methane.

[0025] Methanator effluent **262** is fed to coldbox **270** that is operated under conditions to separate the methanator effluent **262** into a fuel gas portion **272** predominantly comprising methane, hydrogen, and nitrogen, and a purified and cooled syngas with a nitrogen to hydrogen ratio of about 3:1. The fuel gas is preferably fed into the burner of the primary reformer **210**, while the cooled synthesis gas is compressed in syngas compressor **280** before entering the synthesis loop **290**. Synthesis loop **290** produces ammonia product **292** and purge gas **294**, which is optionally combined with fuel gas **272** for combustion in the primary reformer **210**.

[0026] Alternatively, or additionally as depicted in **FIG. 3**, ammonia production may be further improved in a plant **300** where an air separation unit is available. In such configurations, an oxygen-rich gas **306** (i.e., comprising at least 25 mol %, more typically at least 75 mol %, and most typically at least 90 mol % oxygen) may be provided to the secondary reformer **320**, and a nitrogen rich gas **308** (i.e., comprising at least 25 mol %, more typically at least 75 mol %, and most typically at least 90 mol % oxygen) may be introduced to the reformed and/or shift converted gas at a position upstream of the methanator **360**.

[0027] It should be especially appreciated that configurations as depicted in **FIGS. 2 and 3** will generally have little or no effect on the operational requirements of the primary reformer. Moreover, excess nitrogen (i.e., nitrogen above quantities required to obtain a molar ratio of hydrogen to

nitrogen of about 3:1) from the air separation unit (in configurations according to **FIG. 3**) is added upstream of the methanator, which is thought to act as a wash to the syngas and to remove argon and methane in the coldbox while maintaining a molar ratio between hydrogen to nitrogen of about 3:1. Among other things, it should be particularly appreciated that such configurations, and especially when used as an upgrade to an existing ammonia plant, increase in ammonia production may be achieved without hydraulically limiting the plant at the front end.

[**0028**] Still further, it should be especially noted that due to the use of excess air in the secondary reformer (see e.g., **FIG. 2**), or due to the introduction of a nitrogen rich gas at a position upstream of the methanator (see e.g., **FIG. 3**), the nitrogen content in the methanator effluent gas will be more than that required to maintain a 3:1 molar ratio of hydrogen to nitrogen in the feed to the ammonia synthesis loop. Consequently, a coldbox system is contemplated that removes, among other components, excess nitrogen. For example, it is contemplated that suitable coldbox systems may also remove most of the methane and about 30 percent of the incoming argon.

[**0029**] Therefore, it is contemplated that the make-up gas delivered to the ammonia synthesis loop will contain significantly less inerts than before and thus assist in reduction of the ammonia synthesis loop circulation rates and operating pressure (and consequently save energy). Although it has been previously known to employ a cold box with a configuration as described by Grotz et al in existing plants (see e.g., U.S. Pat. No. 3,442,613), upgrading of existing plants with a cold box is frequently problematic. Among other difficulties, configurations as described by Grotz et al typically operate at relatively high pressure drops (up to 30 psi-70 psi in the expander plus 15 psi in the cold box), thereby typically necessitating further modifications in the plant configuration (and thereby incurring additional cost) during upgrading.

[**0030**] A particularly preferred exemplary coldbox system **400** is depicted in **FIG. 4** and typically includes an refrigeration circuit **410** (preferably an external nitrogen circuit) having a compressor and an expander, a low temperature exchanger **420**, and a separation column **430** to remove excess nitrogen and produce an ammonia synthesis make-up gas which contains significantly less inerts (e.g., nitrogen, argon, etc.) than before. Particularly contemplated refrigerants in such systems are substantially devoid (i.e., have less than 5 vol %, more typically less than 1 vol %, and most typically less than 0.1 vol %) of components that could form explosive or otherwise reactive mixtures (e.g.,.oxidizing mixtures) with syngas should a leakage in the system occur. Therefore, an especially preferred refrigerant comprises at least 98 vol % nitrogen, which is partially, and more preferably entirely recycled in the refrigeration circuit. However, in alternative aspects, contemplated refrigerants may also comprise nitrogen in an amount between about 0% to 40%, more preferably between 40% and 70%, and most preferably between 70% and 100%. It should further be appreciated that the raw feed gas in contemplated configurations is at least partially dried using a desiccant.

[**0031**] Alternatively, ammonia syngas is cooled by a tailgas of a separator column as depicted in **FIG. 5**. Here, dry raw feed is provided to the separator column and separated into ammonia syngas and tail gas. At least a portion of the tail gas is then passed through the low temperature exchanger and compressed in a compressor. The compressed tailgas is cooled by expansion in an expander, and the cooled and expanded tailgas is passed back to the low temperature exchanger to cool the raw feed gas. Alternatively, nitrogen may be employed as refrigerant and the tailgas is passed to the fuel gas header.

[**0032**] Thus, it is contemplated that one portion of the waste gas may be recycled within an external refrigeration loop, while another portion of the waste gas is employed as fuel gas. It should especially be recognized that in such configurations the composition of the refrigerant can advantageously be maintained at a substantially constant composition even when the composition of the waste gas varies, and in still further preferred configurations, a control valve controls the amount of waste gas that is fed into the refrigeration loop to compensate for minor compressor seal leakages or other leakages in the refrigeration loop.

[**0033**] An exemplary configuration of such excess nitrogen removal and/or syngas purification is shown in **FIG. 5**. Here, the plant includes a coldbox system **500**, in which the methanator effluent gas stream **502** (or other gas stream depending on the particular application) is cooled using refrigeration circuit **510** and cold exchanger **520**, and separated in a separator **530**. In such configurations, it is contemplated that the separator separates ammonia syngas from the feed gas, and further provides a waste gas stream **504** containing at least part of the excess nitrogen.

[**0034**] In a particularly preferred aspect of the inventive subject matter, the waste gas **504** is split into a first and a second gas stream **506** and **508**, respectively, wherein the first gas stream **506** is used as a fuel gas (e.g., in a reformer), and wherein the second gas stream **508** is employed as a refrigerant via compression, cooling, and expansion in an expander. In especially preferred cold box systems, the refrigeration circuit comprises a compressor and an expander, and at least one of the compressor and the expander is mechanically coupled to a process air compressor. Thus, it should be recognized that at least a portion of the waste gas stream is employed as a refrigerant to cool the methanator effluent gas stream or other gas stream.

[**0035**] In a computer calculation, the impact of installing a contemplated coldbox system in a typical ammonia plant was studied using Pro II™ Software. From this simulation and other calculations (not shown), the inventors contemplate that by employing a cold box system (1) ammonia production in conventional plants can be increased by about 18%, (2) wherein the increase in ammonia production may be achieved by maintaining the same primary reformer fired duty, (3) where higher production rates are achieved, the primary reformer outlet temperature can be lowered about 80° F., thereby achieving a longer primary reformer tube life and radiant heat load, and (4) carbon dioxide production increases by about 23 percent. It is still further contemplated that depending on the particular configuration of contemplated plants, ammonia production in conventional plants can be increased by at least 18%, and more preferably at least 20%, and that consumption of fuel per unit of produced ammonia in an upgrade configuration could be reduced in an amount of between about 0.1% to 25%.

[**0036**] Consequently, particularly preferred plants will include an ammonia synthesis loop that receives an ammo-

nia synthesis make-up gas having a molar ratio of hydrogen to nitrogen of about 3.0 and that is cooled in a refrigeration circuit using a refrigerant other than air and a fuel gas, wherein a separation unit separates a feed gas having a molar ratio of hydrogen to nitrogen of less than 2.5 into a fuel gas and the ammonia synthesis make-up gas. In further particularly preferred configurations, the refrigerant comprises at least some of the fuel gas (tail gas from the separator) or nitrogen or other inert gas, wherein some or all of the refrigerant may be recycled within the refrigeration circuit.

[0037] Another exemplary configuration of contemplated ammonia synthesis plants including a pressure swing absorption unit (PSA) is depicted in **FIG. 6**. Again, installation of a separation system to remove excess nitrogen (and other inert gases) is contemplated to allow operation of the syngas production under conditions that employ addition of significant quantities, and typically up to 20 to 25 percent excess process air (i.e. more than the stoichiometric amount) in the secondary reformer, thereby significantly boosting synthesis gas production. Consequently, more methane can be reformed in the secondary reformer, thereby increasing the plant's net syngas production without raising the primary reformer heat load.

[0038] In a particularly preferred configuration of a plant with a PSA (as shown in **FIG. 6**), plant **600** includes primary and secondary reformers **610** and **620**, respectively, in which the natural gas feed **602** is converted using steam **604**, stoichiometric amounts of process air **605**A, additional process air **605**B, and appropriate catalysts/reaction conditions to produce reformer effluent **626** predominantly comprising carbon monoxide, hydrogen, and nitrogen.

[0039] Heat from the reforming process is recovered in a waste heat recovery unit **630**, and the reformer effluent is shift converted in one or more downstream shift converters (e.g., high and low temperature shift converters) **640** to produce converter effluent **642**, predominantly comprising hydrogen, nitrogen, and carbon dioxide. A subsequent acid gas removal unit (here: carbon dioxide removal unit) **650** removes significant quantities of carbon dioxide, and a methanator **660** downstream of the acid gas removal unit converts residual carbon monoxide and carbon dioxide to methane.

[0040] A first portion of methanator effluent **662**A is fed to the PSA **685** that separates the methanator effluent **662**A into a hydrogen rich stream **662**A' and a waste stream **662**A", predominantly comprising methane, hydrogen, and nitrogen. A second portion of methanator effluent **662**B is fed directly to the syngas compressor **680**, that also compresses hydrogen rich stream **662**A' to form a compressed syngas having a molar ratio of hydrogen to nitrogen of about 3.0. The waste gas is preferably combined with the purge gas from the synloop **690** to combined waste gas stream **672** and fed into the burner of primary reformer **610**, while the synthesis loop **690** produces ammonia product **692**.

[0041] Thus, preferred configurations particularly include those comprising a pressure swing absorption unit that receives a first portion of a feed gas having a molar ratio of hydrogen to nitrogen of less than 3.0 and produces a hydrogen product gas a fuel gas, and,a synthesis loop that receives an ammonia synthesis make-up gas that is formed from at least the hydrogen product gas and a second portion of the feed gas. It should be particularly appreciated that the use of a PSA unit to remove excess nitrogen from the syngas production stream may have various advantages over known systems (e.g., system described in U.S. Pat. No. 5,935,544 to Bhakta). Among other things, by modification of the volume ratio between the first and second portions of the methanator effluent (i.e., the portion that is directly fed to the synloop, and the portion that is fed to the PSA), the nitrogen content of the methanator effluent may vary considerably during operation. Furthermore, use of a PSA unit will typically avoid all or almost all of the difficulties associated with refrigeration (e.g., energy consumption by compressors and potential generation of explosive or otherwise reactive mixtures).

[0042] Consequently, it is contemplated that in preferred configurations, the ratio between the first and second portions of the methanator effluent can be varied between 99:1 (and even higher) and 1:99 (and lower where appropriate). However, the ratio between the first and second portions of the methanator effluent during typical operation will generally be in the range of about 1:3 and about 3:1. With respect to the PSA, it should be recognized that all PSA units are suitable for use herein that will produce a hydrogen product gas, and there are numerous such PSA units known in the art.

[0043] Furthermore, it should be appreciated that the PSA offgas need not necessarily be combined with the purge gas from the synloop to form a combined waste gas. For example, where a particular inert component in the PSA offgas is desired, it is contemplated that such a component may be isolated from the offgas using any suitable methods and/or configurations.

[0044] Still further, it should be recognized that in all of the contemplated configurations various modifications may be made without departing from the inventive concept presented herein. For example, while presence of a methanator is generally preferred (e.g., will significantly increase the fuel value), methanation is not a necessary prerequisite for contemplated configurations. Furthermore, carbon dioxide removal from the gas stream may be achieved using various methods known in the art, and all of the known methods and configurations are contemplated suitable for use herein. Consequently, suitable carbon dioxide removal may include use of physical or chemical solvents, or membranes. Moreover, contemplated acid gas removal also includes removal of compounds other than carbon dioxide, and contemplated compounds especially include hydrogen sulfide and other sulfur containing compounds.

[0045] Thus, specific embodiments and applications of improved ammonia plant configurations and methods have been disclosed. It should be apparent, however, to those skilled in the art that many more modifications besides those already described are possible without departing from the inventive concepts herein. The inventive subject matter, therefore, is not to be restricted except in the spirit of the appended claims. Moreover, in interpreting both the specification and the claims, all terms should be interpreted in the broadest possible manner consistent with the context. In particular, the terms "comprises" and "comprising" should be interpreted as referring to elements, components, or steps in a non-exclusive manner, indicating that the referenced elements, components, or steps may be present, or utilized, or combined with other elements, components, or steps that are not expressly referenced.

What is claimed is:

1. A plant comprising:

an ammonia synthesis loop that receives an ammonia synthesis make-up gas having a molar ratio of hydrogen to nitrogen of about 3.0 and that is cooled in a refrigeration circuit using a refrigerant other than air; and

wherein a separation unit separates a feed gas that has a molar ratio of hydrogen to nitrogen of less than 2.5 into a fuel gas and the ammonia synthesis make-up gas.

2. The plant of claim 1 wherein the fuel gas provides refrigeration in the refrigeration circuit.

3. The plant of claim 2 wherein the fuel gas is combusted in a reformer after the fuel gas cooling the ammonia synthesis make-up gas.

4. The plant of claim 1 wherein the refrigerant is substantially devoid of a component that forms an explosive or reactive mixture with the ammonia synthesis make-up gas.

5. The plant of claim 4 wherein the refrigerant comprises at least 98 vol % nitrogen.

6. The plant of claim 4 wherein at least a portion of the refrigerant is recycled within the refrigeration circuit.

7. The plant of claim 1 wherein the refrigeration circuit functionally cooperates with a plant configuration as an upgrade that increases an ammonia production of the plant configuration in an amount of between about 0.1% to 25%.

8. The plant of claim 1 wherein the ammonia synthesis make-up gas is produced from a natural gas via a primary and secondary reformer, wherein an air separation unit provides an oxygen rich stream to the secondary reformer, and wherein the air separation unit further provides a nitrogen rich stream to the ammonia synthesis make-up gas at a position upstream of the separation unit.

9. A plant comprising:

a pressure swing absorption unit that receives a first portion of a feed gas with a molar ratio of hydrogen to nitrogen of less than 3.0 and produces a hydrogen product gas a fuel gas; and

a synthesis loop that receives an ammonia synthesis make-up gas that is formed from at least the hydrogen product gas and a second portion of the feed gas.

10. The plant of claim 9 wherein the feed gas is produced from a natural gas via a primary and secondary reformer, and wherein additional process air is provided to the secondary reformer.

11. The plant of claim 10 further comprising a methanator upstream of the pressure swing absorption unit.

12. The plant of claim 10 further comprising an acid gas removal unit upstream of the pressure swing absorption unit.

13. The plant of claim 10 wherein the synthesis loop produces a purge gas, and wherein at least one of the purge gas and the fuel gas are combusted in the primary reformer.

14. The plant of claim 9 wherein the ammonia synthesis make-up gas has a molar ratio of hydrogen to nitrogen of about 3:1.

15. The plant of claim 9 wherein at least a portion of nitrogen, argon, and methane contained in the feed gas is removed from the feed gas in the pressure swing absorption unit via the fuel gas.

16. The plant of claim 9 wherein the pressure swing absorption unit functionally cooperates with a plant configuration as an upgrade that increases an ammonia production of the plant configuration in an amount of between about 0.1% to 25%.

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(54) **VERFAHREN ZUR GEWINNUNG VON WASSERSTOFF AUS EINEM METHANHALTIGEN GAS, INSBESONDERE ERDGAS UND ANLAGE ZUR DURCHFÜHRUNG DES VERFAHRENS**

METHOD FOR EXTRACTING HYDROGEN FROM A GAS CONTAINING METHANE, ESPECIALLY NATURAL GAS AND SYSTEM FOR CARRYING OUT SAID METHOD

PROCEDE POUR PRODUIRE DE L'HYDROGENE A PARTIR D'UN GAZ CONTENANT DU METHANE, EN PARTICULIER A PARTIR DE GAZ NATUREL, ET DISPOSITIF POUR LA MISE EN OEUVRE DE CE PROCEDE

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Beschreibung

[0001] Die Erfindung betrifft ein Verfahren zur Gewinnung von Wasserstoff aus einem methanhaltigen Gas, insbesondere Erdgas.

[0002] Aus US 5 131 930 ist eine konventionelle Wasserstoffanlage bekannt, die mit Erdgas als Einsatzstoff betrieben wird. In der Anlage erfolgt zunächst eine im allgemeinen mit Wasserdampf betriebene katalytische Spaltung von im Erdgas enthaltenen Kohlenwasserstoffen in einem beheizten Reformer zur Erzeugung von Kohlenmonoxid und wasserstoffhaltigem Synthesegas. Danach erfolgt eine katalytische Konvertierung des Kohlenmonoxids zu Wasserstoff und anschließend die Reindarstellung des Wasserstoffes mit Hilfe einer Druckwechseladsorptionsanlage. Die Abgase der Adsorptionsanlage werden zur Brennkammer des Reformers zurückgeführt und dort gemeinsam mit zusätzlich zugeführtem Erdgas verbrannt. Es ist auch bekannt, als zusätzlichen Brennstoff Raffineriegas oder andere Brenngase einzusetzen. Durch die Dampfspaltung des Methans wird eine signifikante Menge Kohlendioxid gemäß dem Wassergasgleichgewicht

$$CO + H_2O \Rightarrow H_2 + CO_2$$

erzeugt, die sich in der Konvertierungsstufe durch die Kohlenmonoxid-Konvertierung weiter auf eine Konzentration von im allgemeinen ca. 16 vol. % (trocken) erhöht. Diese Kohlendioxidmenge gelangt über den Kamin der Brennkammer zusammen mit dem durch die Feuerung von zusätzlichen kohlenstoffhaltigen Brennstoffen erzeugten Kohlendioxid in die Atmosphäre.

[0003] Der CO_2-Gehalt im Rauchgas liegt im allgemeinen über 20 vol. % (trocken). In einer Raffinerie stellt somit eine derart konzipierte Wasserstoffanlage einen der größten Kohlendioxid-Emittenten dar.

[0004] Aus US 4 553 981 ist ein Verfahren zur Gewinnung von Wasserstoff bekannt, bei dem ein kohlenwasserstoffhaltiges Gas mit Dampf reformiert und konvertiert wird. In einer Wäsche wird danach aus dem konvertiertem Gasstrom ein CO_2-Abgasstrom abgetrennt. Anschließend erfolgt eine Isolierung von Wasserstoff mit Hilfe einer Druckwechseladsorptionsanlage. Der Abgasstrom der Adsorptionsanlage wird verdichtet und in die Reformierung bzw. die Konvertierung zurückgeführt. Hierdurch entstehen große Kreislaufströme. Zur Vermeidung einer Akkumulation von Inertgasen, wie z. B. Stickstoff, muss dem Abgasstrom der Druckwechseladsorptionsanlage ein Purgestrom entnommen werden. Die Befeuerung des Reformers erfolgt auf konventionelle Weise. Das Verfahren ist ferner aufwendig und teuer.

[0005] Der Erfindung liegt die Aufgabe zu Grunde, ein einfaches und kostengünstiges Verfahren zur Gewinnung von Wasserstoff aus einem methanhaltigen Gas, insbesondere Erdgas anzugeben, bei dem nur geringe Mengen an Kohlendioxid in die Umgebung abgegeben werden.

[0006] Gegenstand der Erfindung und Lösung dieser Aufgabe ist ein Verfahren zur Gewinnung von Wasserstoff aus einem methanhaltigen Gas, insbesondere Erdgas, nach Anspruch 1. In dem Gas enthaltende Kohlenwasserstoffe werden in einem Reformer mittels Wasserdampf katalytisch in Wasserstoff, Kohlenmonoxid und Kohlendioxid gespalten werden, und in einer nachgeschalteten Konvertierungsstufe erfolgt mit Wasserdampf eine katalytische Konvertierung der entstandenen Kohlenmonoxide zu Kohlendioxid und Wasserstoff. Das Kohlendioxid wird mittels einer Gaswäsche aus dem konvertiertem Gasstrom entfernt, und der gewaschene wasserstoffreiche Gasstrom wird anschließend in einer Druckwechseladsorptionsanlage in einen aus Wasserstoff bestehenden Produktgasstrom und einen Abgasstrom getrennt. Der Abgasstrom wird zusammen mit Wasserstoff, der hinter der Gaswäsche aus dem Gasstrom abgezweigt wird, als weitgehend kohlenstofffreies Brenngas dem Reformer zugeführt und dort verbrannt.

[0007] Während in dem Reformer eine nahezu vollständige Spaltung der Kohlenwasserstoffe in Wasserstoff, Kohlenmonoxid und Kohlendioxid erfolgt, wird anschließend in der Konvertierungsstufe das entstandene Kohlenmonoxid zu Kohlendioxid umgesetzt, welches in der nachfolgenden Gaswäsche entfernt wird. Das Abgas der Druckwechseladsorptionsanlage enthält daher im Wesentlichen Wasserstoff und nur noch geringe Mengen an Kohlenstoff. Gleiches gilt für den Wasserstoff, der hinter der Gaswäsche aus dem Gasstrom abgezweigt wird. Bei der gemeinsamen Verbrennung dieser beiden Gasströme im Reformer entsteht daher ein überwiegend aus Stickstoff und Wasser bestehendes Abgas, während der Kohlendioxidgehalt gering ist. Durch die Gasrückführung entfällt eine Zusatzfeuerung des Reformers mit kohlenstoffhaltigen Brennstoffen, so dass die Kohlendioxidemmission deutlich sinkt. Im Vergleich zu konventionellen Verfahren kann der Kohlendioxidausstoßes um ca. 75 % gesenkt werden. Bei den verfahrenstechnischen Schritten, die im Rahmen der erfindungsgemäßen Lehre zur Anwendung kommen, handelt es sich ausnahmslos um ausgereifte Technologien, die in der Wasserstoffherstellung bereits seit längerer Zeit erfolgreich eingesetzt werden. Der Aufwand, der für die Erzielung der beschriebenen Kohlendioxid-Reduktion erforderlich ist, ist vergleichsweise gering. Es besteht daher auch die Möglichkeit, eine vorhandene konventionelle Wasserstoffanlage umzurüsten, um mit ihr das erfindungsgemäße Verfahren zu betreiben.

[0008] Vorzugsweise wird für die Konvertierungsstufe ein bei mittlerer Temperatur betriebener Konvertierungsreaktor oder ein Hochtemperaturkonvertierungsreaktor mit nachgeschaltetem Tieftemperaturkonvertierungsreaktor verwendet. Hierdurch wird eine nahezu vollständige Konvertierung des entstandenen Kohlenmonoxids zu Kohlendioxid gewährlei-

stet, welches nachfolgend über die Gaswäsche aus dem Gasstrom entfernt werden kann. Bei der Verwendung eines nachgeschalteten Tieftemperaturkonvertierungsreaktors besteht der Vorteil, dass der Hochtemperaturkonvertierungsreaktor einer vorhandenen Wasserstoffanlage weiter genutzt werden kann, wodurch die Umrüstungskosten für eine vorhandene Anlage deutlich gesenkt werden.

[0009] Vorzugsweise wird in der Gaswäsche technisch reines Kohlendioxid abgetrennt, welches für technische Anwendungen genutzt oder zu einem Produkt mit einer in der Lebensmittelindustrie einsetzbaren Qualität weiter verarbeitet wird. Neben der Verwendung als Einsatzstoff für die Lebensmittelindustrie kommt als Verwendung des technisch reinen Kohlendioxids beispielsweise die Befüllung einer Erdölbohrung als Maßnahme zur effizienten Erdölförderung in Frage. Alternativ kann das Kohlendioxid auch als Rohstoff für eine Methanolsynthese eingesetzt werden. Die Kohlendioxidwäsche kann hierbei mit bekannten physikalischen Verfahren, wie z. B. Rectisol, Selexol oder Genosorb, oder aber mit einem chemischen bzw. physikalisch/chemischen Verfahren, z. B. aMDEA (wässrige Lösung von N-Methyldiethanolamin) oder Sulfinol, betrieben werden.

[0010] Wird eine bestehende H_2-Anlage zum Zwecke der CO_2-Minimierung umgerüstet, wird zweckmäßigerweise der konvertierte Gasstrom vor Eintritt in die neu zu bauende CO_2-Wäsche verdichtet, um den dadurch entstehenden Druckverlust auszugleichen. Hierdurch wird die Wirksamkeit der CO_2-Wäsche erhöht.

[0011] Gegenstand der Erfindung ist auch eine Anlage gemäß Anspruch 4 zur Durchführung des Verfahrens. Bevorzugte Ausführungen dieser Anlage sind in den Unteransprüchen 5 und 6 beschrieben.

[0012] Im Folgenden wird die Erfindung anhand einer lediglich ein Ausführungsbeispiel darstellenden Zeichnung ausführlich erläutert. Es zeigen schematisch:

Fig. 1 ein Blockschaltbild eines erfindungsgemäßen Verfahren,

Fig. 2 ein Blockschaltbild eines erfindungsgemäßen Verfahrens nach Umrüstung einer konventionellen Wasserstoffanlage.

[0013] Die Fig. 1 zeigt ein erfindungsgemäßes Verfahren zur Gewinnung von Wasserstoff aus einem methanhaltigen Erdgas. Einem Erdgasstrom 1 wird ein Wasserdampfstrom 2 beigemischt. Die im Erdgas enthaltenen Kohlenwasserstoffe, insbesondere Methan, werden in einem mit einer Brennkammer 3 ausgerüsteten Reformer 4 mit Hilfe des beigemischten Wasserdampfstromes 2 katalytisch in Wasserstoff, Kohlenmonoxid und Kohlendioxid gespalten. Diese Reformierung erfolgt nahezu vollständig, so dass am Austritt des Reformers 4 praktisch keine kohlenwasserstoffhaltigen Gase mehr vorliegen. In einem nachgeschalteten, bei mittlerer Temperatur betriebenen Konvertierungsreaktor 5 erfolgt mit Hilfe des Wasserdampfes eine katalytische Konvertierung des entstandenen Kohlenmonoxids zu Kohlendioxid und Wasserstoff. Auch diese Reaktion verläuft nahezu vollständig, so dass der Kohlenmonoxidgehalt des aus dem Konvertierungsreaktor 5 austretenden Gasstromes 8 kleiner als 1 vol. % (trocken) ist. Anschließend wird das entstandene Kohlendioxid mit Hilfe einer Gaswäsche 7 nahezu vollständig aus dem Gasstrom 8 entfernt. Im Ausführungsbeispiel wird die Gaswäsche 7 mit einer wässrigen Lösung von N-Methyldiethanolamin (aMDEA) als Waschflüssigkeit betrieben. Im Rahmen der Erfindung liegt es jedoch auch, andere bekannte Wäscheverfahren, wie z. B. Rectisol, Selexol, Genosorb oder Sulfinol, einzusetzen. Das in der Wäsche 7 gewonnene Kohlendioxid 18 wird in einer weiteren Reinigungsstufe 9 auf eine in der Lebensmittelindustrie einsetzbare Reinheit weiter aufkonzentriert. Der gewaschene Gasstrom 10 enthält nur noch sehr geringe Mengen an Kohlenstoff und wird anschließend in einer Druckwechseladsorptionsanlage 11 in einen aus Wasserstoff 12 bestehenden Produktgasstrom und einen Abgasstrom 13 getrennt. Der Produktgasstrom 12 weist einen Wasserstoffgehalt von mehr als 99 vol. % auf. Der Abgasstrom 13 enthält im Wesentlichen ebenfalls Wasserstoff und nur geringfügige Mengen an nicht bzw. nur teilweise umgesetzten Kohlenwasserstoffen. Gemeinsam mit einem hinter der Wäsche 7 über eine Einrichtung 19 abgezweigten, im Wesentlichen ebenfalls aus Wasserstoff bestehenden Teilstrom 14, wird der Abgasstrom 13 über eine Leitung 17 der Brennkammer 3 des Reformers 4 zugeführt und dort verbrannt. Die Menge des Teilstromes 14 wird hierbei so eingestellt, dass sie bei der gemeinsamen Verbrennung mit dem Abgasstrom 13 den Energiebedarf des Reformers 4 deckt. Da sowohl der Abgasstrom 13 als auch der Teilstrom 14 überwiegend aus Wasserstoff bestehen und nur geringe Mengen an Kohlenstoff enthalten, weist das Abgas 15 der Brennkammer 4 einen hohen Wasserdampfgehalt und nur einen geringen Kohlendioxidanteil auf. Gegenüber konventionellen Verfahren zur Wasserstoffgewinnung, bei denen die Brennkammer mit kohlenstoffhaltigen Brennstoffen, wie z. B. Erdgas und kohlenwasserstoffhaltigen Abgasen, befeuert wird, zeichnet sich das erfindungsgemäße Verfahren somit durch eine geringe Kohlendioxidemission auf.

[0014] Bei den beschriebenen Verfahrensschritten, die im Rahmen der erfindungsgemäßen Lehre zur Anwendung kommen, handelt es sich durchweg um technisch ausgereifte Technologien, die sich sowohl bei der Herstellung von Wasserstoff als auch bei der Produktion von Ammoniak bewährt haben. Der Reformer 4 muss lediglich ausreichend groß bemessen sein, um die H_2-Produktion einschließlich der Brenngasversorgung nach der CO_2-Wäsche zu gewährleisten. Der Konvertierungsreaktor 5 wird bei mittlerer Temperatur betrieben, um eine nahezu vollständige Konvertierung des entstandenen Kohlenmonoxids zu Kohlendioxid sicherzustellen. Das im Ausführungsbeispiel mittels der Reinigungs-

stufe 9 gewonnene Kohlendioxid 21 kann in der Lebensmittelindustrie weiter verarbeitet werden. Alternativ hierzu besteht jedoch auch die Möglichkeit, das in der Wäsche 7 gewonnene technisch reine Kohlendioxid 18 direkt für technische Anwendungen zu nutzen. Hierbei kommt beispielsweise die Befüllung einer Erdölbohrung als Maßnahme zur effizienten Erdölförderung oder aber auch die Verwendung als Rohstoff für eine Methanolsynthese in Frage.

[0015] Der Aufwand zur Durchführung des beschriebenen Verfahrens ist vergleichsweise gering. Insbesondere besteht die Möglichkeit, eine vorhandene konventionelle Wasserstoffanlage so umzurüsten, dass mit ihr das erfindungsgemäße Verfahren betrieben werden kann. Die Fig. 2 zeigt eine erfindungsgemäß umgerüstete konventionelle Wasserstoffanlage. Die bereits vorhandenen Anlagenkomponenten sind mit durchgezogenen Linien gekennzeichnet, während die im Rahmen der Umrüstung hinzugefügten Bestandteile gestrichelt dargestellt sind. Die konventionelle Wasserstoffanlage weist einen mit einer Brennkammer 3' ausgerüsteten Reformer 4' zur katalytischen Spaltung von gasförmigen Kohlenwasserstoffen mit Wasserdampf auf. Dahinter ist ein Hochtemperaturkonvertierungsreaktor 5' zur katalytischen Konvertierung von Kohlenmonoxid mit Wasserdampf zu Kohlendioxid und Wasserstoff angeordnet. Hieran schließt sich eine Druckwechseladsorptionsanlage 11' zur Isolierung von Wasserstoff 12' aus dem konvertierten Gasstrom 8' mit angeschlossener Gasleitung 17' zur Brennkammer 3' zwecks Befeuerung des Reformers 4' mit einem aus der Adsorptionsanlage 11' austretenden Abgasstrom 13' an. Im Rahmen der Umrüstung wurde die Kapazität des Reformierungsschrittes durch einen dem Reformer 4' vorgeschalteten Pre-Reformer 4" sowie einem dem Reformer 4' nachgeschalteten Post-Reformer 4"' um ca. 20 % erhöht. Gegebenenfalls reicht es jedoch auch aus, nur einen der beiden zusätzlichen Reformer 4", 4"' vorzusehen. Der Hochtemperaturkonvertierungsreaktor 5', welcher im allgemeinen bei Temperaturen zwischen 360 und 500°C arbeitet, wurde durch einen nachgeschalteten, im Bereich von ca. 210 bis 270°C arbeitenden, Niedertemperaturkonvertierungsreaktor 5" ergänzt, um eine möglichst vollständige Konvertierung des Kohlenmonoxids zu Kohlendioxid zu erreichen. Alternativ hierzu kann der bestehende Hochtemperaturkonvertierungsreaktor 5' auch durch einen bei mittlerer Temperatur arbeitenden Konvertierungsreaktor ersetzt werden. Zwischen der Konvertierungsstufe und der Druckwechseladsorptionsanlage 11' wurde ein Gaskompressor 16' zur Verdichtung des Gasstromes 6' sowie eine Gaswäsche 7' zur Abtrennung des entstandenen vorgesehen, wobei im Ausführungsbeispiel das in der Gaswäsche 7' gewonnene Kohlendioxid 18' direkt einer technischen Anwendung zugeleitet wird. Zwischen der Wäsche 7' und der Druckwechseladsorptionsanlage 11' wurde eine zusätzliche Einrichtung 19' für die Rückführung eines Teils 14' des den Gaswäscher verlassenden wasserstoffreichen Gasstromes 10' in die Brennkammer 3', 3", 3"' der Reformer 4', 4", 4"' vorgesehen. Abschließend erfolgte eine Anpassung des vorhandenen Reformers 4' an die Verbrennung sowie die Abwärmenutzung des nun wasserstoffreichen Brennstoffes. Die vorhandene Gasleitung 20 für die Zuführung von kohlenwasserstoffhaltigen Brenngasen in die Brennkammer 3' des Reformers 4' wird nicht mehr genutzt. Die Darstellung in Fig. 2 zeigt, dass mit vergleichsweise geringem Aufwand eine konventionelle Wasserstoffanlage derart umrüstbar ist, dass mit ihr das erfindungsgemäße Verfahren betrieben werden kann. Hierdurch wird die Attraktivität des erfindungsgemäßen Verfahrens weiter erhöht.

Patentansprüche

1. Verfahren zur Gewinnung von Wasserstoff aus einem methanhaltigen Gas, insbesondere Erdgas,
   wobei in dem Gas enthaltene Kohlenwasserstoffe in einem Reformer (4) mittels Wasserdampf katalytisch in Wasserstoff, Kohlenmonoxid und Kohlendioxid gespalten werden und in einer nachgeschalteten Konvertierungsstufe mit Wasserdampf eine katalytische Konvertierung des entstandenen Kohlenmonoxids zu Kohlendioxid und Wasserstoff erfolgt,
   wobei das Kohlendioxid mittels einer Gaswäsche (7) aus dem konvertierten Gasstrom (8) entfernt und der gewaschene wasserstoffreiche Gasstrom (10) anschließend in einer Druckwechseladsorptionsanlage (11) in einen aus Wasserstoff bestehenden Produktgasstrom (12) und einen Abgasstrom (13) getrennt wird und
   wobei der Abgasstrom (13) zusammen mit Wasserstoff (14), der hinter der Gaswäsche (7) aus dem Gasstrom (10) abgezweigt wird, als weitgehend kohlenstofffreies Brenngas dem Reformer (4) zugeführt und dort verbrannt wird.

2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** für die Konvertierungsstufe ein bei mittlerer Temperatur betriebener Konvertierungsreaktor (5) oder ein Hochtemperaturkonvertierungsreaktor (5') mit nachgeschaltetem Tieftemperaturkonvertierungsreaktor (5") verwendet wird.

3. Verfahren nach Anspruch 1 oder 2, **dadurch gekennzeichnet, dass** in der Gaswäsche (7) technisch reines Kohlendioxid (18) abgetrennt wird, welches für technische Anwendungen genutzt oder zu einem Produkt (21) mit einer in der Lebensmittelindustrie einsetzbaren Qualität weiter verarbeitet wird.

4. Anlage zur Durchführung des Verfahrens nach einem der Ansprüche 1 bis 3 mit

- mindestens einem mit einer Brennkammer (3) ausgerüsteten Reformer (4) zur katalytischen Spaltung von gasförmigen Kohlenwasserstoffen mit Wasserdampf,
- einer Konvertierungsstufe mit mindestens einem Konvertierungsreaktor (5) zur katalytischen Konvertierung von Kohlenmonoxid mit Wasserdampf zu Kohlendioxid und Wasserstoff,
- einer Gaswäsche (7) zur Abtrennung von Kohlendioxid aus dem die Konvertierungsstufe verlassenden Gastrom (8) und
- einer nachgeschalteten Druckwechseladsorptionsanlage (11) zur Isolierung von Wasserstoff (12), an die eine zur Brennkammer (3) zurückgeführte Gasleitung (17) zur Befeuerung des Reformers mit einem aus der Adsorptionsanlage austretenden Gastrom angeschlossen ist,

wobei eine zusätzliche Einrichtung (19) für die Rückführung eines Teils (14) des die Gaswäsche (7) verlassenden wasserstoffreichen Gasstromes (10) in die Brennkammer (3) des Reformers (4) vorgesehen ist.

5. Anlage nach Anspruch 4, **dadurch gekennzeichnet, dass** die Konvertierungsstufe einen bei mittlerer Temperatur betriebenen Konvertierungsreaktor (5) oder einen Hochtemperaturkonvertierungsreaktor (5') mit nachgeschaltetem Tieftemperaturkonvertierungsreaktor (5") umfasst.

6. Anlage nach Anspruch 4 oder 5, **dadurch gekennzeichnet, dass** sich an den Kohlendioxidabgang der Gaswäsche (7) eine Reinigungsstufe (9) zur Aufkonzentrierung des abgetrennten Kohlendioxids (18) anschließt.

Claims

1. Method for extracting hydrogen from a methane-containing gas, in particular natural gas, wherein hydrocarbons contained in the gas are catalytically split into hydrogen, carbon monoxide and carbon dioxide in a reformer (4) by means of steam, and catalytic conversion of the resulting carbon monoxide to carbon dioxide and hydrogen takes place in a downstream conversion stage by means of steam,
wherein the carbon dioxide is removed from the converted gas stream (8) by means of a gas scrubber (7), and the scrubbed hydrogen-rich gas stream (10) is then separated in a pressure swing adsorption system (11) into a product gas stream (12) consisting of hydrogen and a waste gas stream (13), and
wherein the waste gas stream (13), together with hydrogen (14) which is branched off from the gas stream (10) behind the gas scrubber (7), is passed to the reformer (4) as a combustion gas that is largely free of carbon, and burned there.

2. Method according to Claim 1, **characterized in that**, for the conversion stage, use is made of a conversion reactor (5) which is operated at medium temperature or of a high-temperature conversion reactor (5') with a downstream low-temperature conversion reactor (5").

3. Method according to Claim 1 or 2, **characterized in that** technically pure carbon dioxide (18) is separated in the gas scrubber (7), which is used for technical applications or processed further to produce a product (21) having a quality that can be used in the food industry.

4. System for carrying out the method according to one of Claims 1 to 3, comprising

- at least one reformer (4) equipped with a combustion chamber (3), for catalytic splitting of gaseous hydrocarbons by means of steam,
- a conversion stage comprising at least one conversion reactor (5) for catalytic conversion of carbon monoxide by means of steam to give carbon dioxide and hydrogen,
- a gas scrubber (7) for separating carbon dioxide from the gas stream (8) which leaves the conversion stage, and
- a downstream pressure swing adsorption system (11) for isolating hydrogen (12), to which there is connected a gas line (17) which is passed back to the combustion chamber (3) in order to fire the reformer with a gas stream which exits from the adsorption system,

wherein an additional device (19) is provided for passing back, into the combustion chamber (3) of the reformer (4), part (14) of the hydrogen-rich gas stream (10) which leaves the gas scrubber (7).

5. System according to Claim 4, **characterized in that** the conversion stage comprises a conversion reactor (5) which is operated at medium temperature or a high-temperature conversion reactor (5') with a downstream low-temperature

conversion reactor (5").

6. System according to Claim 4 or 5, **characterized in that** a purification stage (9) for concentrating the separated carbon dioxide (18) follows the carbon dioxide exit of the gas scrubber (7).

Revendications

1. Procédé de production d'hydrogène à partir d'un gaz renfermant du méthane, en particulier de gaz naturel, dans lequel des hydrocarbures contenus dans le gaz sont soumis à un craquage catalytique à la vapeur d'eau dans un réacteur de réformage (4) en hydrogène, oxyde de carbone et gaz carbonique et une conversion catalytique de l'oxyde de carbone formé en gaz carbonique et hydrogène est effectuée dans un étage de conversion aval avec de la vapeur d'eau,
dans lequel le gaz carbonique est éliminé du flux de gaz converti (8) au moyen d'un lavage de gaz (7) et le flux de gaz riche en hydrogène (10) lavé est ensuite séparé dans une installation d'absorption modulée en pression (11) en un flux de gaz produit (12) composé d'hydrogène et en un flux de gaz de combustion (13) et
dans lequel le flux de gaz de combustion (13) avec l'hydrogène (14), dérivé du flux de gaz (10) en aval du lavage de gaz (7), est recyclé dans le réacteur de réformage (4) sous forme de combustible gazeux largement exempt de carbone et y est brûlé.

2. Procédé suivant la revendication 1, **caractérisé en ce qu'**un réacteur de conversion (5) exploité à température moyenne ou un réacteur de conversion à haute température (5') avec un réacteur de conversion à basse température aval (5") est utilisé pour l'étage de conversion.

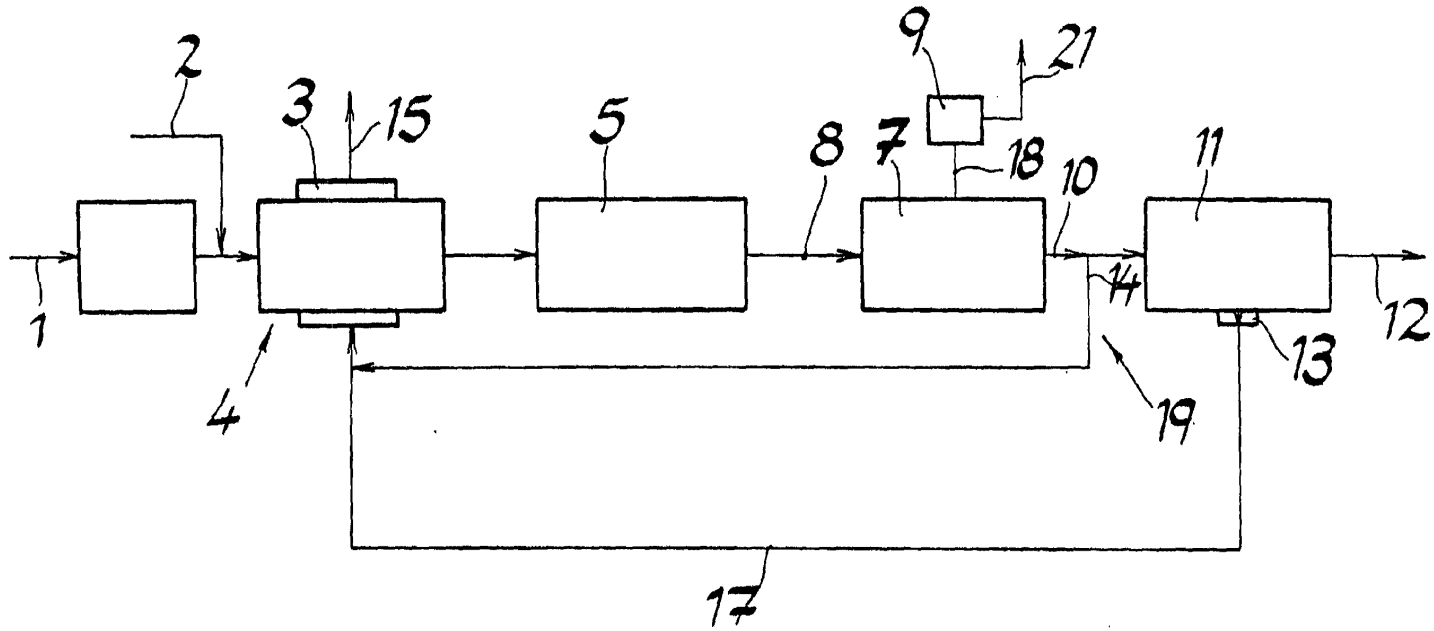
3. Procédé suivant l'une des revendications 1 ou 2, **caractérisé en ce que** du gaz carbonique techniquement pur (18) est séparé dans le lavage de gaz (7), lequel gaz carbonique est utilisé pour des applications industrielles ou est traité ultérieurement en un produit (21) d'une qualité utilisable dans l'industrie alimentaire.

4. Installation pour la mise en oeuvre du procédé suivant l'une des revendications 1 à 3 comprenant
au moins un réacteur de réformage (4) équipé d'une chambre de combustion (3) pour le craquage catalytique d'hydrocarbures gazeux à la vapeur d'eau,
un étage de conversion avec au moins un réacteur de conversion (5) pour la conversion catalytique d'oxyde de carbone à la vapeur d'eau en gaz carbonique et hydrogène,
un lavage de gaz (7) pour séparer le gaz carbonique du flux de gaz (8) sortant de l'étage de conversion et
une installation d'adsorption modulée de pression (11) aval pour l'isolation d'hydrogène (12), à laquelle se raccorde une conduite de gaz (17) renvoyée dans la chambre de combustion (3) pour le chauffage du réacteur de réformage par un flux de gaz sortant de l'installation d'adsorption,
dans laquelle il est prévu un dispositif supplémentaire (19) pour le recyclage d'une partie (14) du flux de gaz riche en hydrogène (10), sortant du lavage de gaz (7), dans la chambre de combustion (3) du réacteur de réformage (4).

5. Installation suivant la revendication 4, **caractérisée en ce que** l'étage de conversion comprend un réacteur de conversion (5) exploité à température moyenne ou un réacteur de conversion à haute température (5') avec un réacteur de conversion à basse température (5") aval.

6. Installation suivant l'une des revendications 4 ou 5, **caractérisée en ce qu'**un étage d'épuration (9) pour la concentration du gaz carbonique (18) séparé se raccorde à la sortie de gaz carbonique du lavage de gaz (7).

Fig.1



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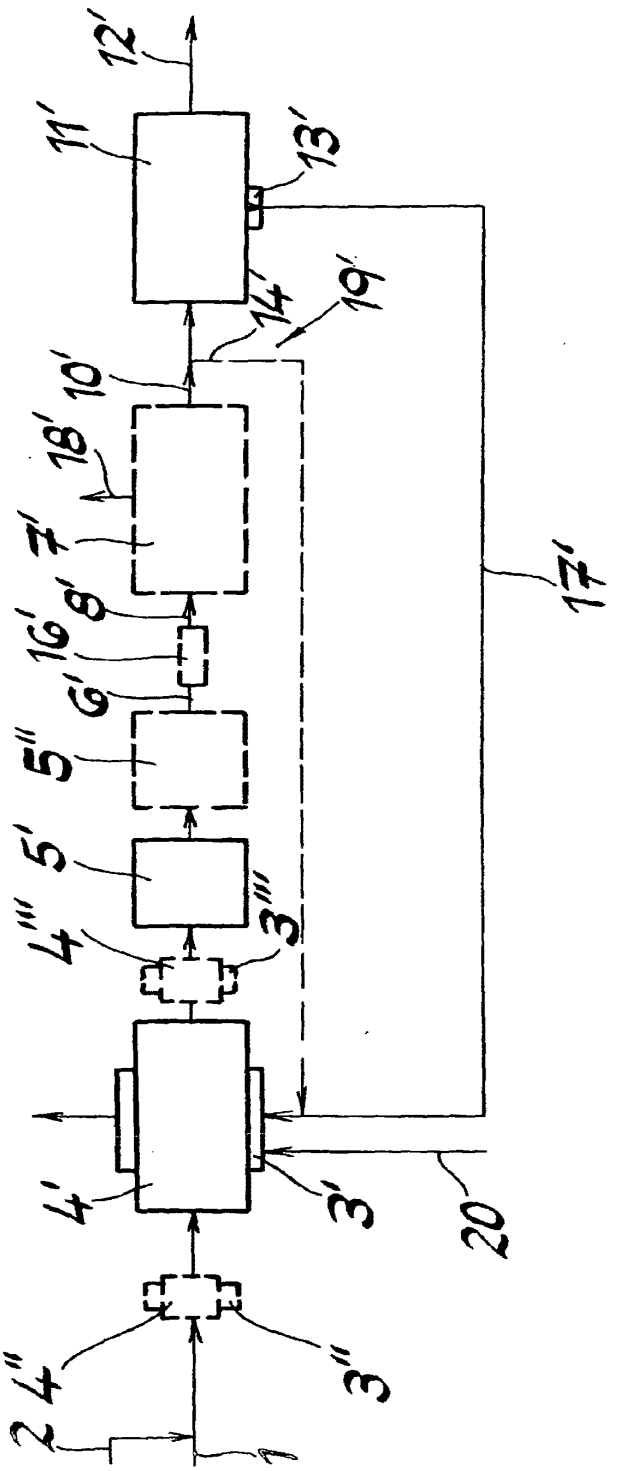


Fig. 2

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Method for extracting hydrogen from a gas containing methane, especially natural gas and system for carrying out said method

Abstract

The invention relates to a method for extracting hydrogen from a gas containing methane, especially natural gas. Hydrocarbons contained in the gas are catalytically broken down in a reformer (4) by steam in order to form hydrogen, carbon monoxide and carbon dioxide. Catalytic conversion of the obtained carbon monoxide with steam occurs in a downstream conversion step in order to form carbon monoxide and water. Carbon dioxide is removed from the converted gas flow (8) by gas washing (7), and the washed hydrogen-rich gas flow (10) is subsequently divided in a pressure-swing adsorption system (11) into a product gas flow (12) made of hydrogen and a waste gas flow (13). The waste gas flow (13) is introduced with hydrogen (14), which is separated from the gas flow (10) after gas washing, into a reformer (4) which is essentially a carbon-free combustible gas, and is combusted there. The invention also relates to a system for carrying out said method.

Images (2)



Classifications

B01D53/04 Separation of gases or vapours; Recovering vapours of volatile solvents from gases; Chemical or biological purification of waste gases, e.g. engine exhaust gases, smoke, fumes, flue gases, aerosols by adsorption, e.g. preparative gas chromatography with stationary adsorbents

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Other languages: German, French

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External links: Espacenet, EPO GPI, EP Register, Global Dossier, Discuss

Claims (6)

Hide Dependent

1. Method for extracting hydrogen from a methane-containing gas, in particular natural gas,
wherein hydrocarbons contained in the gas are catalytically split into hydrogen, carbon monoxide and carbon dioxide in a reformer (4) by means of steam, and catalytic conversion of the resulting carbon monoxide to carbon dioxide and hydrogen takes place in a downstream conversion stage by means of steam,
wherein the carbon dioxide is removed from the converted gas stream (8) by means of a gas scrubber (7), and the scrubbed hydrogen-rich gas stream (10) is then separated in a pressure swing adsorption system (11) into a product gas stream (12) consisting of hydrogen and a waste gas stream (13), and
wherein the waste gas stream (13), together with hydrogen (14) which is branched off from the gas stream (10) behind the gas scrubber (7), is passed to the reformer (4) as a combustion gas that is largely free of carbon, and burned there.

2. Method according to Claim 1, **characterized in that**, for the conversion stage, use is made of a conversion reactor (5) which is operated at medium temperature or of a high-temperature conversion reactor (5') with a downstream low-temperature conversion reactor (5").

3. Method according to Claim 1 or 2, **characterized in that** technically pure carbon dioxide (18) is separated in the gas scrubber (7), which is used for technical applications or processed further to produce a product (21) having a quality that can be used in the food industry.

4. System for carrying out the method according to one of Claims 1 to 3, comprising

- at least one reformer (4) equipped with a combustion chamber (3), for catalytic splitting of gaseous hydrocarbons by means of steam,

- a conversion stage comprising at least one conversion reactor (5) for catalytic conversion of carbon monoxide by means of steam to give carbon dioxide and hydrogen,

- a gas scrubber (7) for separating carbon dioxide from the gas stream (8) which leaves the conversion stage, and

- a downstream pressure swing adsorption system (11) for isolating hydrogen (12), to which there is connected a gas line (17) which is passed back to the combustion chamber (3) in order to fire the reformer with a gas stream which exits from the adsorption system,

wherein an additional device (19) is provided for passing back, into the combustion chamber (3) of the reformer (4), part (14) of the hydrogen-rich gas stream (10) which leaves the gas scrubber (7).

5. System according to Claim 4, **characterized in that** the conversion stage comprises a conversion reactor (5) which is operated at medium temperature or a high-temperature conversion reactor (5') with a downstream low-temperature conversion reactor (5").

6. System according to Claim 4 or 5, **characterized in that** a purification stage (9) for concentrating the separated carbon dioxide (18) follows the carbon dioxide exit of the gas scrubber (7).

Description

translated from German

The invention relates to a process for obtaining hydrogen from a methane-containing gas, in particular natural gas.

From US 5 131 930 a conventional hydrogen plant is known, which is operated with natural gas as a feedstock. in the plant initially carried out in general with steam-operated catalytic cracking of hydrocarbons contained in natural gas in a heated reformer for the production of carbon monoxide and hydrogen-containing synthesis gas. This is followed by a catalytic conversion of the carbon monoxide to hydrogen and then the purification of the hydrogen by means of a pressure swing adsorption. The exhaust gases of the adsorption system are returned to the combustion chamber of the reformer and burned there together with additionally supplied natural gas. It is also known to use refinery gas or other fuel gases as an additional fuel. By the steam splitting of the methane becomes a significant amount of carbon dioxide according to the water gas equilibrium

$$CO + H_2O \Rightarrow H_2 + CO_2$$

produced in the conversion stage by the carbon monoxide conversion to a concentration of generally about 16 vol. % (dry) increased. This amount of carbon dioxide passes through the chimney of the combustion chamber together with the carbon dioxide generated by the firing of additional carbonaceous fuels into the atmosphere.

The CO_2 content in the flue gas is generally above 20 vol. % (dry). In a refinery, a hydrogen plant designed in this way represents one of the largest carbon dioxide emitters.

From US 4 553 981 a process for recovering hydrogen is known in which a hydrocarbon-containing gas is reformed with steam and converted. in a wash, a CO_2 exhaust gas stream is then separated from the converted gas stream. This is followed by isolation of hydrogen by means of a pressure swing adsorption plant. The exhaust stream of the adsorption is compressed and returned to the reforming or conversion. This results in large circulation streams. To avoid accumulation of inert gases, such. As nitrogen, a purge gas must be removed from the exhaust stream of the pressure swing adsorption. The firing of the reformer is done in a conventional way. The method is also complicated and expensive.

The invention is based on the object to provide a simple and inexpensive method for recovering hydrogen from a methane-containing gas, in particular natural gas, in which only small amounts of carbon dioxide are released into the environment.

The invention and solution to this problem is a method for recovering hydrogen from a methane-containing gas, in particular natural gas, according to claim 1. in the gas-containing hydrocarbons are catalytically split into hydrogen, carbon monoxide and carbon dioxide in a reformer by means of water vapor, and in a downstream conversion stage is carried out with steam, a catalytic conversion of the resulting carbon monoxide to carbon dioxide and hydrogen. The carbon dioxide is removed by gas scrubbing from the converted gas stream, and the scrubbed, hydrogen-rich gas stream is then converted to hydrogen from a pressure swing adsorption unit Product gas stream and an exhaust stream separated. The exhaust gas stream is fed together with hydrogen, which is branched off from the gas stream behind the scrubbing gas as largely carbon-free fuel gas to the reformer and burned there.

While in the reformer almost complete cleavage of the hydrocarbons into hydrogen, carbon monoxide and carbon dioxide takes place, the resulting carbon monoxide is subsequently converted in the conversion stage to carbon dioxide, which is removed in the subsequent gas scrubbing. The exhaust gas of the pressure swing adsorption plant therefore contains essentially hydrogen and only small amounts of carbon. The same applies to the hydrogen, which is diverted from the gas stream behind the gas scrubber. In the common combustion of these two gas streams in the reformer, therefore, a predominantly consisting of nitrogen and water exhaust gas, while the carbon dioxide content is low. Due to the gas recirculation, an additional firing of the reformer with carbon-containing fuels is dispensed with, so that the carbon dioxide emission drops markedly Compared to conventional processes, carbon dioxide emissions can be reduced by about 75%. The procedural steps that are used within the scope of the teaching according to the invention are without exception mature technologies which have already been successfully used in hydrogen production for some time. The effort required to achieve the described carbon dioxide reduction is comparatively low. It is therefore also possible to convert an existing conventional hydrogen plant in order to operate with it the inventive method.

Preferably, a medium-temperature conversion reactor or a high-temperature conversion reactor with a downstream low-temperature conversion reactor is used for the conversion stage. This will result in an almost complete conversion of the resulting Guarantees carbon monoxide to carbon dioxide, which can be subsequently removed via the gas scrubbing from the gas stream. When using a downstream cryogenic conversion reactor, there is the advantage that the high temperature conversion reactor of an existing hydrogen plant can continue to be used, thereby significantly reducing the cost of retrofitting an existing plant.

Preferably, in the gas scrubbing technically pure carbon dioxide is separated, which is used for technical applications or further processed into a product with a usable quality in the food industry. In addition to the use as feedstock for the food industry comes as a use of technically pure carbon dioxide, for example, the filling of a petroleum well as a measure for efficient oil production in question. Alternatively, the carbon dioxide can also be used as a raw material for a methanol synthesis. The carbon dioxide washing can be done with known physical methods such B. Rectisol, Selexol or Genosorb, or with a chemical or physical / chemical method, eg. B. aMDEA (aqueous solution of N-methyldiethanolamine) or sulfinol operated.

If an existing H_2 plant is converted for the purpose of CO_2 minimization, the converted gas stream is expediently compressed before it enters the CO_2 scrub to be newly built in order to compensate for the resulting pressure loss. This increases the effectiveness of CO_2 scrubbing.

The invention is also a plant according to claim 4 for carrying out the method Preferred embodiments of this system are described in the subclaims 5 and 6

Fig. 1
ein Blockschaltbild eines erfindungsgemäßen Verfahren,
Fig. 2
ein Blockschaltbild eines erfindungsgemäßen Verfahrens nach Umrüstung einer konventionellen Wasserstoffanlage.

In the following the invention will be explained in detail with reference to a drawing showing only one embodiment. They show schematically:

a block diagram of a method according to the invention,

Fig. 2

a block diagram of a method according to the invention after conversion of a conventional hydrogen plant.

Fig. 1 shows an inventive method for the production of hydrogen from a methane-containing natural gas. A natural gas stream 1, a steam stream 2 is added. The hydrocarbons, in particular methane, contained in the natural gas are catalytically split into hydrogen, carbon monoxide and carbon dioxide in a reformer 4 equipped with a combustion chamber 3 with the aid of the admixed steam stream 2. This reforming is almost complete, so that there are virtually no hydrocarbon-containing gases at the outlet of the reformer 4. In a downstream, operated at medium temperature conversion reactor 5 is carried out using the steam, a catalytic conversion of the resulting carbon monoxide to carbon dioxide and hydrogen. Also, this reaction is almost complete, so that the carbon monoxide content of emerging from the conversion reactor 5 gas stream 8 is less than 1 vol. % (dry). Subsequently, the resulting carbon dioxide is almost completely removed from the gas stream 8 with the aid of a gas scrubber 7. In the exemplary embodiment, the gas scrubber 7 is operated with an aqueous solution of N-methyldiethanolamine (aMDEA) as a scrubbing liquid. In the context of the invention, however, it is also known other washing methods such. As Rectisol, Selexol, Genosorb or sulfinol use. The carbon dioxide 18 obtained in the laundry 7 is further concentrated in a further purification stage 9 to a usable purity in the food industry. The washed gas stream 10 contains only very small amounts of carbon and is then in a pressure swing adsorption 11th separated into a hydrogen gas 12 existing product gas stream and an exhaust gas stream 13. The product gas stream 12 has a hydrogen content of more than 99 vol. % on. The exhaust stream 13 also contains substantially hydrogen and only minor amounts of unreacted or partially reacted hydrocarbons. Together with a downstream of the laundry 7 via a device 19 branched, substantially also consisting of hydrogen partial stream 14, the exhaust gas stream 13 is fed via a line 17 of the combustion chamber 3 of the reformer 4 and burned there. The amount of the partial flow 14 is in this case adjusted so that it covers the energy requirement of the reformer 4 in the common combustion with the exhaust gas stream 13. Since both the exhaust stream 13 and the partial stream 14 predominantly consist of hydrogen and contain only small amounts of carbon, the exhaust gas 15 of the combustion chamber 4 has a high water vapor content and only a small proportion of carbon dioxide. Compared to conventional methods for hydrogen production, in which the combustion chamber with carbonaceous fuels such. B. natural gas and hydrocarbon-containing exhaust gases, is fired, the inventive method is thus characterized by a low carbon dioxide emission.

in the described process steps, which are used in the context of the teaching of the invention, are all technically mature technologies that have proven themselves both in the production of hydrogen and in the production of ammonia. The reformer 4 need only be sized large enough to ensure H_2 production including fuel gas supply after CO_2 scrubbing. The conversion reactor 5 is operated at medium temperature to ensure almost complete conversion of the resulting carbon monoxide to carbon dioxide. The carbon dioxide 21 obtained in the exemplary embodiment by means of the purification stage 9 can be further processed in the food industry. Alternatively, there is but also the possibility to use the obtained in the laundry 7 technically pure carbon dioxide 18 directly for technical applications. In this case, for example, the filling of an oil well as a measure for the efficient extraction of crude oil or else the use as raw material for a methanol synthesis in question.

The effort to carry out the method described is comparatively low. In particular, it is possible to convert an existing conventional hydrogen plant so that it can be operated with the inventive method. FIG. 2 shows a conventional hydrogen plant retrofitted according to the invention. The existing system components are marked with solid lines, while the components added as part of the retrofitting are shown in dashed lines. The conventional hydrogen plant has a reformer 4 'equipped with a combustion chamber 3' for the catalytic splitting of gaseous hydrocarbons with water vapor. Behind it is a high temperature conversion reactor 5 'arranged for the catalytic conversion of carbon monoxide with steam to carbon dioxide and hydrogen. This is followed by a pressure swing adsorption 11 'for the isolation of hydrogen 12' from the converted gas stream 8 'with connected gas line 17' to the combustion chamber 3 'for firing the reformer 4' with a from the adsorption 11 'exiting exhaust stream 13'. As part of the conversion, the capacity of the reforming step by a reformer 4 'upstream pre-reformer 4 "and a reformer 4' downstream post-reformer 4 '" increased by about 20%. If necessary, however, it is also sufficient to provide only one of the two additional reformers 4 ", 4". The high-temperature conversion reactor 5 ', which generally operates at temperatures between 360 and 500 ° C, was supplemented by a downstream, in the range of about 210 to 270 ° C working, low-temperature conversion reactor 5 "to the fullest possible conversion of the Carbon monoxide to achieve carbon dioxide. Alternatively, the existing high temperature conversion reactor 5 'may be replaced by a medium temperature conversion reactor. Between the conversion stage and the pressure swing adsorption 11 'was a gas compressor 16' for compressing the gas stream 6 'and a gas scrubbing 7' provided for the separation of the resulting, wherein in the embodiment, the obtained in the gas scrubber 7 'carbon dioxide 18' is fed directly to a technical application. Between the laundry 7 'and the pressure swing adsorption 11' was an additional means 19 'for the return of a portion 14' of the gas scrubber leaving hydrogen-rich gas stream 10 'in the combustion chamber 3', 3 ", 3"of the reformer 4', 4 ", 4 "provided. Finally, an adaptation of the existing reformer 4 'to the combustion and the waste heat utilization of the now hydrogen-rich fuel. The existing gas line 20 for the supply of hydrocarbon-containing fuel gases in the combustion chamber 3 'of the reformer 4' is no longer used. The illustration in FIG. 2 shows that with comparatively little effort, a conventional hydrogen plant can be converted in such a way that the process according to the invention can be operated with it. As a result, the attractiveness of the method according to the invention is further increased.

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(54) Steam-Hydrocarbon Reforming with Reduced Carbon Dioxide Emissions

(57) A process for producing a hydrogen-containing product gas with reduced carbon dioxide emissions compared to conventional hydrogen production processes. A hydrocarbon and steam are reformed in a reformer and the resulting reformate stream is shifted in one or more shift reactors. The shifted mixture is scrubbed to remove carbon dioxide to form a carbon dioxide-depleted stream. The carbon dioxide-depleted stream is separated to form a hydrogen-containing product gas and a by-product gas. A portion of the hydrogen containing product gas is used as a fuel in the reformer and a portion of the by-product gas is recycled back into the process. The process may optionally include reforming in a prereformer and/or an oxygen secondary reformer.

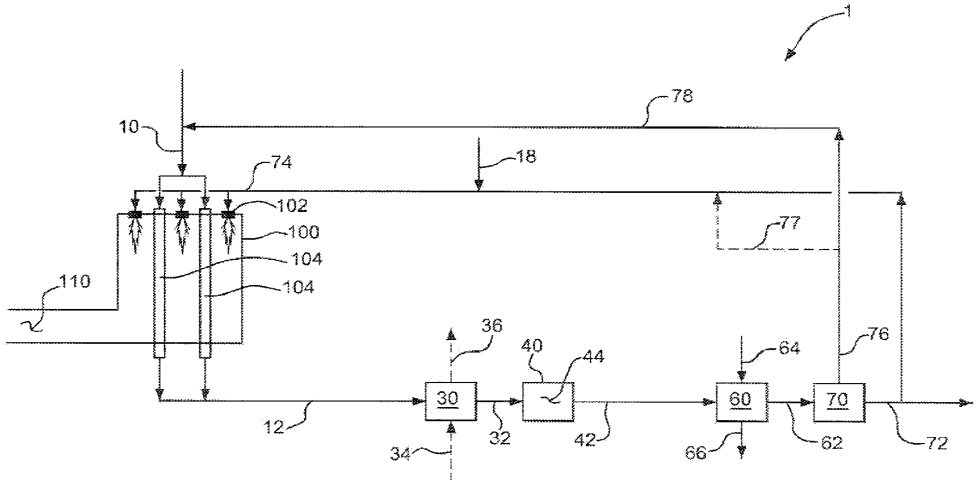


FIG. 1

EP 2 266 922 A1

Description

BACKGROUND

[0001] There is growing pressure to reduce carbon dioxide emissions from industrial processes. A large hydrogen production plant may produce up to 900,000 metric tons of carbon dioxide per year, thus it may be considered a significant source of carbon dioxide.

[0002] In Europe, Canada, and California, carbon dioxide reduction regulations are being phased in gradually. This means that greenhouse gas (GHG) legislation remains a key consideration in projects in the 2012-2015 timeframe. The current understanding on this issue is that new plants will have to plan for carbon dioxide capture but may not be required to install and operate such systems at the project on-stream date. Therefore, industry desires a flexible carbon dioxide capture ready design that may be implemented when needed.

[0003] Industry desires to produce hydrogen by steam-hydrocarbon reforming while capturing carbon dioxide thereby decreasing or eliminating carbon dioxide emissions.

[0004] Industry desires to adjust the amount of carbon dioxide capture based on regulations and economics.

[0005] Industry desires an energy efficient large-scale hydrogen production process with decreased carbon dioxide emissions compared to conventional processes.

BRIEF SUMMARY

[0006] The present invention relates to a process for producing a hydrogen-containing product gas. The process comprises:

(a) introducing a process stream comprising steam and at least one hydrocarbon selected from the group consisting of methane, ethane, propane, butane, pentane, and hexane into a plurality of catalyst-containing reformer tubes in a reformer furnace and reacting the process stream inside the plurality of catalyst-containing reformer tubes at a first temperature ranging from 700°C to 1000°C and a first pressure ranging from 2 to 50 atmospheres (0.2 to 5 MPa) to form a reformate stream comprising hydrogen, carbon monoxide, methane and steam and withdrawing the reformate stream from the plurality of catalyst-containing reformer tubes;

(b) reacting the reformate stream in the presence of a shift catalyst at a second temperature ranging from 190°C to 500°C and a second pressure ranging from 2 to 50 atmospheres (0.2 to 5 MPa) to form a second process stream comprising carbon dioxide, hydrogen, carbon monoxide and methane;

(c) scrubbing the second process stream with a wash stream to form a carbon dioxide-depleted stream and a carbon dioxide-loaded wash stream;

(d) separating the carbon dioxide-depleted stream to form the hydrogen-containing product gas and a by-product gas comprising methane and carbon monoxide;

(e) introducing a portion of the by-product gas into the process stream at a location upstream of the plurality of catalyst-containing reformer tubes and/or into the reformate stream at a location upstream of a reforming catalyst in a secondary reforming reactor; and

(f) combusting a fuel gas comprising a portion of the hydrogen-containing product gas, optionally a portion of the by-product gas, and optionally a supplementary fuel in the reformer furnace external to the plurality of catalyst-containing reformer tubes to supply energy for reacting the process stream inside the plurality of catalyst-containing reformer tubes, and withdrawing a flue gas from the reformer furnace.

[0007] 50% to 98% by volume of the by-product gas formed in step (d) may be introduced into the process stream in step (e).

[0008] The process may comprise reacting the process stream in the presence of a second reforming catalyst in an unfired reactor at a third temperature ranging from 425°C to 600°C and a third pressure ranging from 2 to 50 atmospheres (0.2 to 5 MPa) to form carbon dioxide and hydrogen in the process stream prior to introducing the process stream into the plurality of catalyst containing reformer tubes. The portion of the by-product gas may be introduced into the process stream upstream of the unfired reactor. The process stream reacted in the unfired reactor may comprise a portion of the by-product gas.

[0009] The process may comprise:

introducing an oxygen-rich gas into the reformate stream after withdrawing the reformate stream from the plurality of catalyst-containing reformer tubes to partially oxidize the reformate stream; and

reacting the partially oxidized reformate stream in the presence of the reforming catalyst in the secondary reforming reactor under reaction conditions sufficient to form reaction products comprising carbon monoxide and hydrogen in the reformate stream before reacting the reformate stream in the presence of the shift catalyst.

[0010] The portion of the by-product gas may be introduced into the reformate stream at the location upstream of the secondary reforming reactor. The reformate stream may comprise at least a portion of the by-product gas.

[0011] The process may comprise:

introducing a feed gas comprising at least one hydrocarbon and optionally steam into the reformate stream after withdrawing the reformate stream from the plurality of catalyst-containing reformer tubes, the at least one hydrocarbon selected from the group consisting of methane, ethane, propane, butane, pentane, and hexane;

introducing an oxygen-rich gas into the reformate stream after withdrawing the reformate stream from the plurality of catalyst-containing reformer tubes to partially oxidize the reformate stream; and

reacting the partially oxidized reformate stream in the presence of the reforming catalyst in the secondary reforming reactor under reaction conditions sufficient to form reaction products comprising carbon monoxide and hydrogen in the reformate stream before reacting the reformate stream in the presence of the shift catalyst.

[0012] The process may further comprise reacting the second process stream in the presence of a second shift catalyst at a fourth temperature ranging from 190°C to 300°C and a fourth pressure ranging from 2 to 50 atmospheres (0.2 to 5 MPa) to form carbon dioxide and hydrogen in the second process stream prior to the step of scrubbing the second process stream. The second shift catalyst may comprise copper.

[0013] The fuel gas may comprise 30 volume % to 98 volume % hydrogen-containing product gas and 2 volume % to 70 volume % by-product gas.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

[0014]

FIG. 1 is a process flow diagram for a process for producing a hydrogen-containing product gas with reduced carbon dioxide emissions.

FIG. 2 is another process flow diagram for a process for producing a hydrogen-containing product gas with reduced carbon dioxide emissions.

FIG. 3 is another process flow diagram for a process for producing a hydrogen-containing product gas with reduced carbon dioxide emissions.

FIG. 4 is a process flow diagram for a prior art process for producing a hydrogen-containing product gas.

DETAILED DESCRIPTION

[0015] The articles "a" and "an" as used herein mean one or more when applied to any feature in embodiments of the present invention described in the specification and claims. The use of "a" and "an" does not limit the meaning to a single feature unless such a limit is specifically stated. The article "the" preceding singular or plural nouns or noun phrases denotes a particular specified feature or particular specified features and may have a singular or plural connotation depending upon the context in which it is used. The adjective "any" means one, some, or all indiscriminately of whatever quantity.

[0016] The phrase "at least a portion" means "a portion or all."

[0017] As used herein, "plurality" means at least two.

[0018] For the purposes of simplicity and clarity, detailed descriptions of well-known devices, circuits, and methods are omitted so as not to obscure the description of the present invention with unnecessary detail.

[0019] The present invention relates to a process for producing a hydrogen-containing product gas. The process is particularly useful for producing a hydrogen-containing product gas with reduced carbon dioxide emissions compared

to conventional steam/hydrocarbon reforming processes.

[0020] With reference to FIGS. 1-3, the process comprises introducing a process stream 10 comprising steam and at least one hydrocarbon selected from the group consisting of methane, ethane, propane, butane, pentane, and hexane into a plurality of catalyst-containing reformer tubes 104 in a reformer furnace 100 and reacting the at least one hydrocarbon and steam inside the plurality of catalyst-containing reformer tubes 104 at a temperature ranging from 700°C to 1000°C and a pressure ranging from 2 to 50 atmospheres (0.2 to 5 MPa) to form hydrogen and carbon monoxide in the process stream 10 and withdrawing a reformate stream 12 from the plurality of catalyst-containing reformer tubes 104.

[0021] As used herein, a reformate stream is any stream comprising hydrogen and carbon monoxide formed from the reforming reaction of a hydrocarbon and steam.

[0022] The process stream 10 may contain more than one hydrocarbon. The process stream may be initially formed from natural gas and steam, liquefied petroleum gas (LPG) and steam, naphtha and steam and/or other feedstocks known in the art. As described in more detail below, the process stream 10 may be processed in a prereformer prior to introducing the process stream 10 into the plurality of catalyst-containing reformer tubes 104.

[0023] Reformer furnaces with a plurality of catalyst-containing reformer tubes, i.e. tubular reformers, are well known in the art. Suitable materials and methods of construction are known. Catalyst in the catalyst-containing reformer tubes may be any suitable catalyst known in the art, for example, a supported catalyst comprising nickel.

[0024] The reformate stream 12 withdrawn from the plurality of catalyst-containing reformer tubes 104 is cooled in a heat exchanger 30 which may be a boiler to produce steam 36 from a water-containing stream 34 by indirect heat transfer and thereby remove heat from the reformate stream 12. Reformate stream 32 is withdrawn from the boiler 30. Reformate stream 12 may be passed to the heat exchanger 30 to remove heat from the reformate stream 12 and improve the thermal efficiency of the process.

[0025] The reformate stream is passed to shift reactor 40. The process further comprises reacting carbon monoxide and steam in the reformate stream 32 in the presence of a shift catalyst 44 at a temperature ranging from 190°C to 500°C and a pressure ranging from 2 to 50 atmospheres (0.2 to 5 MPa) to form a second process stream 42 comprising carbon dioxide, hydrogen, carbon monoxide and methane.

[0026] Shift reactors and suitable shift catalysts are known in the art. The shift catalyst may be an iron-based high temperature shift catalyst, or a copper-based medium temperature shift catalyst, or a copper-based low temperature shift catalyst. Any suitable shift catalyst may be used. One skilled in the art can readily select a suitable shift catalyst.

[0027] The shift catalyst 44 may comprise iron oxide and the reaction temperature may be from 310°C to 500°C or 310°C to 400°C.

[0028] The shift catalyst 44 may comprise copper and the reaction temperature may be from 200°C to 400°C or 200°C to 350°C.

[0029] The process further comprises scrubbing the second process stream 42 with a wash stream 64 to form a carbon dioxide-depleted stream 62 and a carbon dioxide-loaded wash stream 66. Scrubbing may be done in a so-called gas scrubber 60. Carbon dioxide scrubbing is also known in the art as acid gas removal. The wash stream 64 may be any scrubbing fluid known in the art, for example N-methyl diethanolamine (aMDEA). Other scrubbing fluids associated with other scrubbing methods, for example, Rectisol®, Selexol®, Genosorb®, and sulfinol are known in the art,.

[0030] The term "depleted" means having a lesser mole % concentration of the indicated component than the original stream from which it was formed. This means that carbon dioxide-depleted stream has a lesser mole % concentration of carbon dioxide than the second process stream which was introduced into the scrubber 60. The wash stream, having an affinity for carbon dioxide will become "loaded" with carbon dioxide. Carbon dioxide will become absorbed or otherwise taken in by the wash stream 64.

[0031] The carbon dioxide-depleted stream 62 contains only a small amount of carbon dioxide.

[0032] Water may also be removed from the second process stream 42 prior to the gas scrubber 60 and/or in the gas scrubber 60.

[0033] The process further comprises separating the carbon dioxide-depleted stream 62 in a separator 70 to form the hydrogen-containing product gas 72 and a by-product gas 76 comprising methane and carbon monoxide. The step of separating the carbon dioxide-depleted stream may be done by pressure swing adsorption and/or temperature swing adsorption. The separator 70 may be a pressure swing adsorber and/or temperature swing adsorber. Construction and operation of pressure swing adsorbers and temperature swing adsorbers are known in the art. Suitable devices and operating conditions may be selected by one skilled in the art.

[0034] Simpler and less efficient pressure swing adsorbers and/or temperature swing adsorbers and their associated processes may be used since a portion of the hydrogen-containing product gas 72 may be blended with the by-product gas 76 for use as a fuel in the reformer furnace (described below).

[0035] More water may be removed from the carbon dioxide-depleted stream 62 prior to separating the carbon dioxide-depleted stream. Water removal is conventional and water may be removed by any suitable method and suitable water removal device known in the art.

[0036] With reference to FIGS. 1-3, the process further comprises introducing a portion 78 of the by-product gas 76

into the process stream 10, 14 at a location upstream of the plurality of catalyst-containing reformer tubes 104 and/or into the reformate stream 12 at a location upstream of a reforming catalyst in a secondary reforming reactor 20 (described later). The portion 78 of the by-product gas 76 may be introduced into the process stream at one or more locations in the process. The portion 78 of the by-product gas 76 may be introduced into the process stream 10, 14 at a location upstream of the plurality of catalyst-containing reformer tubes 104. The portion 78 of the by-product gas 76 may be introduced into the reformate stream 12 at a location upstream of a reforming catalyst in a secondary reforming reactor 20. The portion 78 of the by-product gas 76 may be introduced into the process stream 10, 14 at a location upstream of the plurality of catalyst-containing reformer tubes 104 and introduced into the reformate stream 12 at a location upstream of a reforming catalyst in a secondary reforming reactor 20.

[0037] The portion 78 of the by-product gas 76 may be a divided portion of the by-product stream 76 formed from the separation of the carbon dioxide-depleted stream 62 and thereby have the same composition as the by-product stream 76 formed from the separation of the carbon dioxide-depleted stream 62. As used herein a "divided portion" of a stream is a portion having the same chemical composition as the stream from which it was taken.

[0038] By introducing the by-product gas back into the process stream for further processing, additional carbon in the stream may be converted to carbon dioxide and removed via the scrubbing step. Any by-product gas from the separator that is recycled back to the process feed stream reduces the CO_2 emitted from the overall hydrogen production process.

[0039] 50% to 98% by volume of the by-product gas 76 formed by the separation of the carbon dioxide-depleted stream 62 in separator 70 may be introduced into the process stream 10, 12, and/or 14. The amount of CO_2 emitted from the hydrogen production process can be effectively reduced by increasing the amount of by-product gas that is recycled back to process feed stream.

[0040] The process further comprises combusting a fuel gas 74 comprising a portion of the hydrogen-containing product gas 72, optionally a portion 77 of the by-product gas 76, and optionally a supplementary fuel 18 in the reformer furnace 100 external to the plurality of catalyst-containing reformer tubes 104 to supply energy for reacting methane and steam inside the plurality of catalyst-containing reformer tubes 104. Flue gas 110 is withdrawn from the reformer furnace 100, and because the fuel gas 74 comprises hydrogen in an amount greater than conventional reformer furnaces, the flue gas will contain a reduced amount of carbon dioxide compared to conventional reformer furnaces. The supplementary fuel 18 is often called a trim fuel and may be, for example, natural gas. The portion of the hydrogen-containing product gas 72 and the portion of the by-product gas 76 may be divided portions of the respective gases.

[0041] The amount of carbon dioxide emissions in the flue gas 110 can be adjusted by the amount of hydrogen-containing product gas 72, the amount of by-product gas 76 and the amount of supplementary fuel 18 that are used as fuel.

[0042] For the case where most of the by-product gas 76 is recycled to the process stream and the fuel gas 74 consists essentially of the hydrogen-containing product gas 72, the carbon dioxide emissions in the flue gas 110 will be substantially reduced. The fuel gas may comprise 90 volume % to about 98 volume % hydrogen-containing product gas 72. For practical purposes, at least a portion of the by-product gas 76 may be used as fuel 74 to prevent the build up of inert gases (e.g. N_2 and Ar) in the process streams. Alternatively, and less desirably, a portion of the by-product gas 76 may be used in another process and/or disposed.

[0043] FIG. 2 and FIG. 3 show additional optional features, for example a so-called prereformer 80, an oxygen secondary reformer 20, and a second shift reactor 50.

[0044] A prereformer is defined herein as any unfired vessel that converts hydrocarbon feedstock by reaction with steam over a catalyst with or without heating. A prereformer may be an adiabatic fixed bed reactor. A prereformer may be a tubular reactor. A prereformer generally employs a different type of catalyst than a primary reformer, for example a high activity, high nickel content catalyst. Temperatures in a prereformer may be in the range of about 400°C to about 600°C. Heat to a prereformer may be provided from exhaust gases from a reformer or other source, but is characterized by the lack of direct heating by a combustion flame. A prereformer and a reformer may be physically connected.

[0045] As shown in FIG. 2 and FIG. 3, prior to introducing the process stream 10 into the plurality of catalyst-containing reformer tubes 104, the process may further comprise introducing the process stream 14 comprising steam and at least one hydrocarbon selected from the group consisting of methane, ethane, propane, butane, pentane and hexane into reactor 80 and reacting the at least one hydrocarbon and steam in the process stream 14 in the presence of a reforming catalyst 84 in an unfired reactor (prereformer) at a temperature ranging from 400°C to 600°C and a pressure ranging from 2 to 50 atmospheres (0.2 to 5 MPa) prior to introducing the process stream 10 comprising steam and at least one hydrocarbon selected from the group consisting of methane, ethane, propane, butane, pentane, and hexane into the plurality of catalyst containing reformer tubes 104.

[0046] As used herein, the "process stream" includes the stream comprising steam and at least one hydrocarbon upstream of the optional prereformer 80, if present, to the exit from the plurality of catalyst-containing reformer tubes 104, where it becomes the "reformate stream." In case the optional prereformer 80 is not present, the process stream includes the stream comprising steam and at least one hydrocarbon upstream of the inlet of the plurality of catalyst-containing reformer tubes 104 to the exit of the plurality of catalyst-containing reformer tubes.

[0047] The hydrocarbon composition may vary as process stream 10, 14 is reacted. For example, the at least one

hydrocarbon may initially include propane and butane and after reacting in a prereformer, the at least one hydrocarbon in the process stream may be methane.

[0048] Reforming catalyst 84 may be any suitable reforming catalyst known in the art for so-called "prereforming." Prereforming is a term used to describe reforming before the main reforming step, for example in a fired reformer. Catalysts for prereforming are commercially available. Since the articles "a" and "the" mean one or more, more than one prereformer and more than one reforming catalyst may be used.

[0049] Reforming catalyst 84 may comprise at least one metal selected from a group consisting of nickel, cobalt, platinum, palladium, rhodium, ruthenium, iridium and mixtures thereof.

[0050] Reforming catalysts suitable for prereforming are discussed in patents US 4,105,591, US 3,882,636, US 3,988,425, GB 969,637, GB 1,150,066, and GB 1,155,843.

[0051] Reforming catalyst 84 may be in a wide variety of shapes or forms, for example cylindrical pellets, Raschig rings, multi-hole shaped catalyst, etc. or other form known in the art. The catalyst size may range from about 1 mm to about 15 mm in diameter. The length of the catalyst may range from about 3 mm to 10 mm. The ideal size for a given application depends on a number of factors including the catalyst shape and nickel loading, the operating temperature, pressure, and feed composition, and the allowable pressure drop. A catalyst with a multi-hole shape with a diameter in the range from 5 mm to 25 mm and a height to diameter ratio of 0.5 to 1.2 will be suitable for reforming catalyst 102. One skilled in the art is able to select suitable catalyst with a suitable shape for reforming catalyst 84.

[0052] Reforming catalyst 84 may also be structured packing catalyst where the catalyst is applied as a washcoat on a structured packing. Structured packing is known in the art. As used herein, the term "structured packing" means a flow guide having a plurality of substantially parallel passages. Substantially parallel means parallel within manufacturing tolerances. Davidson, U.S. Pat. No. 4,340,501 describes a structure in a reactor vessel where the fluid is intermittently but controllably brought into contact with the vessel walls.

[0053] As shown in FIG. 2 and FIG. 3, a portion of by-product gas 76 may be recycled back to the reactor 80. Process stream 14 may comprise a portion of the by-product gas 76.

[0054] FIG. 2 and FIG. 3 also show an optional secondary reforming reactor 20 located in the process between the plurality of catalyst-containing tubes 104 and the shift reactor 40. The process may further comprise introducing an oxygen-rich gas 26 into the reformate stream 12 after withdrawing the reformate stream 12 from the plurality of catalyst-containing reformer tubes 104 to partially oxidize the reformate stream, and reacting the partially oxidized reformate stream 12 in the presence of a reforming catalyst 24 in the secondary reforming reactor 20 under reaction conditions sufficient to form reaction products comprising carbon monoxide and hydrogen in the reformate stream 22. The oxygen-rich gas 26 may be introduced into the reformate stream 12 before reactor 20 or may be introduced into the reformate stream 12 in reactor 20, for example through a burner.

[0055] Secondary reforming reactors are well-known in the art and used widely for the production of ammonia and methanol. Secondary reforming reactors are refractory lined vessels with one or more burners and a reforming catalyst bed. Heat required for the reforming reaction is provided by partial oxidation (combustion) of a portion of the feed.

[0056] Effluent from the primary reformer is fed to the secondary reforming reactor where it is mixed with oxygen fed through a burner. Partial oxidation reactions occur in a combustion zone proximate or just below the burner. The partially oxidized mixture then passes through a catalyst bed where the mixture is substantially thermodynamically equilibrated over the reforming catalyst.

[0057] U.S. Pat. No. 3,479,298, incorporated herein by reference, discloses a secondary reformer for the production of a hydrogen-containing gas, and discloses that if oxygen is used instead of air, the process gas leaving the secondary reformer is a gas suitable for further treatment to yield methanol or high purity hydrogen.

[0058] Tindall et al., "Alternative technologies to steam-methane reforming," Hydrocarbon Processing, pp. 75-82, November, 1995, also disclose a oxygen secondary reformer for producing hydrogen.

[0059] As used herein, an oxygen-rich gas is an oxygen-containing gas having an oxygen concentration of 98 volume % to 100 volume %, for example industrial grade oxygen. Oxygen is added in an amount for incomplete combustion of any hydrocarbons in the reformate stream. The resulting stream 22 is rich in hydrogen and carbon monoxide.

[0060] The reforming catalyst 24 may be any conventional gas feed type of steam reforming catalyst suitable for promoting the reaction of methane and steam to produce hydrogen. Typical suitable reforming catalysts include nickel catalysts such as nickel and/or nickel oxide supported on a carrier such as alumina. The nickel catalyst generally contains 8 to 30 weight percent nickel calculated as NiO and may additionally contain other metal or metal compound promoters. Suitable catalysts may be readily selected by one skilled in the art.

[0061] Reaction conditions sufficient to form reaction products in the secondary reforming reactor 20 include a temperature ranging from 800°C to 1200°C, or 900°C to 1100°C, and a pressure ranging from 2 to 50 atmospheres (0.2 to 5 MPa).

[0062] As shown in FIG. 2 and in FIG. 3, a portion 78 of the by-product gas 76 may be introduced into the process stream 10, 14 at a location upstream of the plurality of catalyst-containing reformer tubes 104 and/or into the reformate stream 12 at a location upstream of the secondary reforming reactor 20. The portion 78 of the by-product gas 76 may

be introduced into one of the locations or subdivided and introduced into two or more locations. For example, the portion 78 of the by-product gas 76 may be introduced into the process stream 10 just upstream of the plurality of catalyst-containing reformer tubes 104. Alternatively, the portion 78 of the by-product gas 76 may be divided with a first portion introduced into the process steam 10 at a location upstream of the plurality of the catalyst-containing reformer tubes and a second portion of the by-product gas introduced into the reformate stream 12 upstream of the secondary reforming reactor 20. The reformate stream 12 may comprise at least a portion of the by-product gas 76.

[0063] Generally, not all of the by-product gas 76 will be recycled to the process stream and/or the reformate stream. Another portion 77 of the by-product stream may be introduced in the fuel gas stream 74 as shown in FIGS. 1-3. This other portion 77 may be required to purge the process of inert gases (e.g. N_2 and Ar).

[0064] As shown in FIG. 2 and FIG. 3, the process may comprise introducing a feed gas 28 into the reformate stream 12 after withdrawing the reformate stream 12 from the plurality of catalyst-containing reformer tubes 104. The feed gas 28 comprises at least one hydrocarbon and optionally steam. The at least one hydrocarbon is selected from the group consisting of methane, ethane, propane, butane, pentane, and hexane. Steam addition is optional in case a suitable amount of steam remains from the primary reformer. The process may further comprise introducing an oxygen-rich gas 26 into the reformate stream after withdrawing the reformate stream from the plurality of catalyst-containing reformer tubes to partially oxidize the reformate stream. The process may then comprise reacting the partially oxidized reformate stream in the presence of the reforming catalyst 24 in the secondary reforming reactor 20 under reaction conditions sufficient to form reaction products comprising carbon monoxide and hydrogen in the reformate stream 12.

[0065] The feed gas 28 may be introduced into the reformate stream 12 before the resultant mixture is introduced into the secondary reforming reactor 20. The feed gas 28 may be introduced into the reformate stream 12 in the secondary reactor 20. Typically, the oxygen-rich gas will be introduced into the secondary reactor 20 separately from the feed gas 28 and the reformate stream 12.

[0066] The hydrocarbon source for the feed gas 28 may be the same as the hydrocarbon source for the process stream 10, 14.

[0067] The benefit of providing a feed gas comprising at least one hydrocarbon and reacting the feed gas in the secondary reforming reactor 20 is that the size of the reformer furnace 100 and correspondingly, the plurality of catalyst-containing reformer tubes, will be smaller. One skilled in the art can suitably optimize the size of and amount of feedstock processed in the reformer furnace 100 and the secondary reforming reactor 20. Another benefit is that fuel requirements in the primary reformer are reduced.

[0068] As shown in FIG. 2 and in FIG. 3, the process may include a second shift reactor 50. The second process stream 42 withdrawn from the shift reactor 40 may be further shifted in the second shift reactor 50. The second process stream may be suitably cooled prior to being introduced into the second shift reactor 50. The process may then further comprise reacting carbon monoxide and steam in the second process stream 42 in the presence of shift catalyst 54 at a temperature ranging from 190°C to 300°C and a pressure ranging from 2 to 50 atmospheres (0.2 to 5 MPa) to form carbon dioxide and hydrogen in the second process stream 52. Shift catalyst 54 may comprise copper. Suitable catalysts may be readily selected by one skilled in the art. This additional process step, if included, would be conducted prior to the step of scrubbing the second process stream 52.

[0069] This sequence of two shift reaction steps may be a high temperature shift followed by a low temperature shift. The high temperature shift is conducted using an iron-based shift catalyst at a temperature ranging from 310°C to 500°C or 310° to 400°C. The low temperature shift is conducted using a shift catalyst comprising copper and optionally zinc oxide at a temperature ranging from 190°C to 300°C.

[0070] As used herein, the "second process stream" includes the stream comprising carbon dioxide, hydrogen, carbon monoxide and methane from the exit of the upstream shift reactor to the exit of the scrubber where a portion becomes the "carbon dioxide-depleted stream."

EXAMPLES

[0071] The present invention will be better understood with reference to the following examples, which are intended to illustrate, but not to limit the scope of the invention; the invention being defined by the claims.

[0072] All of the following examples were simulated using Aspen Plus®. The results are normalized for an output of hydrogen product from the hydrogen production process of 100,000 Nm^3/h. The output of hydrogen product is the total hydrogen produced less any amount used for combustion in the reformer. The scrubbers 60 and 260 are assumed to be 100% effective in the removal of CO_2. Water is also removed in the scrubber.

[0073] The composition of the by-product gas 76, 276 is based on a pressure swing adsorber. A prereformer was not used in any of the examples.

[0074] Natural gas was assumed to be 98 mole % CH_4 and 2 mole % N_2.

Example 1

[0075] FIG. 4 illustrates a process flow diagram for a prior art hydrogen production process. A high temperature shift reactor 240 is used. Fuel for the reformer is provided by the by-product gas 276 and natural gas trim fuel. No hydrogen is used as fuel and none of the by-product gas is recycled back to the process stream. Results are summarized in Table 1.

[0076] CO_2 emissions of 16,167 Nm^3/h were calculated for a hydrogen product output of 100,000 Nm^3/h. Flue gas CO_2 is about 40% of the CH_4 feed. The balance of 60% is removed in the scrubber 260. For ease of comparison with other cases, the molar ratio of CO_2 emissions to the hydrogen product output (100 000 Nm^3/h) is shown in Table 1. The CO_2 /H_2 molar ratio for this base case is 0.162.

TABLE 1

Stream	No Recycle
H_2-containing product gas used as fuel (Nm^3/h)	0
CO_2 in flue gas (Nm^3/h)	16 167
By-product gas recycled (Nm^3/h)	0
By-product gas used as fuel (Nm^3/h)	28 957
Reformer duty (kW)	106 658
CO_2 /H_2	0.162
Mole fraction N_2 in recycle	0.027
CH_4 feed (Nm^3/h)	40 499

Example 2

[0077] Example 2 is based on the process flow diagram shown in FIG. 1. Fuel to fire the reformer 100 is provided by by-product gas 76 and hydrogen-containing product gas 72. The amount of by-product gas and hydrogen-containing gas depends on the amount of by-product gas recycled to the process stream. No natural gas trim fuel is used. A high temperature shift reactor 40 is used. Several cases are summarized in Table 2 representing various amounts of recycling of the by-product gas 76 back to the process stream 10 upstream of the plurality of catalyst-containing reformer tubes 104.

[0078] Table 2 shows the effect of by-product recycle on the molar ratio of CO_2 emissions to the hydrogen product output. With 98% of the by-product gas recycled, the CO_2/H_2 molar ratio is reduced to 0.013 compared to 0.162 for Example 1.

[0079] For this case, small amounts of by-product gas recycle do not appear to improve the molar ratio of CO_2 emissions to the hydrogen product output very much. However, with higher levels of by-product gas recycle and using hydrogen as the trim fuel, the CO_2 emissions can be reduced by an order of magnitude.

[0080] With 98% by-product gas recycle, the N_2 content of the recycle gas is 34 mole %. This represents a large amount of N_2 circulating in the process loop, and the compression power for the system will be increased as a result. The reformer duty also increases with the amount of recycle flow. With additional capital, this stream may be heat exchanged to create steam which will be produced with low CO_2 emissions. This is in contrast to fired boilers, which generate substantial CO_2 emissions.

TABLE 2

Stream	No Recycle	50% by-product gas recycle	90% by-product gas recycle	98% by-product gas recycle
H_2-containing product gas used as fuel (Nm^3/h)	6466	25815	65 108	88298
CO_2 in flue gas (Nm^3/h)	15 081	12000	5 112	1 302
By-product gas recycled (Nm^3/h)	0	21 573	74842	136406
By-product gas used as fuel (Nm^3/h)	30661	21 571	8 315	2 784
Reformer duty (kW)	113 451	126 056	158 178	182 204
CO_2 /H_2	0.151	0.120	0.051	0.013
Mole fraction N_2 in recycle	0.027	0.039	0.109	0.343
CH_4 feed (Nm^3/h)	40499	42 187	45353	47883

Example 3

[0081] Example 3 is based on the process flow diagram shown in FIG. 1 and is similar to example 2, except that a low temperature shift reactor is used along with the high temperature shift reactor. All of the trim fuel is provided by hydrogen-containing product gas.

[0082] Results are summarized in Table 3 for various amounts of recycling of the by-product gas back to the process stream upstream of the plurality of catalyst-containing reformer tubes 104.

TABLE 3

Stream	No Recycle	50% by-product gas recycle	90% by-product gas recycle	98% by-product gas recycle
H_2-containing product gas used as fuel (Nm^3/h)	11 752	32 128	68 683	86 388
CO_2 in flue gas (Nm^3/h)	10 322	7 901	2 844	605
By-product gas recycled (Nm^3/h)	0	17 913	54807	101 108
By-product gas used as fuel (Nm^3/h)	26635	17 913	6 090	2 063

(continued)

Stream	No Recycle	50% by-product gas recycle	90% by-product gas recycle	98% by-product gas recycle
Reformer duty (kW)	114 489	128316	157 495	175 840
CO_2/H_2	0.103	0.079	0.028	0.006
Mole fraction N_2 in recycle	0.031	0.048	0.148	0.455
CH_4 feed (Nm^3/h)	41 314	42 561	45 200	47 055

[0083] The results show that use of a low temperature shift reactor is effective for reducing the amount of CO_2 emissions. Compared to example 2, the CO_2 emissions are lower for each respective amount of by-product gas recycle.

[0084] Table 3 shows the effect of by-product recycle on the molar ratio of CO_2 emissions to the hydrogen product output. With 98% of the by-product gas recycled, the CO_2/H_2 molar ratio is reduced to 0.006, which is substantially lower than example 1 where the CO_2/H_2 molar ratio was 0.162.

[0085] In general, there is greater CO_2 recovery, less CO_2 emissions, lower reformer duty and smaller volumes of recycled gas compared to respective by-product gas recycle percentages in Example 2.

Example 4

[0086] Example 4 is based on the process flow diagram shown in FIG. 2 and is similar to Example 3, except that an oxygen secondary reformer is used. The oxygen for the oxygen secondary reformer 20 is assumed to by 99 vol. % O_2 and 1 vol. % Ar. All of the trim fuel is provided by hydrogen-containing product gas.

[0087] Results are summarized in Table 4 for various amounts of recycling of the by-product gas back to the process stream upstream of the plurality of catalyst-containing reformer tubes 104.

[0088] Table 4 shows the effect of by-product recycle on the molar ratio of CO_2 emissions to the hydrogen product output. With 98% of the by-product gas recycled, the CO_2/H_2 molar ratio is reduced to 0.0003, which is substantially lower than example 1 where the CO_2/H_2 molar ratio was 0.162.

[0089] With the oxygen secondary reformer, the methane slip is very low and even without a recycle stream, the CO_2 emission is nearly as low as in Example 2 with 98% by-product gas recycle.

[0090] This configuration has low reformer duty and low methane feed requirements, but has an oxygen requirement.

[0091] In general, there is greater CO_2 recovery, less CO_2 emissions, lower reformer duty and smaller volumes of recycled gas compared to respective by-product gas recycle percentages in Examples 2 and 3.

TABLE 4

Stream	No Recycle	50% by-product gas recycle	90% by-product gas recycle	98% by-product gas recycle
H2-containing product gas used as fuel (Nm^3/h)	23 200	31 441	39 960	47 078
CO_2 in flue gas (Nm^3/h)	1 524	832	176	32
By-product gas recycled (Nm^3/h)	0	10921	28 101	72796
By-product gas used as fuel (Nm^3/h)	19 557	10922	3 123	1 485

(continued)

Stream	No Recycle	50% by-product gas recycle	90% by-product gas recycle	98% by-product gas recycle
Reformer duty (kW)	84338	82812	83439	94070
CO_2 /H_2	0.015	0.008	0.002	0.0003
Mole fraction N_2 in recycle	0.043	0.078	0.274	0.597
Mole fraction Ar in recycle	0.007	0.013	0.048	0.106
O_2 requirement (Nm^3/h)	13 261	14 118	14 984	15 702
CH_4 feed (Nm^3/h)	42 166	42 366	42 838	44 518

Example 5

[0092] Example 5 is based on the process flow diagram shown in FIG. 3 and is similar to Example 4, except that the by-product gas is recycled to the oxygen secondary reformer instead recycling to the primary reformer 100. The oxygen for the oxygen secondary reformer 20 is assumed to by 99 vol. % O_2 and 1 vol. % Ar. All of the trim fuel is provided by hydrogen-containing product gas.

[0093] Results are summarized in Table 5 for various amounts of recycling of the by-product gas back to the process stream downstream of the plurality of catalyst-containing reformer tubes 104 and upstream of the oxygen secondary reformer 20.

[0094] Table 5 shows the effect of by-product recycle on the molar ratio of CO_2 emissions to the hydrogen product output. With 98% of the by-product gas 76 recycled, the CO_2/H_2 molar ratio is reduced to 0.0003, which is substantially lower than Example 1 where the CO_2/H_2 molar ratio was 0.162. The results are not much different than that of Example 4, except that the oxygen requirement is higher and the natural gas feed is higher. With proper integration of a heat exchanger, more steam may be generated. This steam will be produced with very low CO_2 emissions compared to a fired boiler.

[0095] With the oxygen secondary reformer, the methane slip is very low and even without a recycle stream, the CO_2 emission is nearly as low as in Example 2 with 98% by-product gas recycle.

[0096] In general, there is greater CO_2 recovery, less CO_2 emissions, lower reformer duty and smaller volumes of recycled gas compared to respective by-product gas recycle percentages in Examples 2 and 3.

TABLE 5

Stream	No Recycle	50% by-product gas recycle	90% by-product gas recycle	98% by-product gas recycle
H_2-containing product gas used as fuel (Nm^3/h)	23200	32779	42082	46471
CO_2 in flue gas (Nm^3/h)	1 524	838	173	27
By-product gas recycled (Nm^3/h)	0	11 031	28611	76310
By-product gas used as fuel (Nm^3/h)	19 557	11 032	3 179	1 557

(continued)

Stream	No Recycle	50% by-product gas recycle	90% by-product gas recycle	98% by-product gas recycle
Reformer duty (kW)	84338	85669	87695	92817
CO_2 /H_2	0.015	0.008	0.002	0.0003
Mole fraction N_2 in recycle	0.043	0.078	0.276	0.593
Mole fraction Ar in recycle	0.007	0.013	0.05	0.127
O_2 requirement (Nm^3/h)	13 261	14 333	15 935	19 805
CH_4 feed (Nm^3/h)	42 166	42 832	43 845	46 406

[0097] Although the present invention has been described as to specific embodiments or examples, it is not limited thereto, but may be changed or modified into any of various other forms without departing from the scope of the invention as defined in the accompanying claims.

Claims

1. A process for producing a hydrogen-containing product gas (72), comprising:

   (a) introducing a process stream (10) comprising steam and at least one hydrocarbon selected from the group consisting of methane, ethane, propane, butane, pentane, and hexane into a plurality of catalyst-containing reformer tubes (104) in a reformer furnace (100) and reacting the process stream inside the plurality of catalyst-containing reformer tubes (104) at a first temperature ranging from 700°C to 1000°C and a first pressure ranging from 0.2 to 5 MPa (2 to 50 atmospheres) to form a reformate stream (12) comprising hydrogen, carbon monoxide, methane and steam and withdrawing the reformate stream (12) from the plurality of catalyst-containing reformer tubes (104);
   (b) reacting the reformate stream (12, 32) in the presence of a shift catalyst (44) at a second temperature ranging from 190°C to 500°C and a second pressure ranging from 0.2 to 5 MPa (2 to 50 atmospheres) to form a second process stream (42) comprising carbon dioxide, hydrogen, carbon monoxide and methane;
   (c) scrubbing the second process stream (42) with a wash stream (64) to form a carbon dioxide-depleted stream (62) and a carbon dioxide-loaded wash stream (66);
   (d) separating the carbon dioxide-depleted stream (62) to form the hydrogen-containing product gas (72) and a by-product gas (76) comprising methane and carbon monoxide;
   (e) introducing a portion of the by-product gas (76) into the process stream (10, 14) at a location upstream of the plurality of catalyst-containing reformer tubes (104) and/or into the reformate stream (12) at a location upstream of a reforming catalyst (24) in a secondary reforming reactor (20); and
   (f) combusting a fuel gas (74) comprising a portion of the hydrogen-containing product gas (72), optionally a portion (77) of the by-product gas (76), and optionally a supplementary fuel (18) in the reformer furnace (100) external to the plurality of catalyst-containing reformer tubes (104) to supply energy for reacting the process stream inside the plurality of catalyst-containing reformer tubes (104), and withdrawing a flue gas (110) from the reformer furnace (100).

2. The process of claim 1 wherein 50% to 98% by volume of the by-product gas (76) formed in step (d) is introduced into the process stream (10, 14) in step (e).

3. The process of claim 1 or claim 2 further comprising:

reacting the process stream (14) in the presence of a second reforming catalyst (84) in an unfired reactor (80) at a third temperature ranging from 425°C to 600°C and a third pressure ranging from 0.2 to 5 MPa (2 to 50 atmospheres) to form carbon dioxide and hydrogen in the process stream (10, 14) prior to introducing the process stream (10) into the plurality of catalyst containing reformer tubes (104).

4. The process of claim 3 wherein the portion of the by-product gas (76) is introduced into the process stream (14) upstream of the unfired reactor (80).

5. The process of any one of claims 1-4 further comprising:

introducing an oxygen-rich gas (26) into the reformate stream (12) after withdrawing the reformate stream (12) from the plurality of catalyst-containing reformer tubes (104) to partially oxidize the reformate stream; and
reacting the partially oxidized reformate stream (12) in the presence of the reforming catalyst (24) in the secondary reforming reactor (20) under reaction conditions sufficient to form reaction products comprising carbon monoxide and hydrogen in the reformate stream (22) before reacting the reformate stream (32) in the presence of the shift catalyst (44).

6. The process of any one of claims 1-4 further comprising:

introducing a feed gas (28) comprising at least one hydrocarbon and optionally steam into the reformate stream (12) after withdrawing the reformate stream (12) from the plurality of catalyst-containing reformer tubes (104), the at least one hydrocarbon selected from the group consisting of methane, ethane, propane, butane, pentane, and hexane;
introducing an oxygen-rich gas (26) into the reformate stream (12) after withdrawing the reformate stream (12) from the plurality of catalyst-containing reformer tubes (104) to partially oxidize the reformate stream (12); and
reacting the partially oxidized reformate stream (12) in the presence of the reforming catalyst (24) in the secondary reforming reactor (20) under reaction conditions sufficient to form reaction products comprising carbon monoxide and hydrogen in the reformate stream (12) before reacting carbon monoxide and steam in the reformate stream (32) in the presence of the shift catalyst (44).

7. The process of claim 5 or 6wherein the portion of the by-product gas (76) is introduced into the reformate stream (12) at the location upstream of the secondary reforming reactor (20).

8. The process of any one of claims 1-7 wherein the shift catalyst (44) comprises iron oxide and the second temperature ranges from 310°C to 500°C.

9. The process of any one of claims 1-7 wherein the shift catalyst (44) comprises iron oxide and the second temperature ranges from 310 to 400°C.

10. The process of any one of claims 1-7 wherein the shift catalyst (44) comprises copper and the second temperature ranges from 200°C to 400°C.

11. The process of any one of claims 1-7 wherein the shift catalyst (44) comprises copper and the second temperature ranges from 200 to 350°C.

12. The process of claim 8 or 9, further comprising:

reacting the second process stream (42) in the presence of a second shift catalyst (54) at a fourth temperature ranging from 190°C to 300°C and a fourth pressure ranging from 0.2 to 5 MPa (2 to 50 atmospheres) to form carbon dioxide and hydrogen in the second process stream (52) prior to the step of scrubbing the second process stream (52).

13. The process of claim 12 wherein the second shift catalyst (54) comprises copper.

14. The process of any one of claims 1-13 wherein the fuel gas (74) comprises 30 volume % to 98 volume % hydrogen-containing product gas (72) and 2 volume % to 70 volume % by-product gas (76).

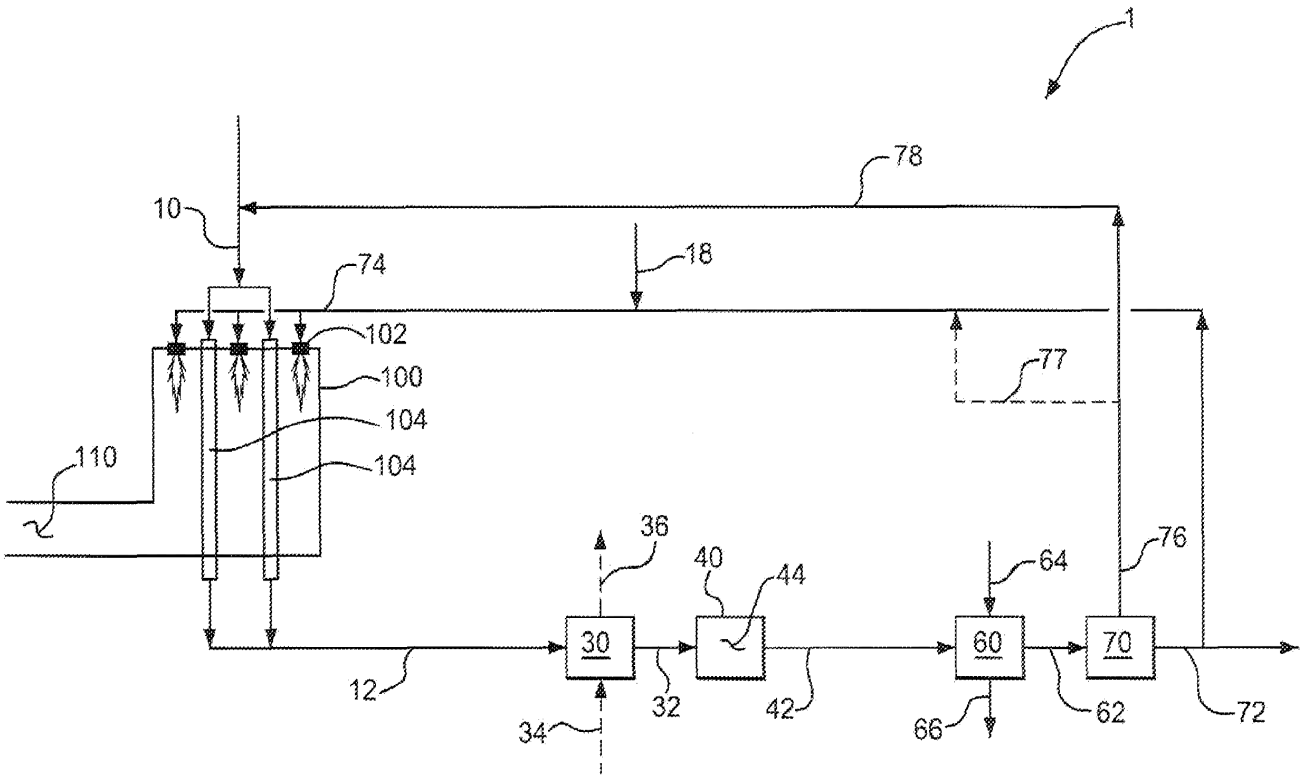

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FIG. 1

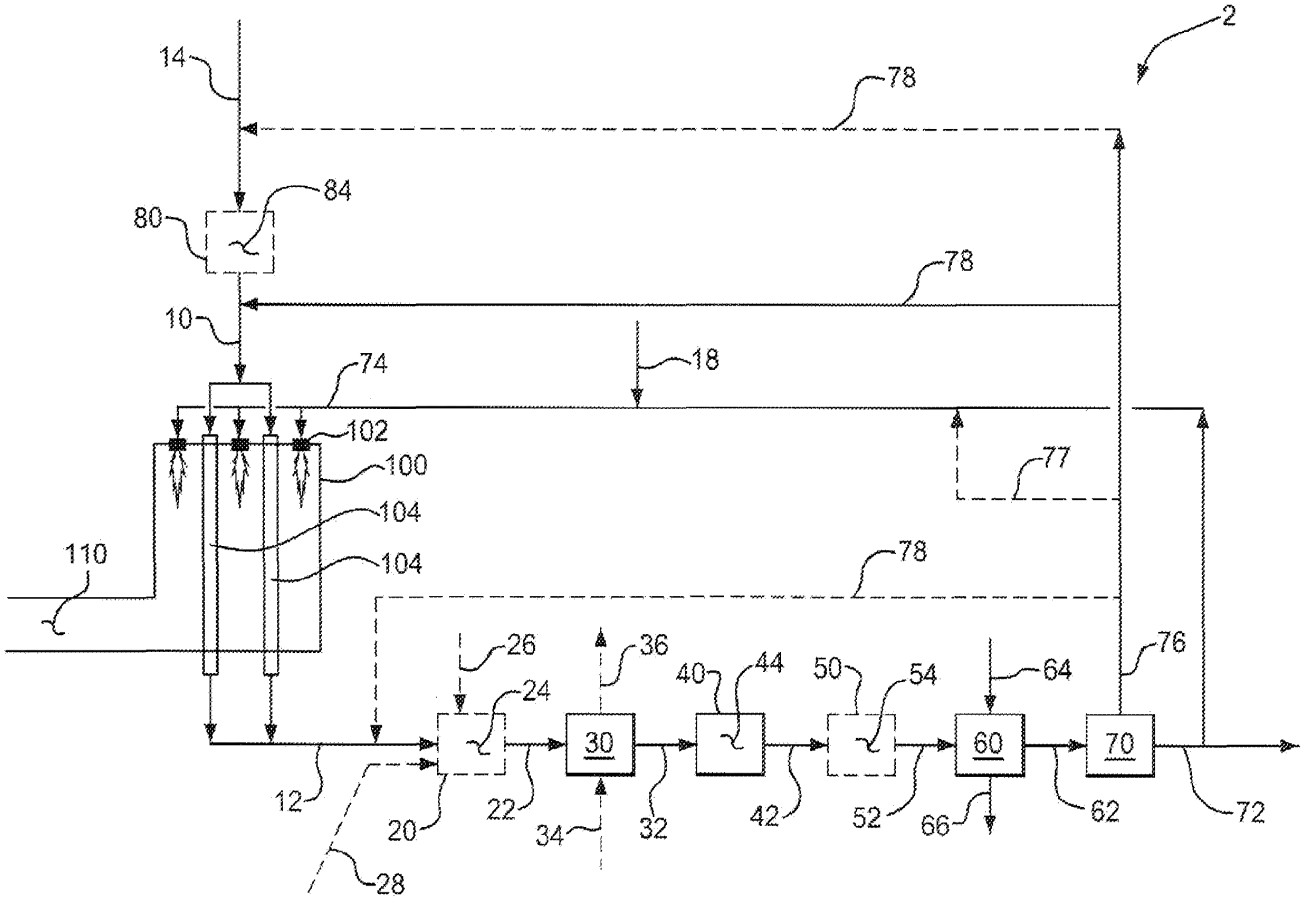

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FIG. 2

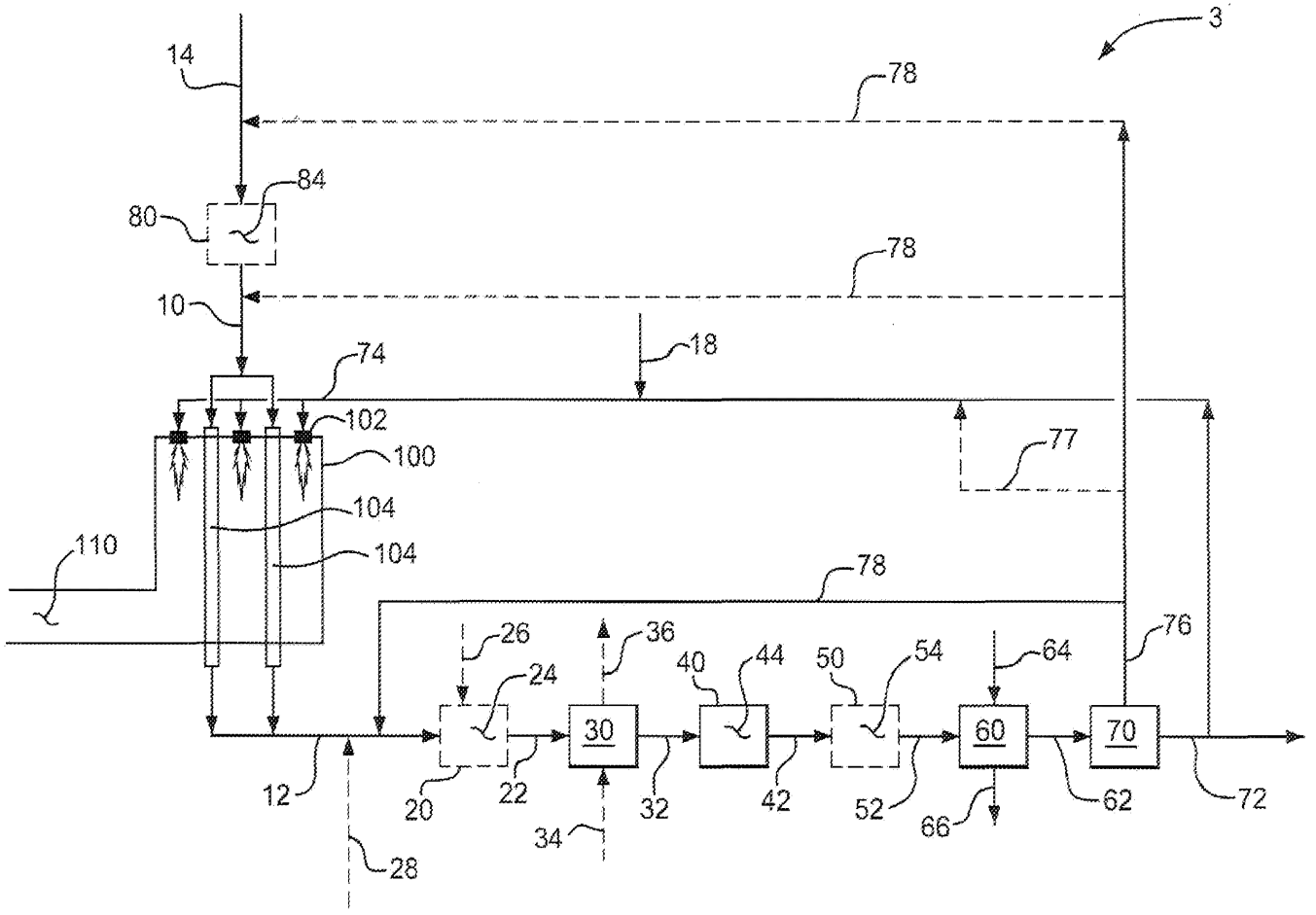

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FIG. 3

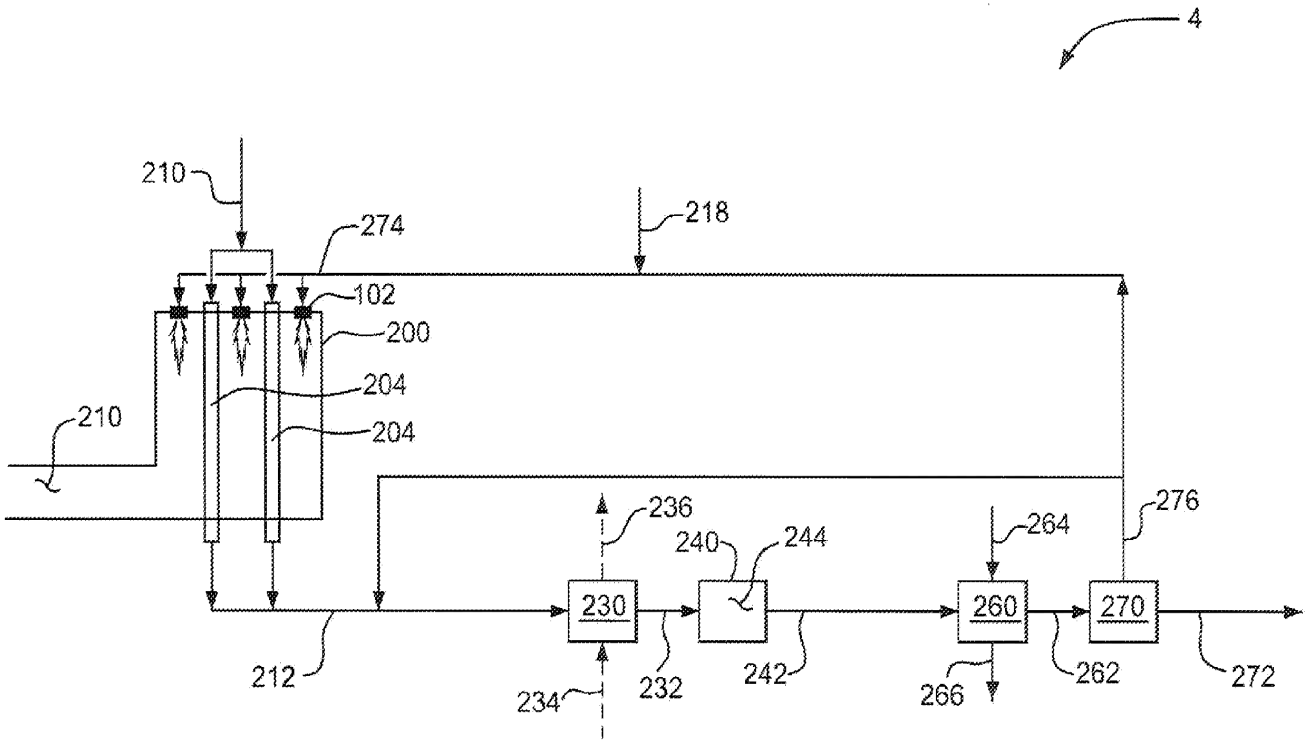


FIG. 4
Prior Art

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EUROPEAN SEARCH REPORT

Application Number
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The present search report has been drawn up for all claims

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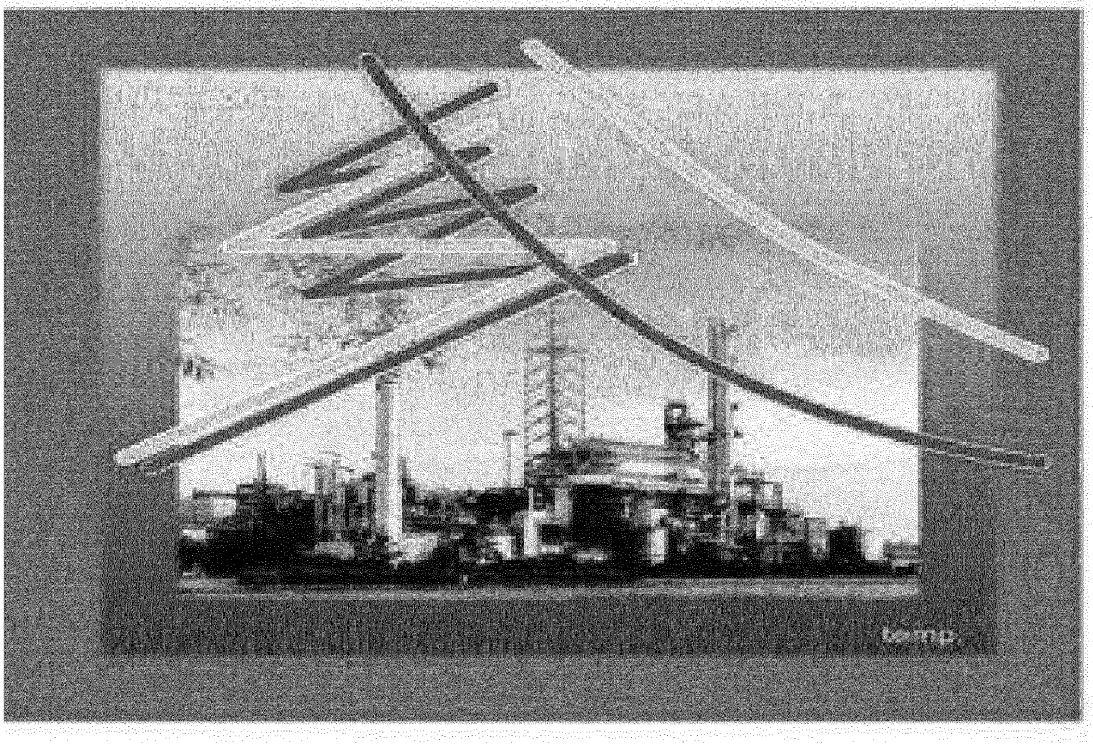
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Preface

The Ullmann's Encyclopedia of Industrial Chemistry is now available on CD Rom and I had the privilege of up-dating and revising the article of ammonia. When reviewing the new ammonia version the publisher WILEY-VCH came up with the idea of using it as a basis for a printed book and extending the subject to the whole ammonia production technology in theory and practice. Consequently, synthesis gas production and purification could be treated in more detail and quite a number of newer publications have been included. For economic aspects of the worldwide ammonia production the newest available data have been used. The extensive bibliography will assist readers in pursuing the subject more intensively but it is of course, not possible to list the enormous number of publications on ammonia exhaustively. Research and technology development are still going on and even with a rather low probability of fundamental technology changes small but economically interesting improvements are still happening.

I would like to thank WILEY-VCH, especially Dr. Th. Kellersohn, for making the publication of this book possible. In particular I should express my thanks to Mrs. Karin Sora and Ms. Ulrike Winter for their exellent editorial work. I am also very much indebted to the authors of the old Ullmann article of 1985, H. Bakemeier, Th. Huberich, R. Krabetz, W. Liebe, M. Schunk, D. Mayer, C. L. Becker. Many thanks for valuable information material and exchange of experience go to all friends and collegues in the industry and the supporting companies which supply it: process licensors, catalyst manufacturers, equipment fabricators, and especially the engineering companies. Additionally, I should mention Alexander More, John French and Bernard Brentnall of British Sulphur who provide a wonderful and continuous documentation of the progress and development in ammonia technology and business through the *Nitrogen* magazine and the regular *Nitrogen Conferences* in Europe, Asia and South America. Especially, I would like to acknowledge the important contribution of the Ammonia Safety Committee of the American Institute of Chemical Engineers and its annual symposium, which provided so much interesting information on technology developments and experience, contributing greatly to the progress of the ammonia industry.

January 1999 Max Appl

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1. Introduction

The name ammonia for the nitrogen–hydrogen compound NH_3 is derived from the oasis Ammon (today Siwa) in Egypt, where Ammonia salts were already known in ancient times and also the Arabs were aware of ammonium carbonate. For a long time only the "sal ammoniacum" was available. Free ammonia was prepared much later (PRIESTLEY, 1774).

In nature ammonia, NH_3 occurs almost exclusively in the form of ammonium salts. Natural formation of ammonia is primarily by decomposition of nitrogen-containing organic materials or through volcanic activity. Ammonium chloride can deposite at the edges of smoldering, exposed coal beds (already observed in Persia before 900 A. D.). Similar deposits can be found at volcanoes, for example, Vesuvius and Etna in Italy. Ammonia and its oxidation products, which combine to form ammonium nitrate and nitrite, are produced from nitrogen and water vapor by electrical discharges in the atmosphere. These ammonium salts supply a significant proportion of the nitrogen needed by growing plants when eventually deposited on the earth's surface. Ammonia and its salts are also byproducts of commercial processing (gasification, coking) of fuels such as coal, lignite and peat (see Fig. 1) Other sources of nitrogen compounds are exhausts from industrial, power-generation, and automotive sectors.

Following the discovery of the nature and value of mineral fertilization by LIEBIG in 1840, nitrogen compounds were used in increasing quantities as an ingredient of mineral fertilizers. At the end of the last century ammonia was recovered in coke oven plants and gas works as a byproduct of the destructive distillation of coal. The produced ammonium sulfate was used as fertilizer. Since these sources of nitrogen were limited in quantity they did not suffice for fertilization. Therefore, it was necessary to use saltpeter from natural deposits in Chile. The earliest source of synthetic nitrogen compunds as fertilizers was the Frank–Caro calcium cyanamide process from 1898 onwards. But the supply was far from sufficient and scientists were concerned with the possibility of future famine because of insufficient agricultural yields. In September

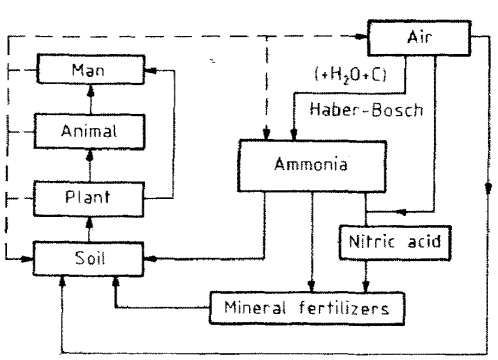


Figure 1. The nitrogen cycle

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1898, in his famous presidential speech to the British Association of Advanced Science, SIR WILLIAM CROOKS adressed the problem and concluded with the prophetic words: "It is the chemist who must come to the rescue of the threatened communities. It is through the laboratory that starvation may ultimately be turned into plenty. Before we are in the grip of actual dearth the chemist will step in and postpone the days of famine to so distant a period that we, our sons and grandsons may live without undue solicitude for the future."

The development of the synthesis of ammonia from its elements is therefore a landmark in the history of industrial chemistry. But this process did not only solve a fundamental problem in securing our food supply by economic production of fertilizers in quantity but also opened a new phase of industrial chemistry by laying the foundations for subsequent high-pressure processes like methanol synthesis, oxo synthesis, Fischer–Tropsch process, coal liquefaction, and Reppe reactions. The technical experience and process know-how gained thereby had an enormous influence on the further development of chemical engineering, metallurgy, process control, fabrication and design of reactors, apparatus, and of course on the theory and practice of heterogeneous catalysis.

Process technology and chemical engineering as we understand it today began with the successful realization of the technical ammonia synthesis. Continuous production with high space velocities and space yields combined with the ammonia oxidation process developed immediately thereafter enabled chemical industry for the first time to compete successfully with a cheap natural bulk product, namely, sodium nitrate from Chile. The synthesis of ammonia thus became exemplary for all subsequent chemical mass production processes.

The development of the ammonia production process was also beginning of systematic catalytic research and widespread use of catalysts in industrial chemistry. Many subsequent achievments in theoretical understanding and practical application of heterogeneous catalysis have their roots in the ammonia synthesis reaction with probably can be considered to be the best understood catalytic process, as demonstrated by the enormous number of publications.

Today ammonia is the second largest synthetic chemical product; more than 90% of world consumption is manufactured from the elements nitrogen and hydrogen in a catalytic process originally developed by FRITZ HABER and CARL BOSCH using a promoted iron catalyst discovered by ALWIN MITTASCH. Since the early days there has been no fundamental change in this process. Even today the synthesis section of every ammonia plant has the same basic configuration as the first plants. A hydrogen–nitrogen mixture reacts over the iron catalyst (today's formulation differs little from the original) at elevated temperature in the range of 400–500 °C (originally up to 600 °C) and pressures above 100 bar with recycle of the unconverted part of the synthesis gas and separation of the ammonia product under high pressure.

BOSCH was already well aware that the production of a pure hydrogen–nitrogen mixture is largest single contributor to the total production cost of ammonia [1]. So, in contrast to the synthesis reaction, dramatic changes happened over the years in the

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technology of synthesis-gas generation, and industrial ammonia processes differ today mainly with respect to synthesis-gas preparation and purification. The elements nitrogen and hydrogen are abundantly available in the form of air and water, from which they can be separated by physical methods and/or chemical reactions using almost exclusively fossil energy. The predominant fossil fuels are natural gas, liquified petroleum gas (LPG), naphtha, and higher petroleum fractions; coal or coke is used today only under special economic and geographical conditions (China, India, South Africa). Recovery of ammonia as byproduct of other production processes, e.g., coke ovens, is no longer of great importance.

Of course, some of the hydrogen comes also from the hydrocarbons themselves (methane has the highest content), and the carbon acts as a reducing agent for water and in some processes may also facilitate the separation of oxygen from nitrogen by formation of carbon dioxide, which can be removed by various operations.

As the ammonia sythesis is the very heart of every ammonia production and is also from a historical point of view the most interesting section it seems to be justified to discuss the fundamentals and the catalysis of this reaction separately and at first.

After this the various techniques used in the individual process steps of industrial ammonia production will be reviewed: gas generation and feedstock pretreatment, carbon monoxide shift conversion, gas purification, compression, and ammonium synthesis. Next the concept and philosophy of integrated single–train ammonia plants will be presented, followed by a review of the commercial processes presently marketed by the various licensors and engineering contractors and of some options for modernization of older plants. Separate chapters are included for the following subjects: integration of other production processes; material considerations for equipment fabrication; handling, storage and transport of ammonia; quality specifications and analysis; environmental, safety and health aspects; chemical reactions and uses; economic aspects; future prospects.

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2. Historical Development

The driving force in the search for methods of nitrogen fixation, of course, was to produce fertilizers. In principle there are three ways of breaking the bond of the nitrogen molecule and fixing the element in a compound:

1) To combine the atmospheric elements nitrogen and oxygen directly to form nitric oxides
2) To combine nitrogen and hydrogen to give ammonia
3) To use compounds capable of fixing nitrogen in their structure under certain reaction conditions.

A vast amount of research in all three directions led to commercial processes for each of them: the electric arc process, the cyanamid process, and ammonia synthesis, which finally displaced the other two and rendered them obsolete.

The availability of cheap hydrolelectric power in Norway and the United States stimulated the development of the *electric arc process*. Air was passed through an electric arc which raised its temperature to 3000 °C, where nitrogen and oxygen combine to give nitric oxide. In 1904 CHRISTIAN BIRKELAND performed successful experiments and, together with SAM EYDE, an industrial process was developed and a commercial plant was built, which by 1908 was already producing 7000 t of fixed nitrogen. Working in parallel, SCHOENHERR at BASF developed a different electric arc furnace in 1905. The Norwegeans and BASF combined forces in 1912 to build a new commercial plant in Norway. However, since at this time pilot-plant operation of ammonia synthesis was already successful, BASF withdrew from this joint venture soon after. Nevertheless, the Norwegian plants operated throughout World War I and had total production of 28 000 t/a of fixed nitrogen with a power consumption of 210 000 kW [2]. The specific energy consumption was tremendous: 60 000 kW per tonne of fixed nitrogen. Had this electricity been generated from fossil fuels this figure would correspond to about 600 GJ/t nitrogen, which is about 17 times the consumption of an advanced steam-reforming ammonia plant in 1996.

The cyanamide process, [2]–[5], developed by FRANK and CARO in 1898, was commercially established by 1910. Calcium carbide, formed from coke and lime in a carbide furnace [6], reacts with nitrogen to give calcium cyanamide, which can be decomposed with water to yield ammonia. The process was energetically very inefficient, consuming 190 GJ per tonne of ammonia. Some other routes via barium cyanide produced from barytes, coke and nitrogen, or using the formation of titanium nitride were investigated in Ludwigshafen by BOSCH and MITTASCH but did not appear promising. In 1934, 11% of world's fixed nitrogen production (about 2×10^6 t/a) [7] was still based on the cyanamid process, and some plants even continued to operate after World War II.

After Berthollet proved in 1784 that ammonia consists of nitrogen and hydrogen and was also able to establish the approximate ratio between these elements, many

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experiments in the 1800s were aimed at its *direct synthesis*, but remained unsuccessful [8] – [10]. One of the reasons for the lack of success was the limited knowledge of thermodynamics and the incomplete understanding of the law of mass action and chemical equilibrium. It was the new science of physical chemistry, which developed rapidly in the late 1800s, that enabled chemists to investigate ammonia formation more systematically.

Around 1900 FRITZ HABER began to investigate the ammonia equilibrium [11] at atmospheric pressure and found minimal ammonia concentrations at around 1000 °C (0.012 %). Apart from HABER, OSTWALD and NERNST were also closely involved in the ammonia synthesis problem, but a series of mistakes and misunderstandings occurred during the research. For example, OSTWALD withdrew a patent application for an iron ammonia synthesis catalyst because of an erroneous experiment, while NERNST concluded that commercial ammonia synthesis was not feasible in view of the low conversion he found when he first measured the equilibrium at 50 – 70 bar [12] – [14].

After a controversy with NERNST, HABER repeated his measurements at atmospheric pressure and subsequently at higher pressures [15] – [18], overcoming his colleague's preoccupation with the unfavorable equilibrium concentrations. HABER concluded that much higher pressures had to be employed and that, perhaps more importantly, a recycle process was necessary.

The amount of ammonia formed in a single pass of the synthesis gas over the catalyst is much too small to be of interest for an economic production. HABER therefore recycled the unconverted synthesis gas. After separating the ammonia by condensation under synthesis pressure and supplementing with fresh synthesis gas to make up for the portion converted to ammonia, the gas was recirculated by means of a circulation compressor to the catalyst-containing reactor. This process, described in the patent DRP 235 421 (1908), became the basis for the industrial manufacture of ammonia and since then the same principle has found widespread application in numerous high-pressure processes. HABER also anticipated the preheating of the synthesis gas to reaction temperature (at that time 600 °C) by heat exchange with the hot exhaust gas from the reactor, the temperature of which would be raised by the exothermic ammonia formation reaction sufficiently (about 18 °C temperature rise for a 1 % increase of the ammonia concentration in converted synthesis gas).

HABER's recycle idea changed the static conception of process engineering in favor of a more dynamic approach. For the first time reaction kinetics were considered as well as the thermodynamics of the system. In addition to the chemical equilibrium, HABER recognized that for industrial realization, reaction rate was a determining factor. Instead of simple yield in a once-through process, which was the usual focus of chemists at that time, he concentrated on space – time yield. Figure 2 illustrates this consideration of equilibrium concentration in combination with space – time yield by comparing ammonia synthesis as a recycle process with the SO_2 oxidation process as a once-through operation.

In 1908 HABER approached BASF (Badische Anilin & Soda Fabrik at that time) to seek support for his work and to discuss the possibilities for the realization of an

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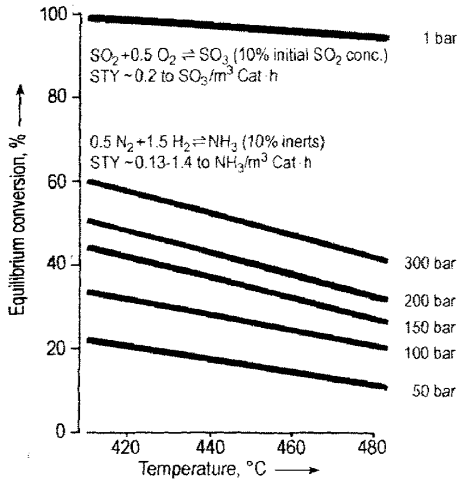


Figure 2. Equilibrium conversion and space time yield for NH_3 and SO_3 production

industrial process. His successful demonstration in April 1909 of a small laboratory scale ammonia plant having all the features described above finally convinced the BASF representatives, and the company's board decided to pursue the technical development of the process with all available resources. In an unprecedented achievement, CARL BOSCH, together with a team of dedicated and highly skilled co-workers, succeeded in developing a commercial process in less than five years [1], [19]–[25]. The first plant started production at Oppau in September 1913 and had a daily capacity of 30 t of ammonia. Expansions increased the capacity to about 250 t/d in 1916/17 and a second plant with a capacity of 36 000 t/a went on stream in 1917 in Leuna. Further stepwise expansions, finally reaching 240 000 t/a, already decided in 1916, came in full production only after World War I [3]. After World War I ammonia plants were built in England, France, Italy and many other countries based on a BASF license or own process developments, with modified process parameters, but using the same catalyst. Figure 3 shows with the example of the BASF plant what the plants looked like in these years. Synthesis gas production was performed from coke by using water gas generators and producer gas generators in parallel. Coal (e.g., lignite) was gasified in Leuna in the subsequently introduced Winkler generators, the first example of fluidized-bed technology. Progress in cryogenic air separation plants with respect to reliability and capacity made it possible to switch the gasification processes from air to oxygen as time went on. Shift conversion was already performed on iron oxide chromium oxide catalysts, water scrubbing was used for CO_2 removal, and residual CO was removed by a copper liquid wash. Gasification, desulfurization, and shift conversion were at normal pressure, CO_2 removal at 25 bar, and copper liquid wash and synthesis at 300 bar. Ammonia was removed from the loop by condensation (from early 1920 onwards; before that by water scrubbing as aqueous ammonia).

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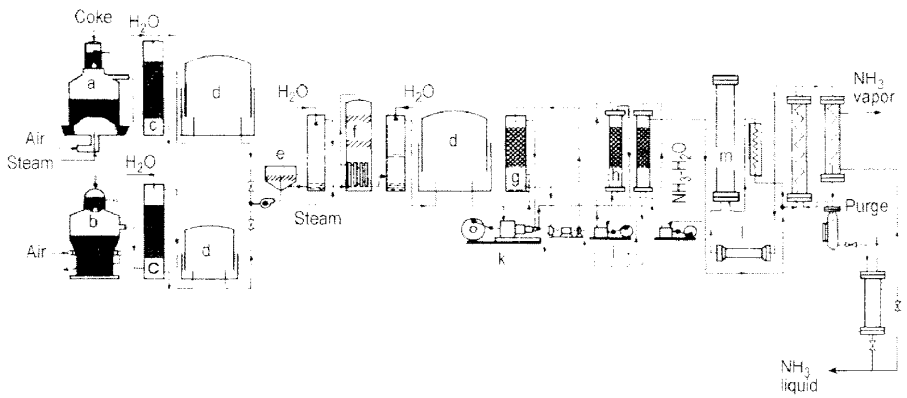


Figure 3. Simplified flow sheet of a coke-based ammonia plant in the 1930s
a) Watergas generator, b) Producer gas generation, c) Scrubber, d) Gas holders, e) Sulfur removal, f) Shift converter g) CO_2 removal, h) CO removal (Co-liq.), i) Copper liq. regeneration, k) Syngas compressor, l) Circulation pump, m) Ammonia converter

Up to the end of World War II, plant capacities were expanded by installing parallel lines of 70 – 120 t/d units, and synthesis-gas generation continued to be based on coal until the 1950s, of course, with improved and now continuously operating designs, as for example the so-called "Abstichgenerator" of BASF [26]. With growing availability of cheap petrochemical feedstocks and novel cost-saving gasification processes (steam reforming and partial oxidation) a new age dawned in the ammonia industry. The development started in the USA, where steam reforming of natural gas was used for synthesis gas production. This process was originally developed by BASF and greatly improved by ICI, who extended it to naphtha feedstocks. Before natural gas became available in large quantities in Europe, partial oxidation of heavy oil fractions was used in several plants. The next revolution in the ammonia industry was the advent of the single-train steam reforming ammonia plants, pioneered by M. W. KELLOGG and others. The design philosophy was to use a single-train for large capacities (no parallel lines) and to be as far as possible energetically self-sufficient (no energy import) by having a high degree of energy integration (process steps in surplus supplying those in deficit). Only through this innovative plant concept with its drastic reduction in feedstock consumption and investment costs, could the enormous increase in world capacity in the following years became possible. Increasing competition and rising feedstock prices in the 1970s and 1980s forced industry and engineering companies to improve the processes further.

The LCA process of ICI (Section 5.1.4.3.) and the KRES/KAAP process (Section 5.1.4.3.), which is the first process since 1913 to use a non-iron synthesis catalyst, are recent advances that make a radical breakaway from established technology.

A short survey of the history of ammonia process technology can be found in [14], [24], [27].

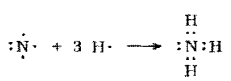
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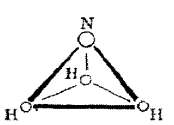
3. Fundamentals of the Synthesis Reaction

3.1. Physical Properties of Ammonia

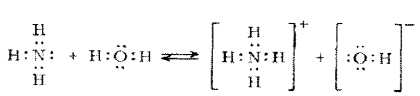
Molecular Properties. Corresponding to its nuclear charge number, the nitrogen atom possesses seven shell electrons. One electron pair in in the ground state 1 *s* (K shell), and five electrons are distributed over the four orbitals with the principal quantum number 2 (L shell). Of these, one electron pair occupies the 2 *s* level and three unpaired electrons, respectively, a half of the remaining three levels, $2p_x$, $2p_y$, $2p_z$. The unpaired electrons can enter into electron-pair bonds with the 1 *s* electron of three hydrogen atoms. Thus, the three half occupied orbitals of the L shell become about fully accupied (formation of an octet of the neon type in accordance with the octet theory of Lewis–Langmuir).



The nitrogen atom is at the apex of a pyramid above the plane of the three hydrogen atoms, which are arranged in an equilateral triangle. The H–N–H bond angle is about 107 ° [28]. Although covalent, the nitrogen–hydrogen bonds have a polar contribution because of a stronger electronegativity of nitrogen relative to hydrogen. Because of polarization of the bonds and the unsymmetrical molecular arrangement, the ammonia molecule has a considerable dipole moment, 1.5 D [29].



As the ammonia molecule possesses the same electron configuration as water (isosterism) and similar bond angles (water vapor bond angle 105 °, dipole moment 1.84 D), ammonia and water behave similarly in many reactions. Ammonia and water are diamagnetic. The dielectric constant of liquid ammonia is about 15 and greater than those of the most condensed gases; therefore, liquid ammonia has a considerable ability to dissolve many substances. The ammonia molecule, with its free electron pair, can combine with a proton.



In the resulting ammonium ion, the nitrogen atom is situated in the middle of a

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terahedron whose corners are occupied by hydrogen atoms. The four hydrogen atoms are equivalent in their behaviour. According to LINUS PAULING, the positive excess charge is distributed about equally over all five atoms.

Physical Data. The results of comprehensive investigations of the physical properties of ammonia have been published in [30] and [31]. Both papers provide numerous equations for physical properties derived from published data, the laws of thermodynamics, and statistical evaluation. These equations are supplemented by lists and tables of thermodynamic quantities and an extensive collection of literature references.

Moreover, data an physical properties and the comples systems important in synthesis may be found in [32]–[35], and of course, in the well-known tabulations *Landolt-Börnstein* [36] and *Handbuch der Kältetechnik* [37], among others. The most important physical data are compiled in Table 1.

***p–V–T* Data.** The $p-V-T$ data in Table 2 are calculated from the equations in [31] and further data in [30], [32]–[37]. Measured $p-V-T$ values for liquid ammonia in the pressure range from 7 to 180 MPa (70–1800 bar) and at temperatures from –20 °C to 40 °C may be found in [38]. Detailed information on compressibility gained from experimental data can be found in [40]–[44]. An equation of state for liquid ammonia is given in [45]; for a more simple form, see [35]. Further data may be found in references [46]–[48]. Properties of liquid ammonia from –50 to 65 °C and from saturation pressure up to 370 bar are reported in [49].

Caloric Data. Enthalpy and entropy of solid ammonia are given in [32]. Enthalpy and entropy may be calculated by the equations in [31]. Further data are given in [37], [50] and [32]–[37]. An enthalpy $\log p$ diagram can be found in [37].

Specific Heat. In the range of –45 °C to 50 °C the specific heat (in kJ $kg^{-1}K^{-1}$) of liquid ammonia can be calculated by using the Equation (1):

$$c_p = -3.787 + 0.0949\,T - 0.3734 \times 10^{-3}\,T^2 + 0.5064 \times 10^{-6}\,T^3 \qquad (1)$$

where $T = \vartheta + 273.15$

Assuming ammonia to be an ideal gas in the range 300–2000 K the following Equation (2) represents the specific heat:

$$c_p = 1.4780 + 2.09307 \times 10^{-3}T - 2.0019 \times 10^{-7}\,T^2 - 8.07923 \times 10^{-11}\,T^3 \qquad (2)$$

The values of the specific heat at constant pressure in Table 3 have been calculated according to [31] and have been extrapolated to 500 °C using data from [31]. Further data can be found in [32]–[36], [52] and [53].

Properties of Saturated Ammonia Liquid and Vapor. Table 4 is derived from [31]. Further data may be found in [30], [34], [36] and [37]. For calculations from reduced data, among others, see [2], [54].

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Table 1. Properties of ammonia

M_r	17.0312
Molecular volume (at 0 °C, 101.3 kPa)	22.08 L/mol
Gas constant R	0.48818 kPa m^3 kg^{-1} K^{-1}
Liquid density (at 0 °C, 101.3 kPa)	0.6386 g/cm^3
Gas density (at 0 °C, 101.3 kPa)	0.7714 g/L
Liquid density (at −33.43 °C, 101.3 kPa)	0.682 g/cm^3
Gas density (at −33.43 °C, 101.3 kPa)	0.888 g/L
Critical pressure	11.28 MPa
Critical temperature	132.4 °C
Critical density	0.235 g/cm^3
Critical volume	4.225 cm^3/g
Critical compressibility	0.242
Critical thermal conductivity	0.522 kJ K^{-1} h^{-1} m^{-1}
Critical viscosity	23.90 × 10^{-3} mPa · s
Melting point (triple point)	−77.71 °C
Heat of fusion (at 101.3 kPa)	332.3 kJ/kg
Vapor pressure (triple point)	6.077 kPa
Boiling point (at 101.3 kPa)	−33.43 °C
Heat of vaporization (at 101.3 kPa)	1370 kJ/kg
Standard enthalpy of formation (gas at 25 °C)	−46.22 kJ/mol
Standard entropy (gas at 25 °C, 101.3 kPa)	192.731 J mol^{-1} K^{-1}
Free enthalpy of formation (gas at 25 °C, 101.3 kPa)	−16.391 kJ/mol
Net heating value, *LHV*	18.577 kJ/g
Gross heating value, *HHV*	22.543 kJ/g
Electrical conductivity	
(at −35 °C), very pure	1 × 10^{-11} $\Omega^{-1}cm^{-1}$
Commercial	3 × 10^{-5} $\Omega^{-1}cm^{-1}$
Ignition temperature acc. to DIN 51794	651 °C
Explosive limits	
NH_3–O_2 mixture (at 20 °C, 101.3 kPa)	15–79 vol% NH_3
NH_3–air mixture	
(at 0 °C, 101.3 kPa)	16–27 vol% NH_3
(at 100 °C, 101.3 kPa)	15.5–28 vol% NH_3

Vapor–Liquid Equilibria for the Ammonia, Hydrogen, Nitrogen, Argon, Methane System (Fig. 4). Because of the great importance of absorption processes in synthesis loop engineering (see Section 4.5.6), these binary and multicomponent systems have been experimentally and theoretically reinvestigated several times. The updates are based mainly on thermodynamic relationships in combination with equations of state.

In [58] various publications are compared with one another and equilibrium methods for the ranges 273–323 K and 4.9–49 MPa (49 to 490 bar) are reported. Inves-

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Table 2. Specific volume of ammonia in L/kg

p,MPa	Temperature, °C											
	−33	−20	−10	0	10	20	50	100	150	200	250	300
0.1	1172.001	1235.492	1284.303	1333.094	1381.870	1430.634	1576.882	1820.589	2064.339	2308.163	2552.061	2796.020
0.5	1.467	1.503	1.533	1.566	257.613	269.524	303.259	356.206	407.353	457.602	507.299	556.610
1	1.466	1.503	1.533	1.565	1.600	1.638	144.981	173.883	200.728	226.667	252.117	277.272
2	1.465	1.501	1.531	1.563	1.598	1.636	64.713	82.476	97.322	111.121	124.391	137.352
3	1.464	1.500	1.530	1.562	1.596	1.634	1.772	51.740	62.785	72.589	81.818	90.721
4	1.463	1.499	1.528	1.560	1.594	1.631	1.768	36.088	45.448	53.305	60.532	67.414
5	1.462	1.498	1.527	1.558	1.592	1.629	1.764	26.361	34.981	41.713	47.754	53.432
6	1.461	1.497	1.526	1.557	1.590	1.627	1.760	19.379	27.944	33.968	39.229	44.109
7	1.460	1.495	1.524	1.555	1.589	1.625	1.756	2.171	22.859	28.422	33.137	37.449
8	1.459	1.494	1.523	1.554	1.587	1.623	1.752	2.151	18.986	24.251	28.565	32.455
10	1.458	1.492	1.520	1.551	1.583	1.618	1.745	2.115	13.375	18.385	22.163	25.467
15	1.453	1.486	1.514	1.543	1.574	1.608	1.727	2.048	4.321	10.478	13.632	16.176
20	1.448	1.481	1.508	1.536	1.566	1.599	1.712	1.999	2.780	6.534	9.408	11.574
25	1.443	1.475	1.501	1.529	1.558	1.590	1.697	1.959	2.516	4.474	6.957	8.863
30	1.438	1.470	1.496	1.522	1.551	1.581	1.684	1.926	2.376	3.540	5.443	7.113
35	1.434	1.465	1.490	1.516	1.544	1.573	1.672	1.898	2.282	3.094	4.494	5.922
40	1.429	1.460	1.484	1.510	1.537	1.565	1.660	1.873	2.211	2.839	3.893	5.088
45	1.424	1.454	1.479	1.504	1.530	1.557	1.650	1.850	2.155	2.670	3.497	4.491
50	1.419	1.449	1.473	1.498	1.523	1.550	1.639	1.830	2.108	2.547	3.221	4.054
55	1.414	1.444	1.468	1.492	1.517	1.543	1.630	1.811	2.068	2.453	3.020	3.727
60	1.409	1.439	1.462	1.486	1.511	1.536	1.620	1.794	2.033	2.377	2.865	3.476

Table 3. Specific heat of ammonia at constant pressure in kJ kg^{-1} K^{-1}

p, MPa	Temperature, °C													
	−33	−20	−10	0	10	20	50	100	150	200	250	300	400	500
0.1	2.324	2.236	2.197	2.175	2.163	2.159	2.174	2.240	2.328	2.422	2.518	2.612	2.797	2.966
0.5	4.468	4.528	4.572	4.618	2.673	2.553	2.383	2.339	2.385	2.459	2.542	2.628	2.815	2.981
1	4.466	4.526	4.569	4.615	4.668	4.736	2.707	2.470	2.456	2.504	2.574	2.653	2.838	2.998
2	4.462	4.521	4.563	4.607	4.659	4.725	3.785	2.787	2.611	2.597	2.636	2.696	2.886	3.028
3	4.458	4.516	4.557	4.600	4.651	4.714	5.039	3.216	2.788	2.697	2.701	2.742	2.934	3.060
4	4.454	4.511	4.552	4.594	4.642	4.703	5.014	3.832	2.994	2.805	2.769	2.788	2.981	3.091
5	4.450	4.506	4.546	4.587	4.634	4.693	4.991	4.826	3.236	2.923	2.840	2.837	3.028	3.121
6	4.446	4.501	4.541	4.580	4.626	4.683	4.969	6.854	3.526	3.050	2.916	2.887	3.067	3.168
7	4.442	4.497	4.535	4.574	4.618	4.673	4.947	6.776	3.882	3.190	2.994	2.939	3.069	3.203
8	4.439	4.492	4.530	4.567	4.610	4.664	4.927	6.551	4.330	3.342	3.077	2.992	3.155	3.238
10	4.432	4.484	4.520	4.555	4.595	4.645	4.889	6.215	5.724	3.695	3.255	3.103	3.242	3.304
15	4.415	4.463	4.496	4.527	4.561	4.603	4.806	5.701	20.410	4.965	3.776	3.407	3.470	3.463
20	4.400	4.444	4.474	4.501	4.530	4.566	4.736	5.396	8.827	6.899	4.399	3.739	3.644	3.607
25	4.387	4.427	4.454	4.477	4.502	4.532	4.676	5.187	6.826	8.074	5.046	4.080	3.812	3.734
30	4.376	4.412	4.435	4.456	4.477	4.502	4.624	5.032	6.048	7.426	5.543	4.397	3.980	3.861
35	4.367	4.399	4.419	4.436	4.454	4.475	4.578	4.912	5.614	6.605	5.741	4.652	4.104	3.967
40	4.361	4.387	4.404	4.418	4.432	4.450	4.538	4.814	5.330	6.033	5.693	4.818	4.229	4.074
45	4.358	4.377	4.391	4.402	4.413	4.427	4.502	4.734	5.128	5.643	5.539	4.894	4.310	4.159
50	4.359	4.369	4.379	4.387	4.395	4.407	4.469	4.665	4.975	5.365	5.364	4.903	4.392	4.244
55	4.367	4.363	4.369	4.374	4.379	4.388	4.440	4.607	4.855	5.157	5.202	4.873	4.442	4.301
60	4.385	4.360	4.361	4.362	4.365	4.370	4.413	4.556	4.757	4.996	5.060	4.824	4.492	4.359

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Table 4. Properties of saturated ammonia liquid and vapor

t, °C	p, kPa	Specific volume		Enthalpy		Heat of vaporization,	Entropy	
		Liquid, L/kg	Vapor, L/kg	Liquid, kJ/kg	Vapor, kJ/kg	kJ/kg	Liquid, kJ kg^{-1} K^{-1}	Vapor, kJ kg^{-1} K^{-1}
−40	71.72	1.4490	1551.6	180.53	1568.7	1388.1	0.8479	6.8017
−35	93.14	1.4620	1215.4	202.80	1576.5	1373.1	0.9423	6.7105
−30	119.49	1.4754	962.9	225.19	1584.1	1358.9	1.0352	6.6241
−25	151.54	1.4892	770.95	247.69	1591.5	1343.8	1.1266	6.5419
−20	190.16	1.5035	623.31	270.31	1598.6	1328.3	1.2166	6.4637
−15	236.24	1.5184	508.49	293.05	1605.4	1312.4	1.3053	6.3890
−10	290.77	1.5337	418.26	315.91	1611.9	1296.0	1.3927	6.3175
− 5	354.77	1.5496	346.68	338.87	1618.0	1279.1	1.4787	6.2488
0	429.35	1.5660	289.39	361.96	1623.6	1261.7	1.5636	6.1826
5	515.65	1.5831	243.16	385.17	1628.9	1243.8	1.6473	6.1188
10	614.86	1.6009	205.55	408.51	1633.7	1225.2	1.7299	6.0571
15	728.24	1.6194	174.74	432.01	1638.1	1206.1	1.8116	5.9972
20	857.08	1.6387	149.31	455.67	1642.0	1186.3	1.8922	5.9390
25	1002.7	1.6590	128.19	479.52	1645.3	1165.8	1.9721	5.8822
30	1166.6	1.6801	110.54	503.57	1648.1	1144.5	2.0512	5.8267
35	1350.0	1.7023	95.699	527.86	1650.3	1122.4	2.1295	5.7722
40	1554.6	1.7257	83.150	522.40	1651.9	1099.5	2.2075	5.7185
45	1781.7	1.7505	72.484	577.22	1652.8	1075.6	2.2849	5.6656
50	2033.0	1.7766	63.373	602.36	1653.0	1050.6	2.3619	5.6131

tigations of binary systems are reported in [56] and [59]–[66] and equations and compilations in [56], [67], and [68], among others. The basis for the saturation concentration (Table 5) and solubilities in liquid ammonia (Table 6) are unpublished BASF calculations produced with the help of the Lee–Kesler equation of state [69] and publications [56], [57]. The ammonia content of the gas may be calculated with the formulas from [63].

A mutual interaction of solubilities exists in all multicomponent systems. The interaction with methane is pronounced. This interdependence is treated in detail in [56], [59], [70] and [71].

Surface Tension. The following equation (Eq. 3), from [72], represents the surface tension of ammonia (σ in Nm^{-1}) over the range −50 to 50 °C.

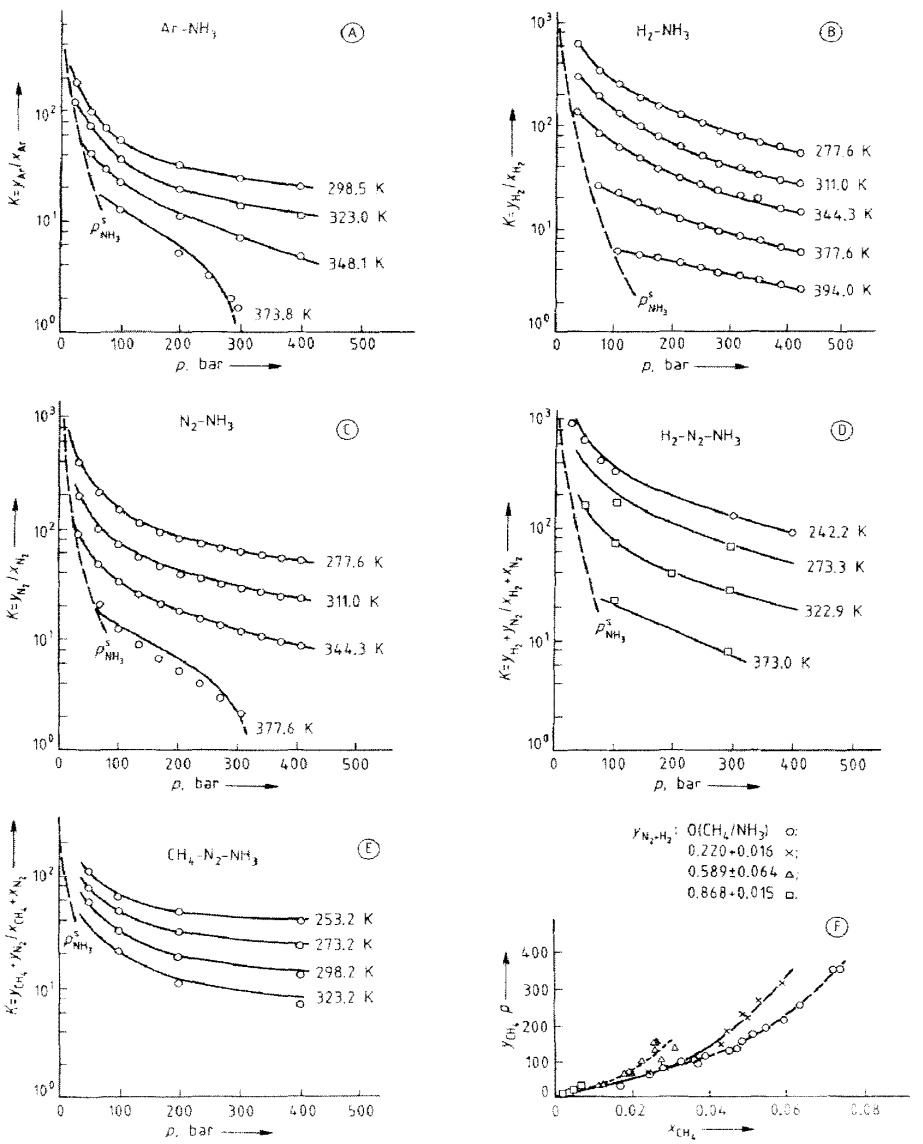
$$\sigma = 26.55 \times 10^{-3} - 2.3 \times 10^{-4}\ \vartheta \qquad (3)$$

Experimental data are given in [73]. The surface tension of aqueous ammonia solutions over the ranges 0.1–1.2 MPa (1–12 bar) and 20–100 °C can be found in [74].

Dynamic Viscosity. A survey on dynamic viscosity data for the ranges 30–250 °C and 0.1–80 MPa (1–800 bar) appears in [34]; further data occur in [75] and [76]. Experimental viscosity data and correlating equations for the range 448–598 K and for pressures up to 12.1 MPa (121 bar) can be found in [77]. Generalized equations for viscosity calculations on refrigerants are presented in [78].

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Figure 4. Equilibrium solubilities (K factors) for argon (A), hydrogen (B), nitrogen (C), hydrogen:nitrogen 3:1 (D), and methane:nitrogen in liquid ammonia (E). F shows the dependance of the methane partial pressure ($p \cdot \gamma CH_4$) on the concentration of methane dissolved in the liquidm χCH_4, for three different gas mixture A – C and E according to [55], F according to [56], D was developed from data reported in [57]



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Table 5. Ammonia concentration at saturation in 1:3 mixtures of nitrogen and hydrogen, in vol%

t, °C	p, MPa							
	5	10	15	20	30	40	50	100
−30	2.9	1.7	1.34	1.15	0.95	0.9	0.87	0.8
−20	4.6	2.70	2.05	1.58	1.5	1.38	1.3	1.2
−10	6.8	4.06	3.10	2.63	2.22	2.03	1.94	1.75
0	10.0	5.80	4.50	3.80	3.20	2.90	2.75	2.5
10	15.0	8.25	6.40	5.36	4.50	4.05	3.84	3.55
20	19.6	11.4	8.6	7.35	6.05	5.55	5.25	4.9
30	20.0	15.2	11.5	9.80	8.20	7.50	7.10	6.70
40	26.5	20.0	15.0	14.0	10.75	9.80	9.40	9.0

Table 6. Solubility of hydrogen and nitrogen in liquid ammonia for 1:3 mixtures of nitrogen and hydrogen in cm^3 gas/g NH_3 (STP)

t, °C		Total pressure, MPa							
		5	10	15	20	30	40	50	100
−30	N_2	0.632	1.161	1.637	2.036	2.743	3.291	3.754	5.317
	H_2	1.291	2.598	3.896	5.157	7.554	8.625	12.380	22.287
−20	N_2	0.864	1.438	2.036	2.568	3.452	4.195	4.195	8.852
	H_2	1.581	3.167	4.759	6.248	9.294	12.518	15.219	33.945
−10	N_2	0.922	1.730	2.488	3.129	4.258	5.207	6.027	8.853
	H_2	1.845	3.869	5.756	7.623	11.444	14.954	18.349	33.945
0	N_2	1.081	2.088	2.994	3.811	5.269	6.457	7.532	11.218
	H_2	2.215	4.560	6.956	9.163	13.740	18.220	22.461	41.863
10	N_2	1.226	2.461	3.583	4.564	6.342	7.800	9.190	14.085
	H_2	2.585	5.490	8.360	11.178	16.590	22.056	27.300	51.783
20	N_2	1.372	2.874	4.414	5.415	7.654	8.303	11.285	17.733
	H_2	2.969	6.423	9.970	13.338	20.142	26.731	33.310	63.530
30	N_2	1.505	3.315	4.954	6.418	9.169	11.619	13.968	22.528
	H_2	3.300	7.557	11.719	15.711	24.272	32.343	40.396	79.345
40	N_2	1.584	3.717	5.767	7.647	10.967	13.954	16.852	28.527
	H_2	3.631	8.761	13.745	18.916	28.028	39.127	49.451	97.253

The following, from [72], is a formula for interpolation along the vapor pressure curve for liquid ammonia (viscosity η in N s m^{-2}):

$$\eta = 1.949 \times 10^{-4} - 1.72 \times 10^{-10}\,\vartheta + 7 \times 10^{-6}\,\vartheta^2 \quad (4)$$

An interpolation formula for ammonia vapor for the temperature range −20 to 150 °C at 0.098 MPa is given in [72]:

$$\eta = 9.83 \times 10^{-6} + 2.75 \times 10^{-8}\,\vartheta + 2.8 \times 10^{-11}\,\vartheta^2 \quad (5)$$

Reference [79] reports viscosity measurements for the hydrogen–ammonia system; [80] for nitrogen–ammonia, oxygen–ammonia, methane–ammonia, and ethylene–ammonia; and [81] for argon–ammonia.

Thermal Conductivity. In [82], experimental data and calculation methods for ammonia liquid and vapor for the ranges 0.1–49 MPa (1–490 bar) and 20–177 °C

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Table 7. Table for determining the percentage ammonia content of aqueous solutions from the density at 15 °C

Density, g/cm³	Ammonia content	Density, g/cm³	Ammonia content
1.000	0.00	0.935	17.12
0.995	1.14	0.930	18.64
0.990	2.31	0.925	20.18
0.985	3.55	0.920	21.75
0.980	4.80	0.915	23.35
0.975	6.05	0.910	24.99
0.970	7.31	0.905	26.64
0.965	8.59	0.900	28.33
0.960	9.91	0.895	30.03
0.955	11.32	0.890	31.73
0.950	12.74	0.885	33.67
0.945	14.17	0.880	35.60
0.940	15.63		

are reported. The anomaly in the thermal conductivity at the critical point is discussed in full detail. A nomogram for these data appears in [83]. A third-degree equation for the range 358–925 K can be found in [84]. For the liquid phase the following formula may be used to interpolate in the range from –10 to 100 °C [72] (thermal conductivity λ in W m^{-1} K^{-1}):

$$\lambda = 0.528 - 1.669 \times 10^{-2}\,\vartheta - 6.2 \times 10^{-6}\,\vartheta^2 \qquad (6)$$

Also from [72] is the formula for ammonia vapor at 101.3 kPa and –20 to 150 °C:

$$\lambda = 0.0217 + 1.17 \times 10^{-4}\,\vartheta + 1.87 \times 10^{-2}\,\vartheta^2 \qquad (7)$$

The thermal conductivities of gas mixtures of ammonia with argon, neon, hydrogen, and methane are reported in [80] and [85]–[87].

Solubility in Water. Tables 7 and 8 and Figures 5 and 6 show miscellaneous information. General physicochemical and chemical engineering handbooks can be consulted for further data.

Reference [88] gives $p-V-T$ values for ammonia containing up to 0.5 wt % water at pressures in the range 113–221 kPa.

3.2. Thermodynamic Data of the Reaction

Ammonia synthesis proceeds according to the following reaction (8):

$$0.5\ N_2 + 1.5\ H_2 \rightleftharpoons NH_3 \qquad \Delta H_{298} = -46.22\ \text{kJ/mol} \qquad (8)$$

To fix a kilogram of nitrogen in ammonia requires reacting 2.4 m^3 (STP) of hydrogen and 0.8 m^3 (STP) of nitrogen. About 3.27 MJ of heat is evolved. Table 9 is a

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Table 8. Heat of solution of ammonia in water, in kJ/mol NH_3

t, °C	Mixture ratio (moles of water per mole ammonia)						
	1	2.33	4	9	19	49	99
0	30.69	34.25	35.17	35.80	36.22	36.47	36.09
20	27.38	32.87	33.66	34.50	34.67	34.83	34.92
40	24.53	31.99	32.91	33.62	33.87	33.95	34

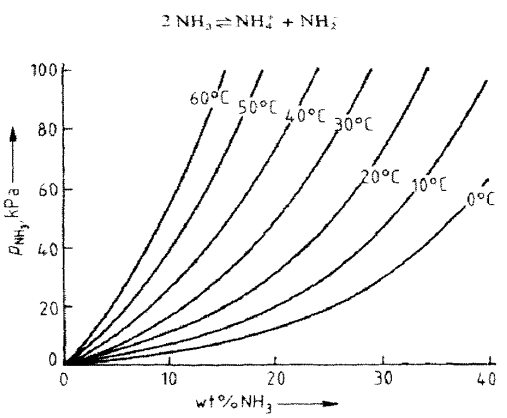


Figure 5. Ammonia partial pressure in aqueous ammonia solutions

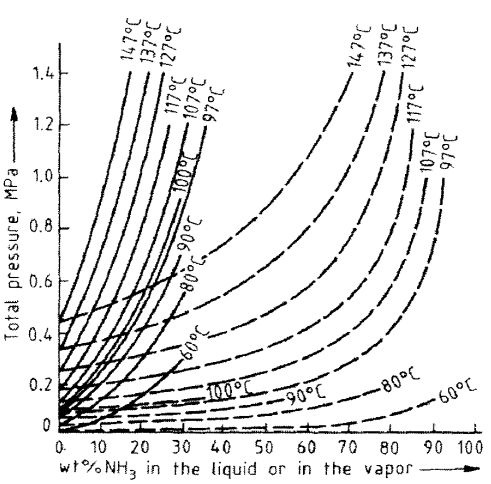


Figure 6. Total vapor pressure and composition of the liquid (——) and vapor (– – –) in the system NH_3–H_2O
Isotherms.

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Table 9. Thermodynamic data for the reaction $0.5\ N_2 + 1.5\ H_2 \rightarrow NH_3$ at atmospheric pressure

	t, K							
	300	400	500	600	700	800	900	1000
ΔH, kJ	−46.35	− 48.48	−50.58	−52.04	−53.26	−54.28	−55.06	−55.68
ΔS, J/K	−99.35	−105.63	−110.03	−112.71	−114.55	−115.89	−116.77	−117.48
$\Delta G/T$, J/K	−55.22	−15.66	8.88	26.25	38.48	48.02	55.56	61.81
c_{p,NH_3}, J mol^{-1}K^{-1}	35.52	38.80	41.97	45.04	47.98	50.80	53.49	56.03
c_{p,H_2}, J mol^{-1}K^{-1}	28.868	29.199	29.278	29.341	29.454	29.634	29.89	30.216
c_{p,N_2}, J mol^{-1}K^{-1}	29.144	29.270	29.601	30.132	30.777	31.451	32.117	32.724

compilation of the most important thermodynamic data for the reaction at atmospheric pressure.

Chemical Equilibrium. The reaction equilibrium has been investigated experimentally and theoretically many times. Today, values for the equilibrium constant are available for pressures up to 350 MPa (3500 bar).

GILLESPIE and BEATTIE [89] (see also [33]) were by far the most successful experimentally in establishing a firm basis for an analytical expression of the equilibrium constant in the range of industrial interest. The values in Tables 10 and 11 were calculated using their equation. A detailed description, with literature data and many tables, appears in [33]. A description of the equilibrium using the REDLICH–KWONG equation of state is given in [90].

Heat of Reaction. HABER investigated the heat of reaction at atmospheric pressure [91]. Numerous authors have estimated the pressure dependence under various assumptions. Today, most people use the Gillespie–Beattie equation [92]. This equation was used in calculating the values in Table 12. For further data see, for example, [33]. Reference [93] contains test results for the range 120–200 MPa (1200–2000 bar) and 450–525 °C. Additional literature can be found in [94].

Physical Properties of the Reactants. Various authors have measured the $p-V-T$ behavior of nitrogen, hydrogen, and 3:1 hydrogen–nitrogen mixtures. Reference [33] contains a survey. For the specific heat, thermal conductivity, and viscosity of the reactants, see [95], [96]. It is to be noted that heats of mixing must be considered for synthesis gas. This applies especially for high pressures and low temperatures. Reference [97] gives viscosities of hydrogen–nitrogen and hydrogen–ammonia mixtures.

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Table 10. Ammonia content (in mol%) in equilibrium synthesis gas; $N_2:H_2=1:3$

t, °C	p_{abs}, MPa										
	5	10	20	30	40	50	60	70	80	90	100
300	39.38	52.79	66.43	74.20	79.49	83.38	86.37	88.72	90.61	92.14	93.39
310	36.21	49.63	63.63	71.75	77.35	81.51	84.73	87.29	89.35	91.03	92.42
320	33.19	46.51	60.79	69.23	75.12	79.53	82.98	85.74	87.98	89.83	91.35
330	30.33	43.45	57.92	66.64	72.79	77.46	81.13	84.09	86.52	88.52	90.20
340	27.64	40.48	55.04	63.99	70.39	75.29	79.18	82.34	84.95	87.12	88.94
350	25.12	37.60	52.17	61.31	67.93	73.04	77.14	80.49	83.28	85.62	87.59
360	22.79	34.84	49.33	58.61	65.41	70.72	75.01	78.55	81.52	84.02	86.15
370	20.64	32.21	46.53	55.89	62.85	68.33	72.80	76.52	79.66	82.33	84.61
380	18.67	29.71	43.79	53.19	60.26	65.89	70.53	74.42	77.72	80.54	82.97
390	16.87	27.36	41.12	50.50	57.66	63.41	68.19	72.23	75.69	78.67	81.25
400	15.23	25.15	38.53	47.86	55.06	60.91	65.81	69.99	73.59	76.71	79.43
410	13.74	23.08	36.04	45.26	52.47	58.39	63.40	67.69	71.42	74.68	77.54
420	12.40	21.16	33.65	42.72	49.91	55.87	60.96	65.36	69.20	72.58	75.57
430	11.19	19.38	31.37	40.26	47.39	53.37	58.50	62.99	66.93	70.43	73.53
440	10.10	17.74	29.20	37.87	44.92	50.88	56.05	60.60	64.63	68.22	71.43
450	9.12	16.23	27.15	35.57	42.50	48.43	53.61	58.20	62.29	65.97	69.28
460	8.24	14.84	25.21	33.36	40.16	46.03	51.19	55.80	59.95	63.69	67.08
470	7.46	13.57	23.39	31.26	37.89	43.67	48.81	53.42	57.60	61.39	64.85
480	6.75	12.41	21.69	29.55	35.71	41.38	46.46	51.06	55.25	59.09	62.60
490	6.12	11.36	20.10	27.34	33.61	39.16	44.17	48.74	52.92	56.78	60.33
500	5.56	10.39	18.61	25.54	31.60	37.02	41.94	46.46	50.62	54.48	58.06
510	5.05	9.52	17.24	23.84	29.68	34.95	39.77	44.22	48.36	52.20	55.80
520	4.59	8.72	15.96	22.24	27.86	32.97	37.68	42.05	46.13	49.96	53.55
530	4.19	8.00	14.77	20.74	26.13	31.07	35.65	39.94	43.96	47.75	51.32
540	3.82	7.34	13.68	19.34	24.49	29.26	33.71	37.89	41.84	45.58	49.13
550	3.49	6.74	12.67	18.02	22.95	27.54	31.85	35.92	39.79	43.47	46.97
560	3.20	6.20	11.74	16.80	21.49	25.90	30.06	34.02	37.80	41.41	44.86
570	2.93	5.70	10.88	15.65	20.13	24.35	28.37	32.20	35.88	39.41	42.81
580	2.69	5.26	10.09	14.59	18.84	22.88	26.75	30.46	34.04	37.48	40.81
590	2.47	4.85	9.36	13.60	17.64	21.50	25.22	28.80	32.26	35.62	38.87
600	2.28	4.48	8.69	12.69	16.52	20.20	23.76	27.22	30.57	33.83	37.00

3.3. General Aspects

Usually, a system having an exothermic heat of reaction under operating conditions should react spontaneously. However, to form ammonia from hydrogen and nitrogen molecules, significant energy input is required for the nitrogen molecule to achieve the activated state. This is because of its high dissociation energy of 941 kJ/mol, which is considerably higher than that of hydrogen. The Gibbs free energy for the dissociation reaction was determinded as $N_2 \rightleftharpoons 2N$ $\Delta F^0_{298} = 911$ kJ/Mol. The distance between the triply bonded nitrogen atoms of 1.098 Å is rather short. The first ionization energy is 1503 kJ/mol.

Because of the high dissociation energy the direct formation of oxides is "endergonisch" [98]. They are thermodynamically unstable compared to N_2 and O_2, which explains why the oxidation route for nitrogen fixation was not competitive.

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Table 11. Equilibrium ammonia content (in mol%) in the presence of inert gases (2.5 mol% Ar; 7.5 mol% CH_4); N_2:H_2=1:3

t, °C	p_{abs}, MPa										
	5	10	20	30	40	50	60	70	80	90	100
300	32.11	43.10	54.27	60.62	64.95	68.12	70.56	72.49	74.03	75.28	76.31
310	29.52	40.51	51.98	58.63	63.20	66.59	69.22	71.31	72.99	74.37	75.51
320	27.05	37.96	49.66	56.57	61.38	64.98	67.79	70.04	71.87	73.38	74.63
330	24.71	35.46	47.32	54.45	59.48	63.29	66.28	68.70	70.67	72.31	73.68
340	22.51	33.03	44.96	52.30	57.52	61.52	64.69	67.27	69.39	71.16	72.65
350	20.46	30.68	42.62	50.11	55.51	59.68	63.02	65.76	68.03	69.93	71.54
360	18.56	28.42	40.30	47.90	53.46	57.79	61.29	64.18	66.59	68.63	70.36
370	16.80	26.27	38.01	45.69	51.37	55.85	59.49	62.52	65.08	67.24	69.10
380	15.19	24.33	35.77	43.48	49.26	53.86	57.64	60.81	63.49	65.79	67.77
390	13.72	22.31	33.59	41.29	47.14	51.85	55.74	59.03	61.84	64.27	66.36
400	12.39	20.50	31.48	39.13	45.02	49.81	53.81	57.21	60.14	62.68	64.89
410	11.18	18.81	29.44	37.01	42.91	47.76	51.84	55.34	58.38	61.03	63.35
420	10.08	17.24	27.49	34.93	40.83	45.71	49.86	53.44	56.57	59.32	61.75
430	9.10	15.79	25.62	32.92	38.77	43.67	47.86	51.52	54.73	57.57	60.09
440	8.21	14.45	23.85	30.97	36.75	41.64	45.87	49.58	52.86	55.78	58.39
450	7.41	13.22	22.17	29.09	34.78	39.65	43.88	47.63	50.97	53.96	56.65
460	6.70	12.09	20.59	27.29	32.87	37.68	41.92	45.68	49.06	52.11	54.87
470	6.06	11.05	19.10	25.56	31.02	35.77	39.97	43.75	47.16	50.25	53.06
480	5.49	10.11	17.71	23.92	29.23	33.90	38.06	41.83	45.25	48.38	51.24
490	4.97	9.24	16.41	22.36	27.51	32.08	36.20	39.94	43.36	46.51	49.40
500	4.51	8.46	15.19	20.89	25.87	30.33	34.37	38.08	41.49	44.64	47.56
510	4.10	7.74	14.07	19.50	24.30	28.64	32.61	36.26	39.65	42.79	45.72
520	3.73	7.09	13.02	18.19	22.81	27.02	30.89	34.49	37.84	40.97	43.90
530	3.40	6.50	12.05	16.96	21.39	25.46	29.24	32.76	36.07	39.17	42.09
540	3.10	5.97	11.16	15.81	20.05	23.98	27.65	31.09	34.34	37.41	40.31
550	2.83	5.48	10.33	14.73	18.79	22.57	26.12	29.48	32.66	35.68	38.56
560	2.59	5.04	9.57	13.73	17.60	21.23	24.67	27.93	31.04	34.01	36.84
570	2.38	4.64	8.87	12.79	16.48	19.96	23.28	26.44	29.47	32.38	35.17
580	2.18	4.27	8.22	11.92	15.43	18.76	21.95	25.01	27.96	30.80	33.54
590	2.01	3.94	7.63	11.12	14.44	17.63	20.69	23.65	26.51	29.28	31.96
600	1.85	3.64	7.08	10.37	13.52	16.56	19.50	22.35	25.12	27.81	30.43

The only reactions of molecular nitrogen at ambient temperature are the formation of lithium nitride Li_3N, reactions with certain transition metal complexes, and nitrogen fixation with nitrogenase in the bacteria of the root nodules of legumes and in blue algae (Sections 14.1.1 and 14.1.2). Above 500 °C nitrogen reacts with some elements, especially with metals (nitride formation).

According to estimates [99], the homogenous reaction of nitrogen with hydrogen to form ammonia in the gas phase requires an activation energy of 230 – 420 kJ/mol. For purely thermal energy supply with a favorable collision yield, this activation barrier requires temperatures well above 800 – 1200 K to achieve measurable reaction rates. However, at such high temperatures and industrially reasonable pressures, the theoretically achievable ammonia yield is extremely small because of the unfavorable position of the thermodynamic equilibrium. In fact, all older attempts to combine molecular nitrogen purely thermally with atomic or molecular hydrogen failed. On the other

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Table 12. Heat of reaction ΔH (in kJ) for the reaction $0.5\ N_2 + 1.5\ H_2 \rightarrow NH_3$, from [89]

t, °C	p_{abs}, MPa										
	0 (ideal)	10	20	30	40	50	60	70	80	90	100
0	44.39	55.20	66.02	76.84	87.66	98.47	109.29	120.11	130.92	141.74	152.56
25	44.92	53.48	62.03	70.59	79.15	87.70	96.26	104.82	113.38	121.93	130.49
50	45.44	52.37	59.30	66.23	73.16	80.09	87.02	93.95	100.88	107.80	114.73
75	45.96	51.69	57.41	63.14	68.86	74.58	80.31	86.03	91.76	97.48	103.20
100	46.47	51.28	56.10	60.91	65.72	70.53	75.34	80.16	84.97	89.78	94.59
125	46.97	51.08	55.19	59.29	63.40	67.51	71.62	75.72	79.83	83.94	88.04
150	47.46	51.02	54.57	58.12	61.68	65.23	68.78	72.34	75.89	79.44	83.00
175	47.95	51.06	54.17	57.28	60.39	63.50	66.61	69.72	72.83	75.94	79.05
200	48.42	51.17	53.92	56.68	59.43	62.18	64.93	67.69	70.44	73.19	75.94
225	48.88	51.34	53.80	56.26	58.71	61.17	63.63	66.09	68.55	71.01	73.47
250	49.33	51.54	53.76	55.97	58.19	60.40	62.62	64.84	67.05	69.27	71.48
275	49.76	51.77	53.79	55.80	57.81	59.82	61.84	63.85	65.86	67.87	69.88
300	50.18	52.02	53.86	55.70	57.54	59.38	61.22	63.06	64.90	66.74	68.59
325	50.59	52.28	53.98	55.67	57.37	59.06	60.75	62.45	64.14	65.83	67.53
350	50.99	52.55	54.12	55.69	57.26	58.82	60.39	61.96	63.53	65.10	66.66
375	51.36	52.82	54.28	55.74	57.20	58.66	60.12	61.58	63.04	64.49	65.95
400	51.73	53.09	54.46	55.82	57.18	58.55	59.91	61.28	62.64	64.00	65.37
425	52.07	53.35	54.64	55.92	57.20	58.48	59.76	61.04	62.32	63.60	64.88
450	52.40	53.61	54.82	56.03	57.23	58.44	59.65	60.86	62.06	63.27	64.48
475	52.71	53.86	55.00	56.14	57.29	58.43	59.57	60.72	61.86	63.00	64.14
500	53.01	54.09	55.18	56.26	57.35	58.43	59.52	60.60	61.69	62.78	63.86
525	53.28	54.31	55.35	56.38	57.42	58.45	59.48	60.52	61.55	62.58	63.62
550	53.53	54.52	55.51	56.50	57.48	58.47	59.46	60.45	61.44	62.42	63.41
575	53.76	54.71	55.66	56.60	57.55	58.50	59.44	60.39	61.33	62.28	63.23
600	53.98	54.88	55.79	56.70	57.61	58.52	59.43	60.34	61.24	62.15	63.06

hand, both ammonia and hydrazine result from reacting atomic nitrogen with atomic hydrogen [99].

At pressures above 200 MPa (2000 bar), the synthesis of ammonia proceeds even in the absence of specific catalysts. At such extreme pressures the vessel walls appear to catalyze the formation of ammonia.

In the homogeneous phase under thermodynamically favorable temperature conditions, the formation of ammonia may be forced by employing other forms of energy, such as electrical energy or ionizing radiation. The principal difficulty with these so-called plasma processes, which also impedes their economic use, is that the energy supplied is useful only in part for ammonia formation. A greater part is transformed in primary collision and exothermic secondary processes into undesirable heat or unusable incidental radiation.

In the catalytic combination of nitrogen and hydrogen, the molecules lose their translational degrees of freedom by fixation on the catalyst surface. This drastically reduces the required energy of activation, for example, to 103 kJ/mol on iron [100]. The reaction may then proceed in the temperature range 250–400 °C. In 1972, it was discovered that electron donor–acceptor (EDA) complexes permit making ammonia with measurable reaction rate at room temperature.

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The following discussion concentrates mainly on the ammonia synthesis reaction over iron catalysts and refers only briefly to reactions with non-iron catalysts. Iron catalysts which are generally used until today in commercial production units are composed in unreduced form of iron oxides (mainly magnetite) and a few percent of Al, Ca, and K; other elements such as Mg and Si may also be present in small amounts. Activation is usually accomplished in situ by reduction with synthesis gas. Prereduced catalysts are also commercially available.

Numerous investigations have been performed to elucidate the mechanism of catalytic reaction of nitrogen and hydrogen to form ammonia. References [101]–[104] give reviews of the older and some of the newer literature. During the past two decades a large variety of surface science techniques involving Auger electron spectroscopy, X-ray photoelectron spectroscopy, work-function measurements, temperature-programmed adsorption and desorption, scanning tunnelling microscopy, and others have been developed [105], [106]. Many of these methods are based on interaction of slow electrons, ions, or neutral particles and exhibit high sensitivity to surface structures. With these powerful tools the kinetics of nitrogen and hydrogen adsorption and desorption could be investigated, and it was also possible to identify adsorbed intermediates. The results of these experiments allow the mechanism of ammonia synthesis in the pressure range of industrial interest to be elucidated [107]–[110].

As with every catalytic gas-phase reaction, the course of ammonia synthesis by the Haber–Bosch process can be divided into the following steps:

1) Transport of the reactants by diffusion and convection out of the bulk gas stream, through a laminar boundary layer, to the outer surface of the catalyst particles, and further through the pore system to the inner surface (pore walls)
2) Adsorption of the reactants (and catalyst poisons) on the inner surface
3) Reaction of the adsorbed species, if need be with participation by hydrogen from the gas phase, to form activated intermediate compounds
4) Desorption of the ammonia formed into the gas phase
5) Transport of the ammonia through the pore system and the laminar boundary layer into the bulk gas stream

Only the portion of the sequence that occurs on the catalyst surface is significant for the intrinsic catalytic reaction. Of special importance is the adsorption of nitrogen. This assumption is decisive in representing the synthesis reaction kinetics. The transport processes occurring in the pores of the catalyst in accordance with the classical laws of diffusion are of importance in industrial synthesis (see also Sections 3.5 and 3.6).

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3.4. Mechanism of the Intrinsic Reaction

Earlier studies [111]–[120] had already suggested that on iron catalysts nitrogen adsorption and dissociation can be regarded as the rate-determining step for the intrinsic reaction. This has now been fully confirmed by microkinetic simulations based on the results of surface science studies [107], [121], [122]. In single-crystal experiments it was found that the activation energy for dissociative nitrogen adsorption is not constant; it increases as the surface becomes increasingly covered with adsorbed nitrogen species. Under reaction conditions it can attain values of 63–84 kJ/mol [109], [112], [113], [123] which are typical for ammonia synthesis. In the case of nitrogen the first step seems to be an adsorption in molecular state followed by chemisorption in the atomic state. From experimental results it was concluded that for hydrogen a direct transition from the gaseous H_2 molecule into the chemisorbed H_{ad} is most likely, and evidence for the stepwise hydrogenation of surface nitrogen atomic species was found. In IR spectroscopic investigations, NH and NH_2 species were identified [124], and secondary ion emissions detecting NH^+ also confirmed the presence of NH species on the surface [125]. It was further shown that at lower temperatures nitrogen becomes adsorbed only in the molecular state, but subsequently dissociates when the temperature is raised. Isotopic experiments with $^{30}N_2$ and $^{29}N_2$ showed that the surface species resulting from low-temperature adsorption was molecular, whereas that from high-temperature adsorption was atomic [126]. Ammonia synthesis is highly sensitive to the orientation of the different crystal planes of iron in the catalyst [127]–[131]. Measurements on defined single crystal surfaces of pure iron performed under ultrahigh vacuum [132]–[134] clearly showed that Fe(111) is the most active surface. This was also demonstrated by the rate of ammonia formation on five different crystallographic planes for unpromoted iron at 20 bar, as shown in Figure 7.

Activation energy, reactivity, adhesion coefficient (the probability that a nitrogen molecule striking the surface will be adsorbed dissociatively) and work function show a clear dependence on surface orientation [135], [136]:

Ammonia synthesis activity:
(111) > (211) > (100) > (210) > (110)
Activation energy of nitrogen adsorption:
(111) > (100) > (110)
Work function:
(210) > (111) > (211) > (100) > (110)
Surface roughness:
(210) > (111) > (211) > (100) > (110)

Ultrahigh-vacuum experiments with single crystals show that the activation energy of nitrogen adsorption at zero coverage increases from about zero for Fe(111) to 21 kJ/mol for Fe(100) and 27 kJ/mol for Fe(110) [107], [112], [137]–[139]. These values increase significantly for higher coverage [138], [139]. Adsorption and desorption

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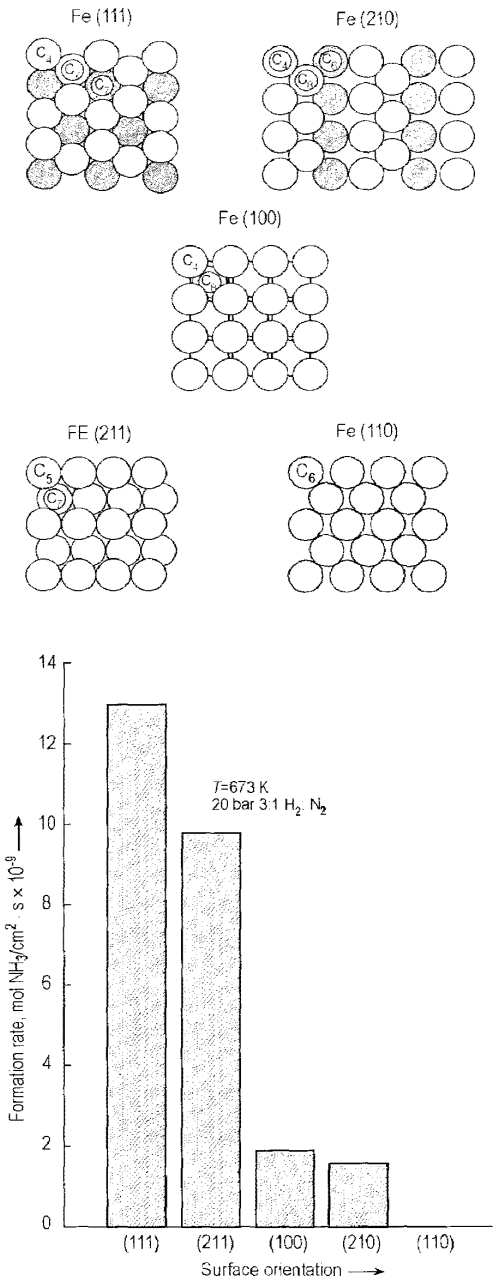


Figure 7. Ammonia formation rate on different iron surfaces [122], [135]

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under higher pressure on finely dispersed catalyst indicate that the reaction is highly activated. Activation energy is 100 kJ/mol under these conditions with high coverage. [111], [140]. According to [137], [138] adsorption on the planes Fe(111) and Fe(110) is associated with a regrouping of the surface atoms.

A possible explanation for the high activity of faces (111) and (211) is that these are the only surfaces which expose C_7 sites (iron with seven nearest neighbors) to the reactant gases. There are theoretical arguments [141] that highly coordinated surface atoms should show increased catalytic activity due to low-energy charge fluctuations in the *d*-bands of these highly coordinated atoms. This argument might probably be the key for the special role of C_7 sites. Other reasons discussed are based on charge transfer and interaction of iron *d*-bands with antibonding 2 π^* orbitals of nitrogen [142].

Promotion with potassium of single iron crystals enhances the sticking probability for nitrogen dissociation much more on the Fe(100) and (110) than on the Fe(111) (factors 280, ca. 1000 and 8, respectively) to the effect that the differences in surface orientation disappear [143]. A similar effect was not found for the ammonia synthesis at 20 bar and catalyst temperature of 400 °C: only a two-fold increase of the ammonia formation rate was measured for Fe(111) and Fe(100), and the face (110) was found to be inactive with and without potassium [135]. Other experiments [144] show that even the least active face Fe(110) becomes as active for the synthesis as Fe(111) after addition of alumina with subsequent annealing with oxygen and water vapor. A proposed mechanism for these findings — backed by X-ray photoelectron spectroscopy, temperature programmed desorption and electron microscopy — assumes that first alumina forms an iron aluminate $FeAl_2O_4$ on the surface. This new surface then may serve as a template on which iron grows with (111) and (211) orientation upon exposure to the synthesis-gas mixture in the reaction [145].

Based on these experimental results a reaction scheme for the ammonia synthesis may be formulated comprising the following sequence of individual steps [107]:

$$H_2 + * \rightleftharpoons 2\,H_{ad} \quad (9)$$

$$N_2 + * \rightleftharpoons N_{2,ad} \quad (10)$$

$$N_{2,ad} \rightleftharpoons 2\,N_{ad} \quad (11)$$

$$N_{ad} + H_{ad} \rightleftharpoons NH_{ad} \quad (12)$$

$$NH_{ad} + H_{ad} \rightleftharpoons NH_{2,ad} \quad (13)$$

$$NH_{2,ad} + H_{ad} \rightleftharpoons NH_{3,ad} \quad (14)$$

$$NH_{3,ad} \rightleftharpoons NH_3 + * \quad (15)$$

The progress of the reaction may be described in the form of an energy profile, as shown in Figure 8. Industrial ammonia synthesis in the homogeneous gas phase is not feasible because of the high dissociation energies for the initial steps. The reaction over a catalyst avoids this problem since the energy gain associated with the surface atom bonds overcompensates these dissociation energies and the first steps have actually become exothermic.

Dissociative nitrogen adsorption remains nevertheless the rate-determinating step, not so much on account of its activation barrier but rather because of the very

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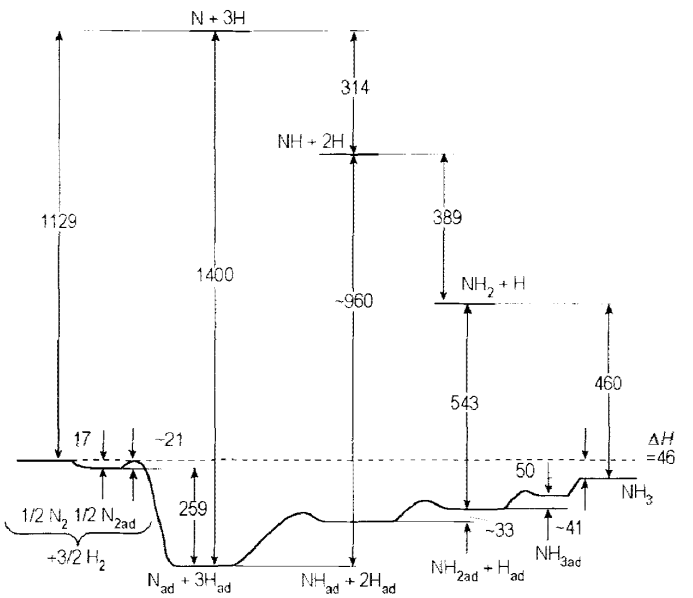


Figure 8. Schematic energy profile of the progress of ammonia synthesis on Fe (energies in kJ/mol) [107]

unfavorable pre-exponential factor in its rate constant. The subsequent hydrogenation steps are energetically uphill, but the energy differences involved can easily be overcome at the temperatures (ca. 700 K) used in industrial ammonia synthesis. It is, however, quite apparent that the rate-controlling step would switch from dissociative nitrogen adsorption to hydrogenation of adsorbed atomic nitrogen species if the temperature were lowered sufficiently because of these differences in activation energy.

Some critics [146] of the above energy diagram question the low net activation barrier from the gas phase. The arguments are based on an analysis of activation energies from early measurements of the nitrogen adsorption kinetics on singly (Al_2O_3) promoted catalysts and on the results of experiments with supersonic molecular beams [147], [148].

An attempt to explain these differences is given in [149]. In more recent investigations of the adsorbed nitrogen species [150]–[153] a second molecularly adsorbed species was detected. This so-called α state was interpreted as a bridge-bonded species with electron donation from the surface to the antibonding π levels of N_2, whereas the γ state is regarded as a terminally bound species. Thus the following picture (16) for the nitrogen adsorption emerges:

$$N_2 \rightarrow S^*- N_2\ (\gamma \text{ state}) \rightarrow S^*-N_2 -S^*\ (\alpha \text{ state}) \rightarrow 2\ S^*-N\ (\beta \text{ state}) \qquad (16)$$

where S* denotes a surface atom.

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For industrial catalysts made by careful reduction of magnetite fused with nonreducible oxide promoters the important role of the (111) face seems to be confirmed [154]. However, the question whether the active industrial catalyst exposes mostly (111) faces remains unresolved. If not, further improvements of the catalyst are at least theoretically possible [155]. A critical evaluation of our present knowledge of the reaction mechanism was recently made by SCHLÖGL [156].

Other reaction mechanisms have been debated for reaction temperatures below 330 °C [130], [157], [158]–[169]. These propose participation of diatomic nitrogen, or of adsorption complexes containing diatomic nitrogen, in the rate-determining step (see [101], [102] for further literature).

NIELSEN et al. investigated ammonia synthesis on a commercial Topsøe catalyst, KM IR, over a wide temperature range. They found evidence that a different reaction mechanism predominates below and above 330 °C [170]. Also, at low temperatures, chemisorbed hydrogen blocks the catalyst surface [171]. The latter finding is in agreement with the observations of ERTL's group [123].

Reaction Mechanism on Non-Iron Catalysts. Non-iron systems which exhibit some potential to catalyze ammonia synthesis can be divided into the following groups [172]:

- Platinum group metals such as Ru, Os Ir, Pt (no nitrides)
- Mn, Co, Ni, Tc, Rh and their alloys (no nitride formation under synthesis conditions)
- Mn, Mo, V (present as nitrides under the reaction conditions)

In the non-iron systems the rate-determining step is also dissociative adsorption of nitrogen and the catalyst effectivity seems to be primarily dictated by the activation energy of the dissociation reaction [172]. This is somewhat surprising in view of the marked differences in the heats of adsorption of nitrogen and the adsorption activation energy. This even holds for tungsten, which has no significant activation energy and a high adsorption enthalpy for nitrogen, so that hydrogenation of adsorbed atomic nitrogen could be expected to be the rate-determining step. The factor common with the iron catalyst is the structure sensitivity.

The only system which seems to be promising for industrial application is ruthenium promoted with rubidium on graphite as carrier (see Section 3.6.2.3). Further information on structure, activity and reaction mechanism of non-iron catalysts is given in [102], [172]–[175]. Specific references: vanadium [176], uranium [177], molybdenum [178]–[180], tungsten [181].

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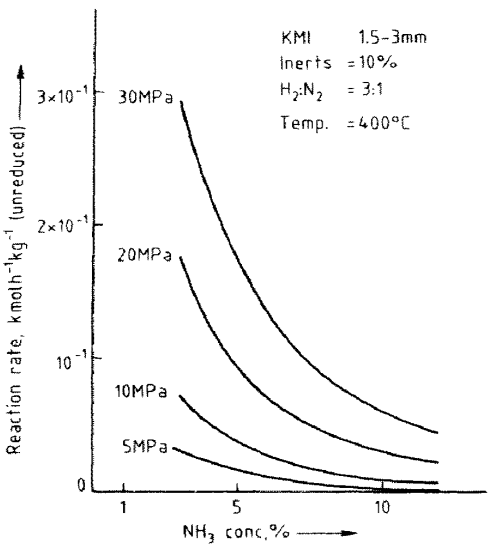


Figure 9. Reaction rate for NH_3 synthesis. Dependence on the ammonia concentration at various pressures.

3.5. Kinetics

Knowledge of the reaction kinetics is important for designing industrial ammonia synthesis reactors, for determining the optimal operating conditions, and for computer control of ammonia plants. This means predicting the technical dependence on operating variables of the rate of formation of ammonia in an integral catalyst volume element of a converter.

High pressure promotes a high rate of ammonia formation; high ammonia concentration in the synthesis gas (recycle gas) restricts it (Fig. 9). High temperatures accelerate ammonia formation but imply a lower value of the equilibrium ammonia concentration and so a lower driving force. Therefore, the rate of formation at first increases with rising temperature but then goes through a maximum as the system approaches thermodynamic equilibrium (Fig. 10). A similar situation exists for the dependence of the reaction rate on the ratio of the hydrogen and nitrogen partial pressures; with lower temperature, the maximum rate shifts to a lower hydrogen – nitrogen ratio (Fig. 11). Figure 11 presents data obtained using a commercial iron catalyst, Topsøe KMIR. The data show a sharp drop in reaction rate with declining temperature at $H_2/N_2 = 3:1$ ratio in contrast to a $H_2/N_2 = 1:1$ ratio. This may be attributed to a hindering effect of adsorbed hydrogen at low temperature [171].

Equations for describing ammonia synthesis under industrial operating conditions must represent the influence of the temperature, the pressure, the gas composition, and the equilibrium composition. Moreover, they must also take into consideration the dependence of the ammonia formation rate on the concentration of catalyst poisons and the influence of mass-transfer resistances, which are significant in industrial ammonia synthesis.

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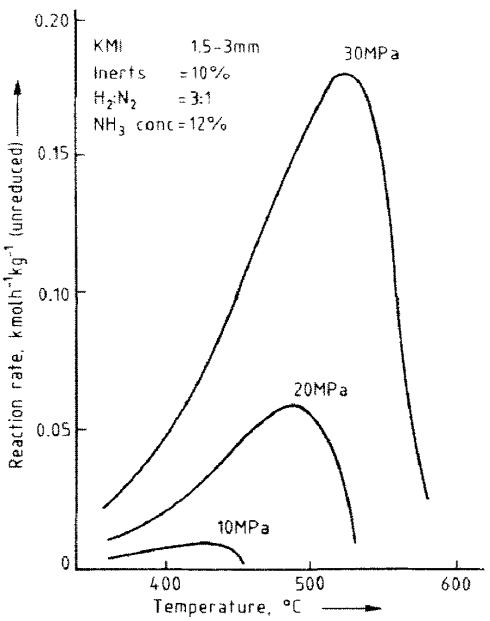


Figure 10. Reaction rate for NH_3 synthesis. Dependence on the temperature at various pressures.

Since the beginning of commercial ammonia synthesis, a large number of different kinetic equations have been suggested, emanating in each case from a proposed reaction mechanism or from empirical evaluations. A critical review of the data and equations published up to 1959 appears in [182]. A discussion of kinetics proposed up to 1970, insofar as they have been based on measurements in the operating range of commercial interest, can be found in [157]. An evaluation of present knowledge is given in [107], [121], [183], [184].

Contradictory data on the kinetics of ammonia synthesis, especially in the earlier literature, in some circumstances may reflect a lack of attention to the influence of impurities in the gas. If oxygen compounds are present in the synthesis gas, reversible poisoning of the adsorbing areas, in accordance with an equilibrium depending on the temperature and the water vapor – hydrogen partial pressure ratio, must be taken into account when developing rate equations (see also Section 3.6.1.5).

Experimental Measurements of Reaction Kinetics. The reaction expressions discussed in the following model the intrinsic reaction on the catalyst surface, free of mass-transfer restrictions. Experimental measurements, usually made with very fine particles, are described by theoretically deduced formulas, the validity of which is tested experimentally by their possibility for extrapolation to other reaction conditions. Commonly the isothermal integral reactor is used with catalyst crushed to a size of 0.5 – 1.5 mm to avoid pore diffusion restriction and heat-transfer resistance in the catalyst particles. To exclude maldistribution effects and back mixing, a high ratio of

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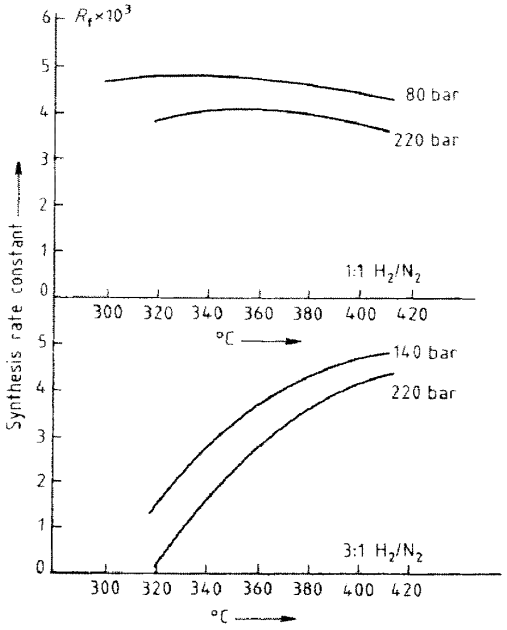
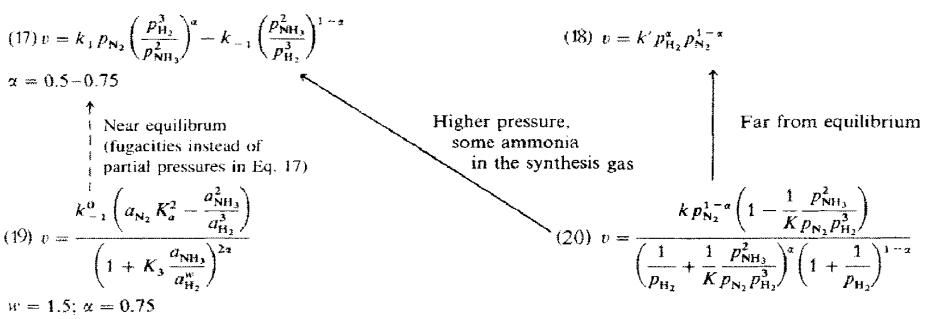


Figure 11. Ammonia synthesis rate constant dependence on hydrogen – nitrogen ratio

bed length to bed diameter is chosen. Sometimes the catalyst is also diluted with inert material. In some investigations, differential reactors were used. To exclude any poisoning by the synthesis gas, very pure reactants were prepared by decomposition of anhydrous ammonia [183].

Classical Expressions for Ammonia Synthesis Kinetics. The first expression useful for engineering purposes was the Temkin – Pyzhev Equation (17) proposed in 1940 [185], [186]. It is based on the assumption that dissociative adsorption is the rate-determining step, that hydrogen and ammonia have no significant influence on nitrogen adsorption, and that the kinetics of nitrogen adsorption and desorption can be described adequately by Elovich-type adsorption on an energetically inhomogeneous surface. For many years this kinetic expression was the basic design equation for ammonia converters. Values for the factors α between 0.5 [187] – [189] and 0.75 [33], [190], [191] were used. A problem with this equation was that the α values (reaction order) were dependent on temperature, and the rate constants on pressure [170], [190] – [194]. More serious (not so much for industrial purposes, where the converter feed has always a certain ammonia content) was the fact that for zero ammonia content, as in some laboratory measurements, the equation gives an infinitely high reaction rate. To avoid this, a simpler expression (Eq. 18) was often used [192], [193].

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An important modification was made by TEMKIN [195] who incorporated hydrogen addition to the adsorbed nitrogen as a second rate-determining step (Eq. 20). ICI demonstrated that this equation gives a better fit with experimental data [196]. It was also shown later that the original Equation (17) is a simplified form of a more general model which can be derived from the concept of energetically homogeneous (Langmuir – Hinshelwood adsorption isotherm) as well as for heterogeneous surfaces (Elovich-type isotherm). The applicability of a particular equation resulting from this concept also depends on the state of reduction of the catalyst [194] and the type of promoter [197]. Equation (19), used by NIELSEN et al. [198], is a combination of these model equations, developed by OZAKI et al. [199], that uses fugacities instead of partial pressures. A similar equation is found in [200]. Additionally, a number of modified equations were proposed and tested with existing experimental data and industrial plant results [201] – [204]. Near the thermodynamical equilibrium, Equation (19) transforms into Equation (17) [157], [170].

Surface science based ammonia kinetics [107], [108], [183], [184] are presently still viewed as an academic exercise rather than as a practical tool for engineering. The large amount of available data on nitrogen and hydrogen adsorption from ultrahigh-vacuum studies on clean iron surfaces, acquired with all the modern spectroscopic techniques, has prompted some research groups, such as BOWKER et al. [205], [206] and STOLTZE and NØRSKOW [207], [208], to attempt the generation of a kinetic expression for ammonia synthesis from a detailed microscopic model of the reaction mechanism consisting of a number of discrete steps at molecular and atomic level. Potential energy diagrams for the various intermediate steps and species, were set up and Arrhenius expressions for each single step with known or estimated values for all pre-factors and activation energies were formulated. The best results have been achieved so far by calculating the overall rate from the rate of dissociation of the adsorbed nitrogen and equilibrium constants for all other reaction steps. The adsorption – desorption equilibria were treated with approximation of competitive Langmuir-type adsorption and by evaluation of the partition functions for the gaseous and adsorbed species. The data from single-crystal experiments for potassium-promoted

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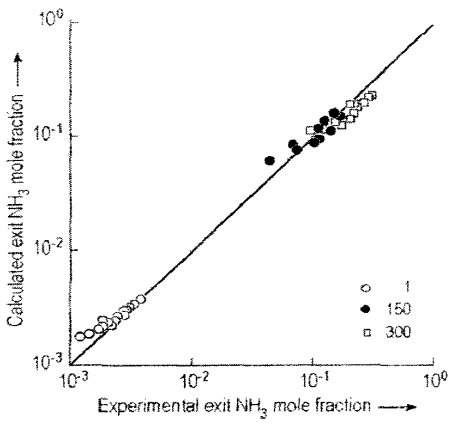


Figure 12. Comparison of ammonia concentrations calculated from surface science kinetics with experimentally measured values [208], [210]

Fe(111) surface were used for the rate of the dissociative nitrogen adsorption. Comparison of the calculated ammonia yields with those determined experimentally on a commercial Topsøe KM1 catalyst showed an agreement within a factor better than 2. Figure 12 demonstrates these encouraging results. These conclusions have been confirmed by calculations results of another independent group [121], [209].

To compete with the empirical models (Temkin and improved expressions) for the best fit to experimental data cannot be the prime objective of the microkinetic approaches. Rather, they are means of checking whether our knowledge and understanding of the elementary steps correspond to the reality of catalysts under industrial synthesis conditions.

Transport Phenomena. For practical application, the above kinetic equations have to be modified to make allowance for mass and energy transfer since the reaction rates actually observed in a commercial converter are lower. One aspect is interparticle mass transfer and heat transfer through the stagnant film which surrounds the catalyst particles. The high velocity of the gas passing through the converter creates sufficient turbulence to keep the film thickness rather small in relation to the catalyst grain size. For this reason the largest concentration gradient (with respect to the concentration in the bulk gas stream) is within the catalyst particles. Since the thermal conductivity of the iron catalysts is much higher than that of the synthesis gas, the major temperature difference is in the external gas film, while the catalyst particles themselves operate under approximately isothermal conditions. As can be seen from Table 13 the differences in temperature and ammonia concentration between the bulk gas stream and the external catalyst surface are small. It also appears that the effects are oppositely directed and will partly compensate each other. So it can be concluded that their combined influence on the reaction rate is negligible compared to inaccuracies of the experimental data for the intrinsic catalyst activity [183].

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Table 13. Mass and heat transfer effects at the external surface of catalyst particle

Position in catalyst bed, vol% from inlet	NH_3 concentration in bulk gas, mol%	NH_3 concentration at catalyst surface, mol%	Temperature in bulk gas, °C	Temperature at catalyst surface, °C
0	2.500	2.592	400.0	401.4
20	4.500	4.288	428.1	429.5
40	5.960	6.045	455.1	456.5
60	7.000	7.778	481.9	483.2
80	9.300	9.361	505.5	506.6
100	10.500	10.536	522.7	523.3

For the particle sizes used in industrial reactors ($\geq$ 1.5 mm), intraparticle transport of the reactants and ammonia to and from the active inner catalyst surface may be slower than the intrinsic reaction rate and therefore cannot be neglected. The overall reaction can in this way be considerably limited by ammonia diffusion through the pores within the catalysts [211]. The ratio of the actual reaction rate to the intrinsic reaction rate (absence of mass transport restriction) has been termed as pore effectiveness factor E. This is often used as a correction factor for the rate equation constants in the engineering design of ammonia converters.

For pore diffusion resistances in reactions having moderate heat evolution, the following phenomena characteristically hold true in industrial ammonia synthesis [212]: in the temperature range in which transport limitation is operative, the apparent energy of activation falls to about half its value at low temperatures; the apparent activation energy and reaction order, as well as the ammonia production per unit volume of catalyst, decrease with increasing catalyst particle size [211], [213]–[215]. For example at the gas inlet to a TVA converter, the effective rate of formation of ammonia on 5.7-mm particles is only about a quarter of the rate measured on very much smaller grains (Fig. 13) [157].

Mathematical models [216] for calculating these effectiveness factors involve simultaneous differential equations, which on account of the complex kinetics of ammonia synthesis cannot be solved analytically. Exact numerical integration procedures, as adopted by various research groups [157], [217]–[219], are rather troublesome and time consuming even for a fast computer. A simplification [220] can be used which can be integrated analytically when the ammonia kinetics are approximated by a pseudo-first-order reaction [214], [215], [221], according to the Equation (21):

$$r = k_v \left(c_{NH_3,\,\text{equilibrium}} - c_{NH_3}\right) \tag{21}$$

For this case, the pore effectiveness factor E is a function of the so-called Thiele modulus m (Eq. 22) [222]:

$$E = \frac{3}{m}\left[\frac{1}{\operatorname{tgh} m} - \frac{1}{m}\right] \tag{22}$$

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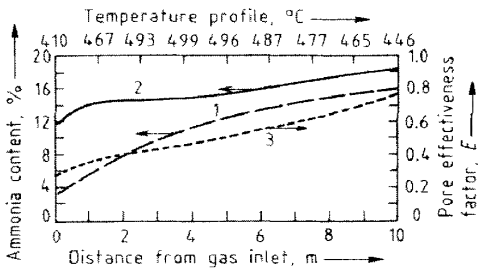


Figure 13. Ammonia content in the bulk stream (1) and in the catalyst pores (at $r = 0.5\ R$) (2) and pore effectiveness factor, E (3)
21.4 MPa; 12% inerts; SV = 15000 h^{-1}; particle diameter, $2\ R = 5.7$ mm

The Thiele modulus m is defined by Equation (23):

$$m = \frac{d_{eff}}{2}\sqrt{\frac{k_v}{D_{eff}}} \tag{23}$$

where

d_{eff} =	effective particle diameter
D_{eff} =	effective diffusion coefficient of ammonia in the catalyst particle
k_v =	reaction rate constant referred to a unit of particle volume
tgh =	tangens hyperbolicus

The practical application of kinetic equations to the mathematical calculation of ammonia synthesis converters is described in [196], [217], [223]–[229].

3.6. Catalysts

The ammonia synthesis catalyst may be viewed as the heart of an ammonia plant. For a given operating pressure and desired production, it determines the operating temperature range, recycle gas flow, and refrigeration requirement. As a result, it directly fixes vessel and exchanger design in the synthesis loop. It also indirectly influences the makeup gas purity requirement, and so the operating pressure, and capital cost, and energy consumption for synthesis gas production and purification. Although the proportionate cost of catalysts compared to the total cost of a modern ammonia synthesis plant is negligible, the economics of the total process are determined considerably by the performance of the ammonia catalyst [230].

Industrial catalysts for ammonia synthesis must satisfy the following requirements:

1) High *catalyst activity* at the lowest possible reaction temperatures in order to take advantage of the favorable thermodynamic equilibrium situation at low temperatures. Average commercial catalysts yield about 25 vol% ammonia when operating at 40 MPa (400 bar) and 480 °C catalyst end temperature, which corresponds to a 535 °C equilibrium temperature. With catalysts that would function at a reaction temperature about 100 K lower, a yield of 45 vol% ammonia can be expected with

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the same approach to equilibrium, or the pressure may be reduced to 15 MPa (compare Tables 9 and 10).

2) The highest possible *insensitivity to oxygen- and chlorine-containing catalyst poisons,* which may be present in even the very effectively purified synthesis gas of a modern process (see Sections 3.6.1.5, and 4.3.2). In assessing the newly developed catalyst systems recommended for operation at very low temperatures (see Section 3.6.2.3), it must be kept in mind that the effect of poisons, for example, oxygen compounds, may become more severe as temperature declines (see Fig. 25).
3) *Long life,* which is determined essentially by resistance to thermal degradation and to irreversible poisoning (see Section 3.6.1.5). In older high-pressure plants (60 – 100 MPa), catalyst life was a big issue; because the catalysts in these plants showed a markedly reduced life owing to the severe operating conditions, the necessary downtime for removing, replacing, and reducing the catalyst had a considerable effect on the ammonia manufacturing cost. In modern single-train ammonia plants, conventional iron catalysts achieve service lifetimes up to 14 years.
4) *Mechanical Strength.* Insufficient pressure and abrasion resistance may lead to an excessive increase in converter pressure drop, and so to a premature plant shutdown. For example, mechanical disintegration during operation along with oxygen sensitivity thwarted the industrial application of uranium carbide catalysts [231].
5) Because of the high and increasing world demand for ammonia, a *reliable primary raw material source.* For example, osmium, which was planned as the first industrial catalyst, is so scarce that, in 1910, as a precautionary measure for this option, BASF had secured almost the total world supply [231].

The ammonia synthesis catalyst problem has been more intensively studied than the catalysis of any other industrial reaction. At BASF, A. MITTASCH et al. started a tremendous experimental programm, in which up to 1911 more than 2500 different formulations were tested in more than 6500 runs. They checked almost all elements of the periodic table for their suitability as ammonia catalysts [8], [232]. The experiments were fially brought to a close in 1922 after a total of 22 000 tests. From these experiments came a series of technical findings, for example, concerning the relationships between catalytic effectiveness and the strength of the nitrogen bond and reducibility, or relating to the mechanism of opposing activation or inactivation in doubly promoted systems.

In principle, metals or metal alloys are suitable as ammonia catalysts, above all those from the transition-metal group [233] (Table 14). Metals or metal compounds for which the chemisorption energy of nitrogen is neither too high nor too low show the greatest effectiveness (Figs. 14, 15), [234], [235], but only the magnetite-based catalyst proved suitable for industrial use.

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Table 14. Effectiveness of various elements as catalysts, promoters, or catalyst poisons

	Catalysts	Promoters	Poisons
I		Li, Na, K, Rb, Cs	
II		Be, Mg, Ca, Ba, Sr	Cd, Zn
III	Ce and rare earths	Al, Y, La, Ce and rare earths	B, Tl
IV	(Ti), (Zr)	Si, Ti, Zr, Th	Sn, Pb, C
V	(V)	Nb, Ta	P, As, Bi
VI	(Cr), Mo, W, U	Cr, Mo, W, U	O, S, Se, Te
VII	(Mn), Re		F, Cl, Br, J
VIII	Fe, Ni, Co, Ru, (Rh), Os, (Ir)		

Table 15. Effect of various elements or their oxides on the activity of iron catalysts in ammonia synthesis

a)	positive: Al, Ba, Be, Ca, Ce, Cr, Er, K, La, Li, Mg, Mn, Mo, Na, Nb, Nd, Rb, Sm, Sr, Ta, Th, Ti, U, V, W, Y, Zr
b)	negative: As, B, Bi, Br, C, Cd, Cl, F, J, P, Pb, S, Sb, Sn, Te, Tl, Zn
c)	doubtful: Au, Co, Cu, Hg, Ir, Ni, Os, Pd, Pt, Si

3.6.1. Classical Iron Catalysts

From the early days of ammonia production to the present, the only catalysts that have been used have been iron catalysts promoted with nonreducible oxides. Recently, a ruthenium-based catalyst promoted with rubidium has found industrial application. The basic composition of iron catalysts is still very similar to that of the first catalyst developed by BASF.

The catalytic activity of iron was already known well before the advent of industrial ammonia synthesis. RAMSAY and YOUNG used metallic iron for decomposing ammonia. PERMAN [236], as well as HABER and OORDT [237], conducted the first catalytic synthesis experiments with iron at atmospheric pressure. NERNST [12] used elevated pressures of 5–7 MPa. Pure iron showed noticeable initial activity which, however, could be maintained for longer operating periods only with extremely pure synthesis gas.

The ammonia synthesis catalyst problem could be considered solved when the catalytic effectiveness of iron in conversion and its onstream life were successfully and substantially improved by adding reduction-resistant metal oxides [232] (Table 15). The iron catalysts promoted with aluminum and potassium oxides proved to be most serviceable [238]. Later, calcium was added as the third activator. Development work in the United States from 1922 can be found in [239].

Modern catalysts additionally contain other promoters that were present in the older catalysts only as natural impurities from the raw materials. Onstream life and performance were enhanced considerably by optimizing the component ratios (Section 3.6.1.1), conditions of preparation (Section 3.6.1.3), and catalyst particle size and form (Section 3.6.1.2). The high-purity gas of modern processes and the trend to lower

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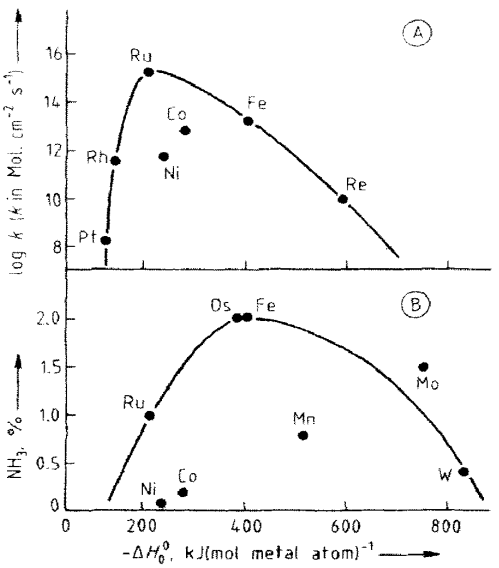


Figure 14. The rate constants of ammonia decomposition (A) on and the ammonia synthesis capacities (B) of metals as a function of $-\Delta H_0^0$. (Mol. denotes molecule, mol denotes mole)

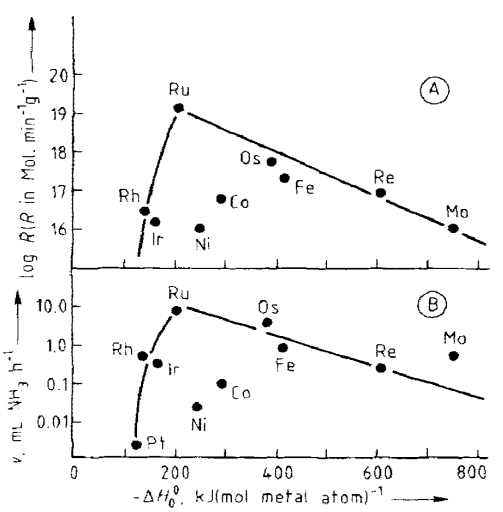


Figure 15. Catalytic activity of carbon-supported metals promoted by metallic potassium as a function of $-\Delta H_0^0$.
A) The rate of isotopic equilibration of N_2 at 623 K, 20 kPa of p_{N_2} (Mol. denotes molecule, mol denotes mole);
B) The rate of ammonia synthesis at 523 K, 80 kPa of total pressure

synthesis pressures especially favor the development of more active and easily reducible types of catalysts, at some sacrifice in temperature stability and resistance to poisons. To some extent even today, ammonia plant operating conditions and types of converters (Section 4.5.3) can differ greatly one from another. Thus, individual catalyst manufacturers now offer several catalyst types in various particle size distributions, in oxidic and prereduced states.

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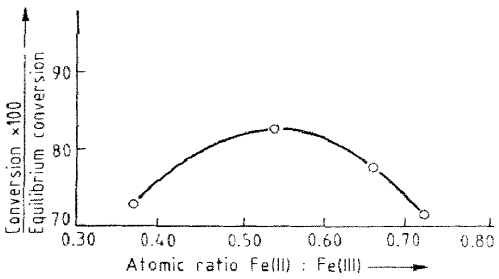


Figure 16. Dependence of the ammonia yield on the degree of oxidation of the iron in the unreduced catalyst

3.6.1.1. Composition

Table 16 gives a composition survey of commercial ammonia catalysts in the years 1964–1966. The principal component of oxidic catalysts is more or less stoichiometric magnetite, Fe_3O_4, which transforms after reduction into the catalytically active form of α-iron.

The degree of oxidation of industrial catalysts has a considerable influence on their catalytic properties. MITTASCH in 1909 established that catalysts manufactured by reducing a magnetite phase were superior to those prepared from other oxides. For industrial catalysts, the highest ammonia yields are observed with an Fe(II) – Fe(III) ratio of 0.5 – 0.6, about the degree of oxidation of stoichiometrically composed magnetite [240] – [242] (Fig. 16). To obtain optimal catalyst composition, careful control of the manufacturing process, especially the melting conditions, which determine the oxygen content, is necessary.

In general, the catalysts contain varying quantities of the oxides of aluminum, potassium, calcium, magnesium, and silicon as promoters. Patents recommend adding sodium [243], beryllium [244], vanadium [245], uranium [246], or platinum [247]. Reference [248] describes cesium-containing catalysts. Catalysts patented by Lummus [249] and Ammonia Casale [250] contain cerium as additional promoter. ICI [251] has developed a cobalt-containing catalyst, as has Grande Paroisse [252].

Nature of the Surface of Commercial Iron Catalysts. Freshly reduced commercial iron catalysts that contain aluminum, potassium, and calcium oxides as basic promoters consist of approximately 30-nm primary crystallites; the spaces between them form an interconnecting system of pores. Besides a maximum at a pore radius of about 10 nm that originates on reduction of the Fe_3O_4 (magnetite) phase of the nonporous oxidic catalyst, the pore distribution curve (Fig. 17) generally shows a peak at 25 – 50 nm that is formed on reduction of the wustite phase [157], [253]. The pore volume measures 0.09 – 0.1 cm^3/g; with an apparent density of 4.8 – 4.9 g/cm^3, accordingly, the pores represent 44 – 46% of the volume of a catalyst granule [33]. The surface of the walls of the pores, the so-called inner surface, amounts to about 15 m^2/g.

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Table 16. Examples of commercial ammonia catalysts from the years 1964 – 1966. Values for the composition in weight%. The numbers at the beginning of the lines are keyed to the catalyst origin.

Origin, type	Fe total	FeO	Fe_2O_3	Al_2O_3	MgO	SiO_2	CaO	K_2O	Other	Particle size, mm	Bulk density, kg/L
1	68.6	36.07	57.85	3.30	0.09	0.75	2.13	1.13	–	2 – 4	2.37
2 normal	60.0	32.91	60.18	2.90	0.37	0.35	2.80	0.54	–	4 – 10	2.94
2	68.2	31.30	62.53	2.90	0.30	0.35	1.65	0.97	–	6 – 10	2.80
2 HT	66.9	32.47	59.18	2.95	1.55	0.40	2.95	0.50	–	6 – 10	2.80
2 prereduced	88.1			3.70	0.43	0.45	3.60	0.70	–	6 – 10	2.30
3	71.3	39.22	58.2	1.80	0.18	0.27	1.43	0.89	–	2 – 4	2.86
4	66.3	22.27	49.0	0.59	4.47	0.77	0.65	0.50	0.7 Cr_2O_3		
4 prereduced	90.6			0.10	6.08	1.23	0.10	0.86	1.05 Cr_2O_3		
5	71.5	33.0	65.5	2.96	1.55	–	0.20	0.01	–		
6 (1964)	69.5	23.85		3.15	0.26	0.40	1.85	1.10	–	3 – 9	2.71
6 (1966)	66.9			2.73	0.29	0.43	1.84	1.15	–	5 – 10	2.73
7 prereduced	90.4			3.12	1.00	0.46	0.25	0.58	0.4 MnO	5/5	2.55
8	68.4	35.35		3.16	0.56	0.50	3.54	0.58	–	2 – 4	2.61
9	70.0	32.14		3.17	0.28	0.10	2.40	0.32	–	2 – 4	2.81
10	70.8	33.62		1.58	0.28	1.14	0.67	1.57	–	2 – 4	2.66
11 normal (1964)	66.7	35.95	56.97	3.27	0.67	0.55	3.00	0.65	–		
11 (1966)	68.2	38.70	54.60	2.42	0.35	0.64	2.85	0.58	–		
11 normal (1964)				3.0	0.3	0.5	2.0	1.0	–		
11 (1966)	69.5	38.20	56.70	2.34	0.35	0.57	1.85	0.57	–		
11 HT	66.3	38.22	52.38	2.94	3.56	0.30	2.66	0.63	–		
11 prereduced	84.9			3.62	0.43	0.94	4.70	0.68	–	5 – 11	2.11
12				3.9	4.0	0.8	2.3	1.8	–		
13		23.15		2.9	0.1	0.42	3.12	0.52	–		
14				4		0.7	3	1			

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Table 17. Composition by volume of an industrial ammonia catalyst in comparison to the surface composition before and after reduction (an approximately 10^{-4} cm^2 size typical surface). Numerical values in atomic % [109]

	Fe	K	Al	Ca	O
Volume composition	40.5	0.35	2.0	1.7	53.2
Surface composition before reduction	8.6	36.1	10.7	4.7	40.0
Surface composition after reduction	11.0	27.0	17.0	4.0	41.0

The composition of the outermost atomic layers of the pore walls deviates considerably from the overall average concentrations. Auger electron spectroscopic (AES) measurements on an industrial catalyst (BASF S 6-10) have shown that a significant enrichment of the promoters into the surface results using the unreduced as well as the reduced catalyst [109] (see Table 17). The free iron surface of the reduced BASF catalyst [109] and Topsøe catalyst KM-I [254] comprises only a fraction of the total surface, as could be deduced from the results of prior investigations [157], [255]–[261].

The aluminum oxide promoter exists partly in the form of larger crystallites and, moreover, is relatively homogeneously distributed over the iron area of the surface, although with low concentration [109], [254]. After reduction, about 1 wt% of the alumina also remains statistically distributed in the form of $FeAl_2O_4$ molecular groups built into the α-iron lattice of the reduced catalyst [262], [263]. According to [109] the potassium, in the form of a K + O adsorbed layer, covers about 20–50% of the iron surface. According to [253], [254], a correlation exists between the distribution of the potassium and that of aluminum and/or silicon. Calcium oxide segregates, essentially at the grain boundaries, into separate regions, probably as a mixture of the silicate and ferrite [110]. Auger spectroscopic investigations on reduced BASF and Topsøe catalysts reveal large local differences in composition [109], [253]. Large, apparently homogeneous regions that have originated from reduction of Fe_3O_4 crystallites alternate with nonhomogeneous regions that are formed by the reduction of FeO crystals or consist of amorphous phases [253].

Extensive studies in the last decade have provided a more refined picture of the morphology of the active catalyst (reduced state) and its precursor (oxidic state). A review is given in [156], [264]. With methods such as scanning transmission electron microscopy (TEM) and electron microdiffraction a textural hierarchy has been modeled. Macroscopic particles in the reduced catalyst are confined by fracture lines running through a system of blocks consisting of stacks of slabs in parallel orientation. This structure is already preformed in the preparation of the catalyst precursor, and in the reduction process a further subdivision of the slabs into even smaller platelets might occur. This texture is stabilized by structural promoters, which act as spacers and "glue", separating neighboring platelets and thus providing voids for the interconnection of the pore system. There is also evidence that the basal plane of many platelets has the Fe(111) orientation [154], [264].

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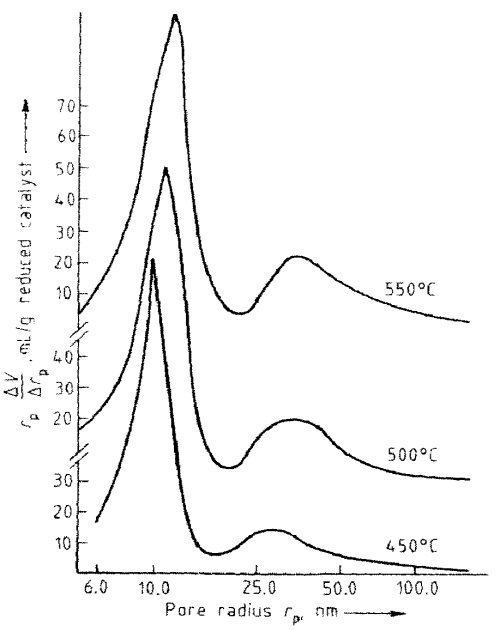


Figure 17. Pore size distribution of a commercial catalyst after reduction at various temperatures [253]

Influence of the Promoters. Promoters can be classified in different groups according to the specific action of the metal oxides:

Structural stabilizers, such as Al_2O_3, produce a high inner surface during reduction and stabilize it under thermal stress by restraining iron crystallite growth [144], [242], [265]. The ability of the various metal oxides to create a high specific surface decreases in the following order [266]:

$$Al_2O_3 > TiO_2 > Cr_2O_3 > MgO > MnO = CaO > SiO_2 > BeO$$

So-called *electronic promoters,* such as the alkali oxides, enhance the specific activity (based on a unit surface) of iron–alumina catalysts. However, they reduce the inner surface or lower the temperature stability and the resistance to oxygen-containing catalyst poisons [267], [268]. In the alkali-metal series, the promoter effect increases with increasing atomic radius, and the destructive effect with decreasing atomic radius [269]. In striving to improve the activity or stability of iron catalysts, a multitude of structural and electronic promoters has been investigated in recent years, among them rare-earth oxides [270], [271], such as Sm_2O_3 [272], Ho_2O_3, Dy_2O_3, and Er_2O_3 [273].

Promoter oxides that are reduced to the metal during the activation process and form an alloy with the iron (see also Section 3.6.2.1) are a special group. Among those in use industrially, cobalt is of special interest [274], [275].

The effect of a given promoter depends on concentration and on the type of promoter combination and the operating conditions, especially the reaction temperature and the synthesis gas purity [245], [267], [269], [276]–[279].

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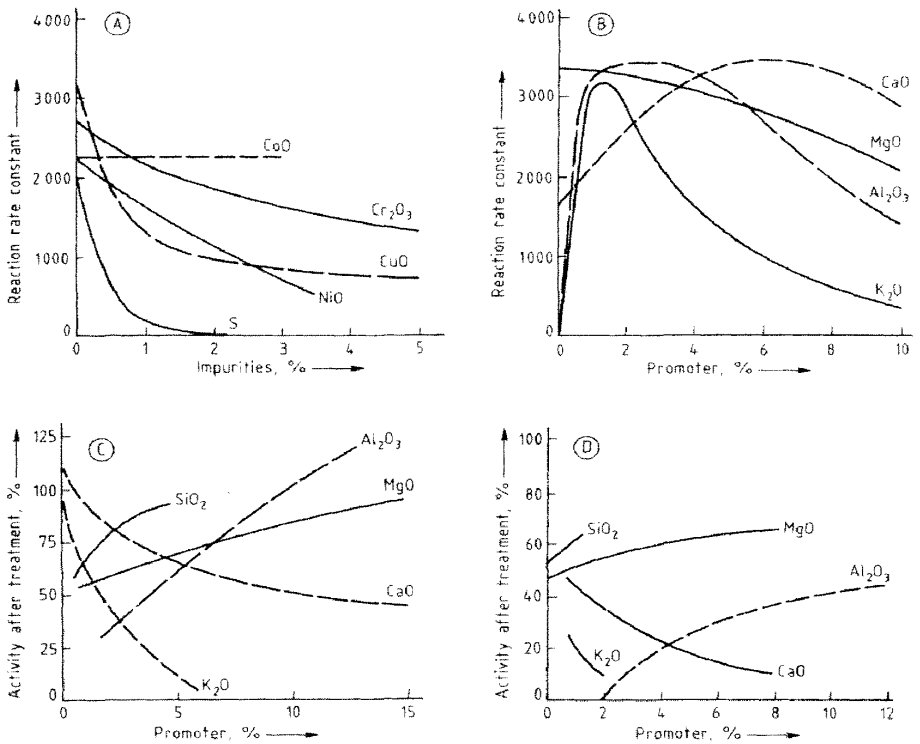


Figure 18. Dependence of the catalyst activity on various factors
A) Concentration of impurities; B) Concentration of promoters; C) Overheating to 700 °C with increasing promoter concentrations; D) Poisoning with water at increasing promoter concentrations

A graphic picture is conveyed in [269] of how the activity of a quadruply promoted (4% Al_2O_3, 1% K_2O, 1% CaO, 1% SiO_2) catalyst changes with varying promoter concentration and operating conditions (Fig. 18). Under normal operating conditions [14–45 MPa, 380–550 °C, 10 000–20 000 $m^3m^{-3}h^{-1}$ (STP)], the optimal activity corresponds to a composition of 2.5–3.5% CaO, 2.3–5.0% Al_2O_3, 0.8–1.2% K_2O, and 0–1.2% SiO_2 (Fig. 18 B). Raising or lowering the concentration of a particular oxide causes a reduction in activity. Changes in the potassium and aluminum oxide concentrations have an especially strong influence. Adding magnesium oxide decreases the catalyst performance. If before the test the catalyst is overheated at 700 °C for 72 h (Fig. 18 C) or poisoned with 2000 cm^3 water vapor per cubic meter of gas at 550 °C (Fig. 18 D), the optimum composition shifts to higher Al_2O_3 and SiO_2 and lower K_2O and CaO concentrations. Magnesium oxide addition now shows a favorable effect.

For ammonia plants operating at pressures up to 35 MPa (350 bar), catalyst end temperatures of 520–530 °C maximum, and with highly purified synthesis gas, the preferred catalysts contain 2.5–4.0% Al_2O_3, 0.5–1.2% K_2O, 2.0–3.5% CaO, 0–1.0% MgO, and a natural content of about 0.2–0.5% SiO_2 [242]. Less active but more

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poison- and temperature-resistant catalysts containing up to 3.6% magnesium oxide were recommended for older plants, for example, classical Casale plants, which operated at up to 80 MPa (800 bar) pressure and in which catalyst end temperature reached 650 °C (see for example [33]). An industrial catalyst for operating temperatures up to 550 °C is stabilized against deterioration by 2–5% V_2O_5 besides 3.5–4.0% Al_2O_3, 2.0–2.5% CaO, and 0.7% K_2O [245]. For higher operating temperatures, still higher V_2O_5 contents are recommended. Silicon dioxide additions shift the optimum potassium oxide concentration to higher values [267]. For example, the Bulgarian catalyst K-31 contains 3.9% Al_2O_3, 2.3% CaO, 0.4% MgO, 0.8% SiO_2, and 1.8% K_2O. An older Norsk Hydro catalyst, besides the usual additives, contained 1.14% SiO_2 and 1.57% K_2O. The ICI catalyst with composition 5.2% CoO, 1.9% CaO, 0.8% K_2O, 2.5% Al_2O_3, 0.2% MgO, 0.5% SiO_2, remainder Fe_3O_4, is substantially more active than the conventional cobalt-free catalysts [251], [280]. Reducing the synthesis pressure and/or the synthesis temperature should enable application of the Lummus [249], [281] and Ammonia Casale [250] cerium-containing catalysts.

The effect of the promoters on the rate of reduction and the temperature required for reducing the iron oxide phase is also significant in industrial practice. The structural promoters, such as Al_2O_3, lower the rate of reduction [264], [282], [283]. Magnesium oxide-activated iron, said to be thermally stable up to 650 °C, needs a higher reduction temperature than aluminum oxide-promoted iron catalyst [284]. Greater differences in reducibility have also been observed in commercial catalysts with similar chemical composition [285] and in connection with particular oxide phases, such as $CaFe_3O_5$ and FeO [285]–[287]. Early work [288] referred to the rough parallels between the reducibility and the thermal stability of catalysts. All published experience appears to demonstrate that it is not possible to combine in a catalyst high thermal stability with easy reducibility and high activity at low temperatures. Hence it may be advantageous to use a combination of active and thermally-resistant catalysts in the same converter.

Mechanism of the Promoter Effect. The action of the so-called structural promoters (stabilizers), such as Al_2O_3, is closely associated with their solubilities in the iron oxide matrix of the unreduced catalyst or with the capability of the regular crystallizing magnetite to form solid solutions with iron–aluminum spinels [33], [289]–[291]. The solid solutions of Fe_3O_4 and the spinel $FeAl_2O_4$ have a miscibility gap below 850 °C [292]; at 500 °C, the solubility limit in the magnetite mixed crystal is a maximum of 7.5% $FeAl_2O_4$, i.e., 3% Al_2O_3, referred to iron. Higher alumina contents lead to separation into two phases, whereby only the portion dissolved in the magnetite phase appears to be responsible for the specific promoter action of alumina [255], [256], [293]. According to [294], there exists a close connection with the mechanism of the reduction which consists schematically of the following partial steps [295]:

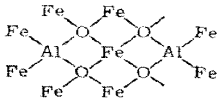
1) Phase-boundary reaction of hydrogen with oxygen ions of the magnetite lattice, with formation of water vapor and release of electrons

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2) Formation of metallic iron nuclei by combination the electrons with Fe^{2-} ions
3) Diffusion of Fe^{2+} ions and electrons to the nuclei and growth of the nuclei to iron crystals of various size

A more detailed discussion of the reduction mechanism is given in Section 3.6.1.4.

In the presence of dissolved aluminum ions, at not too high a temperature, the diffusion rate of the iron ions in the magnetite lattice is low. Hence, nucleus formation proceeds rapidly relative to crystal growth. Therefore, small iron crystallites, about 30 nm, form with correspondingly large specific surfaces. The aluminum probably remains partly in the iron crystallite in the form of very small $FeAl_2O_4$ areas statistically distributed over the lattice [262], [263], [294], [296], where an $FeAl_2O_4$ molecule occupies seven α Fe lattice positions [101].



According to this concept, the stabilizer function of alumina reduces to paracrystalline lattice defects; an analogous effect is to be expected with Cr_2O_3, Sc_2O_3, etc. [262], [296]. Another theory is based on the observation that during reduction part of the alumina precipitates with other promoters into the surface of the iron crystallite in a molecularly dispersed distribution [258], [297] or in small islands [254]. This "patchy" monolayer of alumina acts like a "spacer" between iron atoms of neighboring crystallites and prevents sintering by means of a "skin" effect [263]. (See also [101], [110], [253].)

Insofar as small crystals of nonreducible oxides dispersed on the internal interfaces of the basic structural units (platelets) will stabilize the active catalyst surface Fe(111), the paracrystallinity hypothesis will probably hold true. But the assumption that this will happen on a molecular level on each basic structural unit is not true. The unique texture and anisotropy of the ammonia catalyst is a thermodynamically metastable state. Impurity stabilization (structural promotion) kinetically prevents the transformation of platelet iron into isotropic crystals by Ostwald ripening [154]. Thus the primary function of alumina is to prevent sintering by acting as a spacer, and in part it may also contribute to stabilizing the Fe(111) faces [155], [156], [298].

Calcium oxide, which also acts as a structural promoter [253] has a limited solubility in magnetite. It tends to stretch the magnetite lattice [101]. In the main, on cooling the magnetite melt, it separates at the grain boundaries as $CaFe_3O_5$ (at very rapid cooling rates) [285] and, in the presence of SiO_2, forms poorly reducible intermediate layers of calcium ferrite and silicates [253], [286]. In the reduced catalysts, it segregates between the iron crystallites [260], [299] and so possibly prevents sintering together at high operating temperatures. One may also presume that by partial neutralization of the "acid" components by calcium, more potassium is made available for activating the iron [196].

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Potassium is likewise scarcely soluble in magnetite because of its ionic size [100]. In the unreduced catalysts, separate potassium- and iron-rich regions were found [109]. The appearance of a $K_2Fe_{22}O_{34}$ phase besides an unidentified phase, however, has been proved [300]. According to [301], during reduction, the emerging K_2O migrates to the iron crystallite surface. While doing this it reacts with the more or less homogeneously distributed aluminum (silicon) compounds. In this way, it is distributed over the iron phase. In the reduced catalysts, the potassium exists as a K + O adsorption layer that covers about 20 – 50 % of the iron surface [109]. According to [259], [302], potassium associates partly with the alumina in the surface, partly as KOH with iron [303]. It was found that the enhancement of the catalysts' specific activity by potassium oxide is accompanied by a decrease in the electron work function [302], [304], [305]. The promoting effect of potassium seems to be based on two factors which probably act simultaneously. One mechanism is the lowering of the activation energy for the dissociative adsorption of nitrogen [101], [109]. The explanation is based on an electrostatic model [107], [142], [306]. As indicated by the strong decrease in the work function upon potassium adsorption, there is a considerable electronic charge transfer to the substrate, which creates a $M^{\delta-} - K^{\delta+}$ dipole. A nitrogen molecule adsorbed near such a site will experience a more pronounced back-bonding effect from the metal to its antibonding π orbitals. This will increase the bond strength to the metal and further weaken the N – N bond, as can be seen from a further reduction of the N – N stretching frequency [307]. The other effect consists of lowering the adsorption energy of ammonia, which avoids hindering of nitrogen adsorption by blocking (poisoning) of the catalyst surface by adsorbed ammonia molecules [99], [109]; hence, potassium oxide ought to improve the catalyst performance less at low than at higher operating pressures [190], [308].

The negative effect of K_2O concentrations higher than about 0.58 % has not been explained unequivocally [144]. With increasing potassium concentration, this manifests itself by the increasing size of the average iron crystallite or the decreasing specific surface in the reduced catalyst [267], [300]. Since potassium oxide prevents the formation of solid solutions between alumina and magnetite to a certain extent [309], the recrystallization-promoting effect of higher K_2O concentrations may be attributed to a lowering of the portion of alumina dissolved in the magnetite phase [300]. Remarks in [301] and [310] reveal another possible interpretation: the K_2O located at the phase boundary surface and not bound to acid or amphoteric oxides may be converted by water vapor concentrations over 10^{-2} pm in the synthesis gas into potassium hydroxide or by hydrogen into potassium and potassium hydroxide, which would exist in molten form at operating conditions [301], [303].

An extensive review on promoters can be found in [108], and [156] provides a critical discussion of present theoretical interpretations of the promoter effects.

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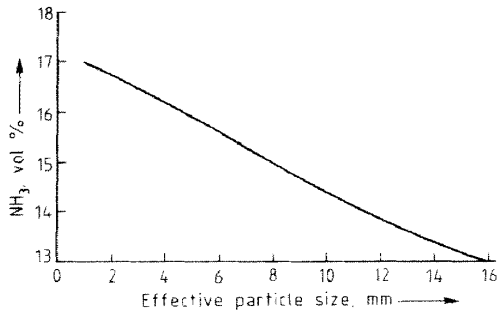


Figure 19. Influence of the particle size on the ammonia production (BASF catalyst).
25 MPa; SV = 12 000 $m^3m^{-3}h^{-1}$ (STP); gas composition (vol %): N_2 20.59, H_2 60.06, NH_3 2.55, Ar 5, CH_4 10

3.6.1.2. Particle Size and Shape

The choice of particle size and shape of commercial ammonia catalysts is determined mainly by two factors:

1) Catalyst performance
2) Pressure drop

From the standpoint of space–time yield, it is desirable to use the finest possible particle, which, practically speaking, is about 1–2 mm (Fig. 19); however, with decreasing particle size, the pressure drop and the risk of destructive fluidization of the catalyst increase (Fig. 20).

For processes operating at pressures of 25–45 MPa (250–450 bar) and at space velocities of 8000–20 000 $m^3m^{-3}h^{-1}$ (STP) a grain size of 6–10 mm is preferred. Larger granulations, for example, 8–15 mm or 14–20 mm, are used only in plants where the lowest possible pressure drop is essential because of very high gas velocities. In catalyst zones in which the ammonia formation rate is so high that the allowable temperature limits are exceeded, it may be advantageous to use coarse particles for suppressing the reaction. Radial-flow converters and the horizontal crossflow Kellogg converter (Fig. 91), which operate at comparatively low gas velocities [311], allow the use of small granulations (1.5–3 or 2–4 mm) with optimal use of the converter volume. Fluidized-bed processes, which have been explored especially in the Soviet Union, have so far been unsuccessful [312], [313].

Two effects cause the low production capacity of coarse-grained catalyst: first, large grain size retards transport of the ammonia from the particle interior into the bulk gas stream, because this proceeds only by slow diffusion through the pore system. Slow ammonia diffusion inhibits the rate of reaction. At the high reaction rate typical for the converter inlet layer, only a surface layer of the catalyst grains, about 1–2 mm thick, participates in the reaction.

The second effect is a consequence of the fact that a single catalyst grain in the oxidic state is reduced from the outside to the interior of the particle [314]: the water vapor produced in the grain interior by reduction comes into contact with already reduced

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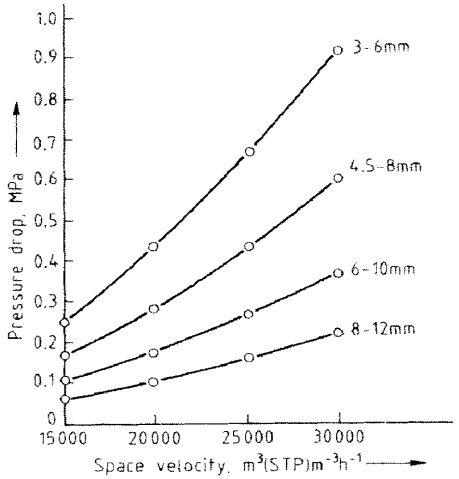


Figure 20. Pressure drop in the catalyst bed for various catalyst particle size ranges, from [33]. Depth of the catalyst bed, 7 m; reaction pressure 27.1 MPa; reaction temperature 450 °C

catalyst on its way to the particle outer surface; this induces a severe recrystallization [33]. The effect is very significant. As an example, if the particle size increases from about 1 to 8 mm, the inner surface decreases from 11 – 16 m^2/g to 3 – 8 m^2/g [315].

To allow for the influence of various particle shapes and size distributions within a defined sieve fraction, in lay-out calculations it is customary to employ an effective particle diameter, d_{eff}, as nominal size [32]. The diameter d_{eff} is defined as the ratio of equivalent diameter Λ and a form factor ψ. Λ is equal to the diameter of a sphere with a volume equal to the (average) volume of the particles, and ψ is the average ratio of the particle surface to the surface of a sphere of equal volume.

Table 18 shows the relation between the catalyst size classification, the equivalent particle diameter, and the percentage saving in catalyst or converter volume relative to the 6 – 10 mm standard size [280].

An irregular grain shape, for example with a shape factor of 1.5, has a more favorable effective activity for the individual particle and for radial intermixing of mass and heat in an industrial converter [316] than a more cubic or spherical shape, with a shape factor close to one. According to a patent by Chemie Linz AG [317], the catalyst particle ought to be 2 – 20 times as long as it is broad, preferably 5 – 10 mm long and 1 – 2 mm thick (broad). On the other hand, regular shapes have the advantages of greater abrasion resistance and lower pressure drop (see Fig. 21) [318].

The advantages of regular catalyst shapes and the need to compensate for the above-described negative effects of larger grain size by a system of macropores in the oxidic and reduced catalyst stimulated various attempts to manufacture shaped, macroporous catalysts. Various manufacturing techniques have been proposed [319] – [328]. As an example, magnetite is melted with the additives at high temperature (> 1600 °C) and the melt is cooled, broken, and ground to powder. After water is added and, if required, a binding agent, such as bentonite [327], or a promoter salt, such as cerium

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Table 18. Effect of catalyst size on catalyst volume

Catalyst size classification, mm	Approximate equivalent particle diameter, mm	Relative catalyst volume, %
6 – 10	7.5	100
4.5 – 8	5.5 – 6.5	92 – 95
3.6	4.5 – 4.7	88 – 90
1.5 – 3	2.0 – 2.2	80 – 82
1 – 1.5	1.2 – 1.3	77 – 79

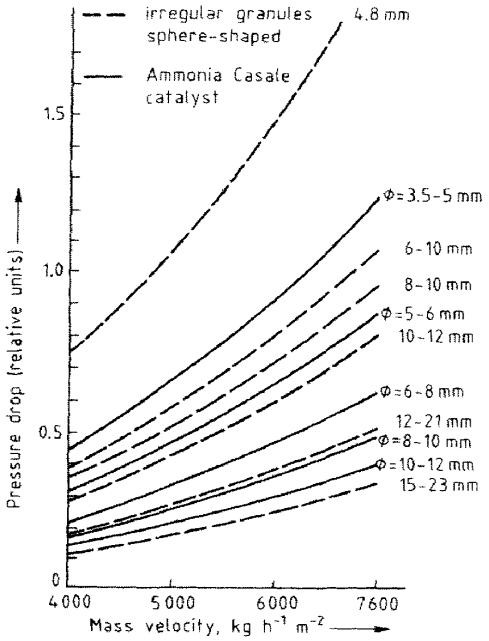


Figure 21. Comparison of the Ammonia Casale spherical catalyst and irregularly shaped catalyst [280]

nitrate [250], the powder is pelletized. The pellets subsequently are dried and sintered in an inert atmosphere at higher temperatures (about 1350 °C).

The application of macroporous catalysts ought to be especially useful for very low synthesis pressures and in plants in which large catalyst particles must be used for reasons of low pressure drop. For example, the performance of the macroporous Topsøe catalyst KMG 6 mm at 5 MPa synthesis pressure is said to be at least equivalent to KM I 1.5 – 3 mm and distinctly superior to KM I 6 – 10 mm [329].

3.6.1.3. Catalyst-Precursor Manufacture

The term "ammonia catalyst" commonly refers to the oxidic form consisting of magnetite and oxidic promoters. In fact this is only the catalyst precursor which is

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transformed into the active catalyst composed of α-iron and promoters by reduction with synthesis gas, usually in situ. The reduction step is very important for catalyst performance.

The first effective catalysts were made by the oxygen-melt process. The purest possible iron (e.g., Swedish charcoal iron), together with the additives, was burned to Fe_3O_4 in a stream of oxygen. This process was largely replaced by melt processes in which natural or, less frequently, synthetic magnetite, together with the activators, was melted electrically or in electric arc furnaces [241], [330]. The cooled melt is ground to the proper granulation and reduced with hydrogen – nitrogen mixtures.

A process developed by Farbenfabriken (formerly Friedrich Bayer) had only local significance and is today only of historical interest. Complex iron cyanides were decomposed thermally in the presence of hydrogen. The hydrodecomposition proceeds via the carbide and nitride, finally to α iron. This is activated in the well-known manner by reduction-resistant metal oxides. The so-called Mont Cenis process employed such catalysts [331]. Repeatedly described as a means of manufacture, although only in the scientific literature, is coprecipitation of the catalyst components, for example, from aqueous solutions of the metal salts, with subsequent calcining and reduction [332] – [335]. With magnesium oxide as support, very small (under 10 nm) iron particles are obtained with high specific iron surfaces [335], similar to those obtained by exchange of magnesium ions by iron ions in the surfaces of magnesium hydroxy carbonate crystals [335], [336]. Granulation and sintering techniques have been used for the preparation of shaped macroporous iron catalysts, described in Section 3.6.1.2, which, however, have not gained industrial importance.

Impregnating the pore surface of prereduced passivated catalysts is a possibility for incorporating promoters into iron ammonia catalysts. A United Kingdom patent [337], by way of example, claims catalysts manufactured by impregnating the reduced catalysts with cerium salts. Improving the performance and life of industrial catalysts by radioactivity and X rays [338], treatment with ultrasound [339], [340], mechanical treatment [341], or high-frequency, alternating-field heating [342] has been attempted also.

The superiority of the catalyst manufacturing processes that use a molten iron oxide stage is mainly due to the fact that above 1000 °C in air, magnetite, Fe_3O_4, is the thermodynamically stable oxide phase of iron [8], [343]. Magnetite leads to especially efficient catalysts, and its electrical conductivity allows the use of economical electrical melting processes.

In 1996 the prices of commercial ammonia catalysts were about 2 $/lb (7 DM/kg) for oxidic and about 5.5 $/lb (20 DM/kg) for prereduced. Therefore, they are among the least expensive catalysts.

Operating conditions in the individual manufacturing steps — proportioning and mixing the raw materials, melting, cooling, crushing or if necessary grinding and preforming, and reduction — influence the quality of the finished catalyst (Fig. 22) [230].

The raw materials — usually, natural magnetite, lime, potash, and alumina — must, as far as possible, be free of catalyst poisons (see Section 3.6.1.5). Many ores have too high a content of free or bound silica, which can be lowered with magnetic separators [344]. Melting is accomplished in electrical resistance or induction furnaces (arc furnaces in the past) operating at 1600 – 2000 °C. The walls of these furnaces should

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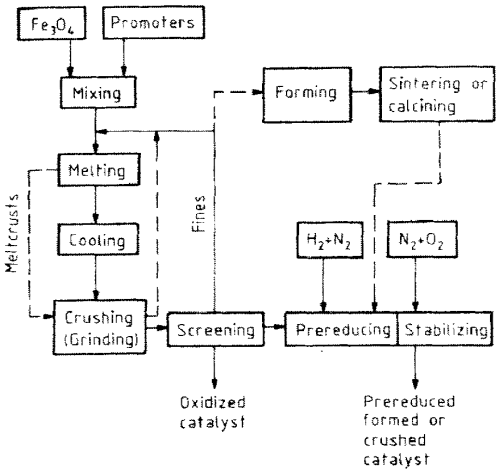


Figure 22. Ammonia catalyst manufacture

consist of a weakly basic tamping material indifferent to the melt, such as magnesium oxide, which is also an activating component of the catalyst [345]. A homogeneous distribution of the promoters in the magnetite melt and a degree of oxidation at or under that of stoichiometric magnetite should be obtained. This is said to be promoted by initially overheating to temperatures up to 3500 °C [346] (Fig. 23). It is claimed to be advantageous to bring the promoters into the melt as common chemical compounds that are isomorphous with magnetite [347].

Induction furnaces are optimal for the melting operation. Their good temperature control permits accurate adjustment of the degree of oxidation. Since the melt is held in constant turbulent motion by the magnetic field produced in the primary coil, it is well mixed, even for short melt times. In comparison to the most frequently used resistance furnaces, plant cost and power consumption are higher.

Another important factor in catalyst manufacture is the melt cooling rate, which is affected by the design and dimensions of the ingot molds. Quenching or fast cooling in thin sheets leads to a less abrasion-resistant, sharp-edged chip after crushing. Very slow cooling results in a more cubic chip, but with inferior catalyst quality (Fig. 23). In practice, slow cooling is avoided.

With falling temperature, both the solubility of the activator oxides (see Section 3.6.1.1) in magnetite and the rate of adjustment to the new phase equilibrium decline. Therefore, by rapid cooling of the melt the activator oxide distribution can be frozen in a condition corresponding to that of a higher temperature [348]. According to [285], there may exist relationships between the melt cooling rate, the appearance of certain phases, and the reducibility of the catalysts.

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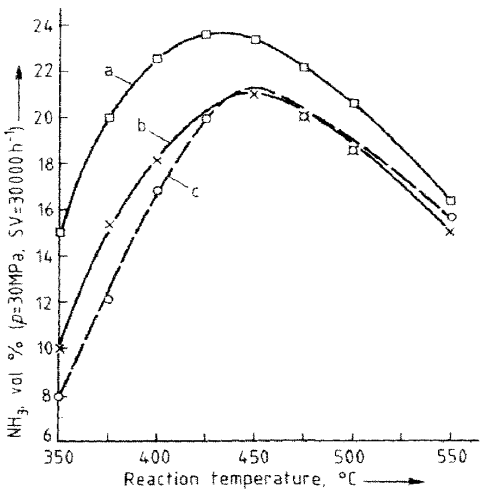


Figure 23. Effect of the melting temperature and rate of cooling of the melt on the activity of ammonia catalysts
a) Melt overheated to 3500 °C (rapid cooling); b) Melt temperature 1800–2000 °C (rapid cooling); c) Melt temperature 1800–2000 °C (slow cooling)

3.6.1.4. Catalyst Reduction

The reduction of oxidic catalyst is generally effected with synthesis gas. The magnetite is converted into a highly porous, high surface area, highly catalytically active form of α-iron. The promoters, with the exception of cobalt, are not reduced [33].

To ensure maximum effectiveness of the catalyst, a defined reduction procedure must be followed. Above all, it is important to hold the partial pressure of the resulting water vapor as low as possible and to insure that the water vapor does not come into contact with regions that have already been reduced [359]. High temperature and high water vapor partial pressure markedly accelerate premature catalyst aging by recrystallization. Therefore, the reduction should be carried out at high gas velocities [about 5000–15 000 $m^3m^{-3}h^{-1}$ (STP)], at the lowest temperatures sufficient for complete reduction, and at not too high pressures (7–12 MPa in low-pressure, 25–30 MPa in high-pressure plants) to hold the exothermic formation of ammonia under better control during the reduction. When the reduction of the oxidic catalyst is carried out in the production plants, long reduction times are needed at low temperatures and low pressures with a consequential loss of production.

In practice, the reduction temperature is raised stepwise by using the exothermic heat of ammonia formation. The progress of the reduction is controlled according to the catalyst temperature and the water concentration by adjustment of the synthesis gas flow. As a rough guideline, the water content of the gas effluent from the catalyst should not exceed 2–3 g/m^3 (STP). Under these conditions, depending on its size and operating pressure, a synthesis converter with a fresh load of oxidic catalyst attains its full production capacity in 4–10 d.

The minimum temperatures necessary for reduction are somewhat different for the various catalyst types. Catalysts conventionally employed in medium-pressure plants

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may be reduced from about 340 to 390 °C, although a slow induction period starts somewhat lower. Generally, temperatures above 440 °C are required to complete the reduction.

The reducibility of industrial catalysts is dependent on both the combination of promoters and the degree of oxidation. The FeO (wustite) phase is reduced faster and at lower temperatures than the Fe_3O_4 (magnetite) phase [285]. According to [285], the rather considerable differences in the reduction rates of commercial catalysts with similar compositions may be attributed to differences in manufacturing methods or operating conditions. Commonly, the manufacturers hold these in strict secrecy.

Some older publications deal with the influence of catalyst granulation on the optimum reducing conditions [349]. Directions for reduction in multibed converters that combine fine- and coarse-grained catalyst appear in [350]. The influence of the hydrogen/nitrogen ratio during reduction on the catalyst performance after reduction is discussed in [351].

The influence of the reduction conditions (gas flow rate, temperature in the range 300 – 600 °C, nitrogen content in the hydrogen in the range 0 – 100 %) on the production capacity of an ammonia catalyst has been investigated [352].

The gas/solid reaction between magnetite and hydrogen has been studied in great detail by rate measurements, microscopy, and X-ray diffraction [353] – [356]; a summary is given in [156] and [264]. According to one model, on an atomic scale the reaction is controlled by two processes:

1) Metallic iron is formed from wustite (Eq. 24) by direct chemical reaction controlled in the initial phase by the reaction rate (activation energy ca. 65 kJ/mol) and in the final stage by diffusion processes involving hydrogen and water on the reaction site:

$$FeO + H_2 \longrightarrow Fe + H_2O \tag{24}$$

2) The chemical reaction creates an iron(II) ion concentration gradient in the solid. This gradient leads to a rapid diffusion of iron(II) ions from magnetite through wustite to the chemical reaction interface, where they are reduced and precipitated as iron nuclei. This is made possible by the structural defects of the wustite. The precipitation of further wustite nuclei on the magnetite/wustite reaction interface seems to be effected by ion/electron diffusion processes rather than by direct contact of magnetite with hydrogen [357] (Eqs. 25, 26):

$$O^{2-} + H_2 \longrightarrow H_2O + 2\ e^- \tag{25}$$

$$Fe_3O_4 + Fe^{2+} + 2\ e^- \longrightarrow 4\ FeO \tag{26}$$

The topotactic reduction process leads to a core and shell structure which is visible under the optical microscope and is shown schematically in Figure 24 (a). Figure 24 (b) shows the wustite/magnetite interface as observed by electron microscopy [264]. This concept was developed for single-crystal magnetite grains, but the shell and core model is also discussed for commercial polycrystalline catalysts [264], [358]. But this model seems to contain too many simplifications [156]. For example, it is difficult to explain with this model why water diffusing through porous iron in contact with oxo anions

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would not reoxidize it. Therefore it might be viewed more as a formal description rather than a mechanical approximation. A more detailed atomistic view of the reduction reaction indicates that migration of electrons and reactants through intrinsic and extrinsic defects will control the kinetics of the reaction. Information in this respect was gained from metallurgical reduction processes [1470]–[1473]. According to this, a gradient in chemical potential of the iron ions is required for a satisfactory progress of the reaction. This gradient is established by iron metal nuclei which are formed from metastable wuestite existing in the mosaic-like crystals of the precursor. Consequently there should be no homogeneous topotactic reaction interface, as assumed in the shell and core model. According to the alternative model, the active catalyst should not grow as a shell around a core of percursor material but as a core within an oxidic matrix. Reaction equations for this reaction may formulated as follows (Eqs. 27–31) [156], [1472], [1473].

$$4\ O^{-2} + 4\ H_2 \longrightarrow 4\ H_2O + 2\ e^- \tag{27}$$

$$Fe_3O_4 + Fe^{2+} + 2\ e^- \longrightarrow 4\ FeO \tag{28}$$

$$4\ FeO \longrightarrow 4\ Fe^{2+} + 4\ O^{2-} \tag{29}$$

$$4\ Fe^{2+} \longrightarrow 8\ e^- + 4\ Fe \tag{30}$$

Overall reaction:

$$4Fe_3O_4 + 4\ Fe + 4\ H_2O \longrightarrow 4\ Fe + 4\ H_2O \tag{31}$$

The equation of the overall reaction suggests the process is at least in some formal way autocatalytic. As all atoms of the activated catalyst should move through the matrix, there will be no structural correlation on an atomic scale between the starting material (precursor) and the product (active catalyst). In contrast to the simple core and shell model, a reproduction of the oxide morphology of the precursor could not be expected for the final reduced catalyst. An explanation of how the desired iron platalet microstructure could be formed is seen in the topochemistry of the iron nuclei which result from a decomposition of wuestite into iron and platalets of secondary magnetite. The presence of wuestite is thus thought to be essential. According to SCHÖGL [156] this could be a first hint of a difference between normal iron and "ammonia iron". Information on the reduction kinetics, including industrial catalysts, can be found in [154], [156], [314], [360], [364]–[367]. Newer findings also seem to question the shell and core model with the topotactic reaction interface [156].

Prereduced, stabilized catalyst types, introduced on the market some years ago, have gained a considerable market share. Prereduced catalysts have the full pore structure of active catalysts, although the pore surface has been oxidized to a depth of a few atomic layers to make these catalysts nonpyrophoric.

Reactivating such catalysts usually takes only 30–40 h. Ammonia formation begins at substantially lower temperatures, so that altogether the downtime of a production unit is reduced markedly. This and further advantages, such as reducing the risk of damaging the catalyst during activation by too high a local concentration of water, the

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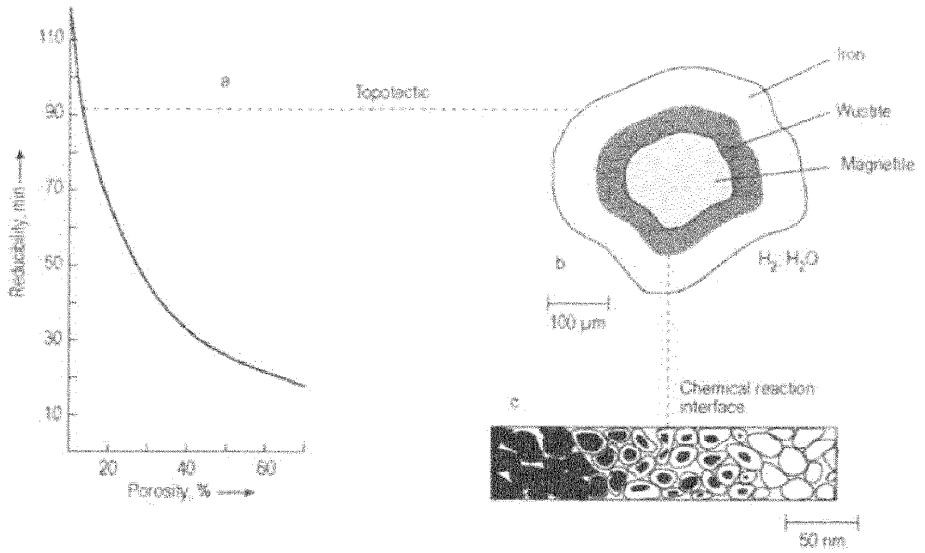


Figure 24. Core and shell mechanism of catalyst reduction [264]
a) Reducibility of catalyst under standard conditions as a function of its porosity; b) Core and shell structure of catalyst; c) Reaction interface

quantitatively lower yield of aqueous ammonia solution (which can be added to the production), as well as the roughly 20% lower bulk weight (which reduces the design loadings and costs of the internals of large converter units), make using prereduced catalysts increasingly attractive, especially in single-train plants, in spite of higher prices. The somewhat inferior mechanical strength is a disadvantage that requires special care when a charge is being loaded into the converter.

Reduced catalyst is pyrophoric in the atmosphere; therefore, it has to be stabilized by passivating the surface with oxygen after the reduction with hydrogen/nitrogen mixture at low to moderate pressure before it can be removed from the reduction reactor for packing and shipping. Usually, the method recommended by BURNETT is used. The reduced charge is treated with nitrogen containing 100 – 1000 ppm oxygen at 50 – 70 °C (maximum 95 °C) and a pressure of 0.1 – 0.2 MPa (1 – 2 bar) and up [368]. The reducible oxygen content of the prereduced catalyst ranges between 2 and 7%. Part of this is only loosely bound and is removed in reactivation even below 200 – 300 °C.

Detailed data on the manufacturing steps most important to the catalyst performance, reduction, prereduction, passivating, and reactivation, appear in [33], including a discussion of the most important literature in this field.

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3.6.1.5. Catalyst Poisons

The activity of an ammonia synthesis catalyst may be lowered by certain substances, commonly referred to as poisons. These substances can be minor gaseous constituents of the synthesis gas or solids introduced into the catalysts during the manufacturing procedure, derived from impurities in the natural magnetite from which the catalyst is made. These latter should not play a major role with catalysts from manufacturers of repute and are not discussed in detail in this section because of the proprietary nature of the production processes. General measures to avoid this sort of contamination include selecting a rather pure magnetite, the application of pre-treatment processes, and the use of high-purity promoters. The melting process itself may also contribute to minimizing the content of some minor impurities. For gaseous poisons in the synthesis gas, a distinction can be made between permanent poisons that cause irreversible damage to the catalyst and temporary poisons which lower the activity while present in the synthesis gas. In contrast to temporary poisons, permanent poisons can be detected on the catalyst by chemical analysis. Oxygen-containing compounds such as H_2O, CO, CO_2 and O_2 are the most common temporary poisons encountered in ammonia synthesis.

Oxygen compounds have a reversible effect on iron catalysts at not too high temperatures. That is, the activity of a damaged catalyst may be practically completely restored by reduction with clean synthesis gas. Equivalent concentrations of oxygen compounds, for example, 100 ppm of O_2 or CO_2 and 200 ppm CO or H_2O, lead to the same degree of poisoning, presumably because as soon as they enter the catalyst bed they rapidly and completely transform into H_2O [33]. The damage depends approximately linearly on the quantity of adsorbed water taken up by the catalyst [369], which is proportional to $\sqrt{p_{H_2O}}\sqrt{p_{H_2}}$ [370]. Corresponding to the adsorption equilibrium, the degree of poisoning therefore rises with growing partial pressure ratio, p_{H_2O}/p_{H_2} and falls with increasing temperature.

Under the assumption of a displacement equilibrium (Eq. 32) in accordance with

$$(N_2)_{ads} + H_2O_{gas} + 2\ H_{2gas} \rightleftharpoons (O)_{ads} + 2\ NH_3 \tag{32}$$

I. A. SMIRNOV et al. set up a rate equation for ammonia synthesis [371], [372] that takes the effect of water vapor into consideration over a wide range of temperature and pressure:

$$v = \frac{k_1 p_{N_2} - k_2 p_{NH_3}^2/p_{H_2}^3}{\left(p_{NH_3}^2/p_{H_2}^2 + C\, p_{H_2O}/p_{H_2}\right)^{1/2}} \tag{33}$$

and found the values of C listed in Table 19.

A more recent investigation [373]–[375] proposed multiplying the rate equation by a correction factor $1-\Theta$, where $\Theta = a + bT + cT \ln X_{H_2O}$ and X_{H_2O} is the molar fraction of H_2O. Some authors assume a different route (Eq. 34) for the formation of adsorbed atomic oxygen [376], [377]:

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Table 19. C values for the ammonia synthesis rate equation

Catalyst	Temperature, °C				
	400	425	450	475	500
$Fe + Al_2O_3$	0.63	0.39	0.24	0.17	0.12
$Fe + Al_2O_3 + K_2O$	0.74	0.46	0.28	0.20	0.14

$$H_2O(g) + 3^* \rightleftharpoons 2\ H^* + O^* \qquad (34)$$

where * denotes a surface site.

Recent reports have confirmed the equivalence of H_2O, CO, CO_2 and O_2 [378] with respect to their poisoning effect.

The experimentally determined effect of water vapor concentrations up to about 30 ppm on the activity of a commercial catalyst (BASF S 6–10) at 30 MPa is evident from Figure 25.

With continuing exposure oxygen compounds also cause irreversible damage to the catalyst activity that is causally linked with growth of the iron primary crystallite [375], [379]. This is probably one of the main causes of the decline in converter performance over the course of the catalyst operating life. This damage depends on the water-vapor partial pressure and is especially serious, in contrast to reversible poisoning, at high temperatures. In a pilot plant, Österreichische Stickstoffwerke (ÖSW), Linz, established that at 30 MPa and a water-vapor content of 250 ppm, for example, the production declined by about 15 % per month. For a carbon monoxide content of 5 ppm, they determined about a 4 – 5 % decrease in activity per year. The influence of the operating temperature is evident from the data. The performance of a catalyst operated at 570 °C is about 35 – 40 % under that of a catalyst charge operated at 520 °C. That is, the higher the temperature, the greater is the harmful effect of oxygen compounds [380]. Corresponding to the data, they established that above all, temperatures above 500 – 520 °C must be avoided in order to achieve a converter charge operating period of more than 2 – 3 years. If the temperature is kept at this level, generally recommended for modern plants, then even at CO concentrations of 20 ppm in the recycle loop gas, no serious deterioration of the catalyst performance is observed after a month of operation. With the highly purified synthesis gas of modern synthesis processes (with final gas purification by methanation the carbon monoxide level is lowered to below 5 ppm), operating periods of up to 14 years can be achieved for a converter charge without significant loss of activity (Fig. 26).

As already mentioned in Section 3.6.1.1, the concentration and combination of promoters affect the degree of irreversible damage. This must be considered in the choice of catalyst for a particular plant.

Sulfur, Phosphorus, and Arsenic Compounds. Sulfur, occasionally present in synthesis gases from coal or heavy fuel oil, is more tightly bound on iron catalysts than oxygen. For example, catalysts partially poisoned with hydrogen sulfide cannot be regenerated under the conditions of industrial ammonia synthesis. Compounds of phosphorus and arsenic are poisons but are not generally present in industrial synthesis gas. There are

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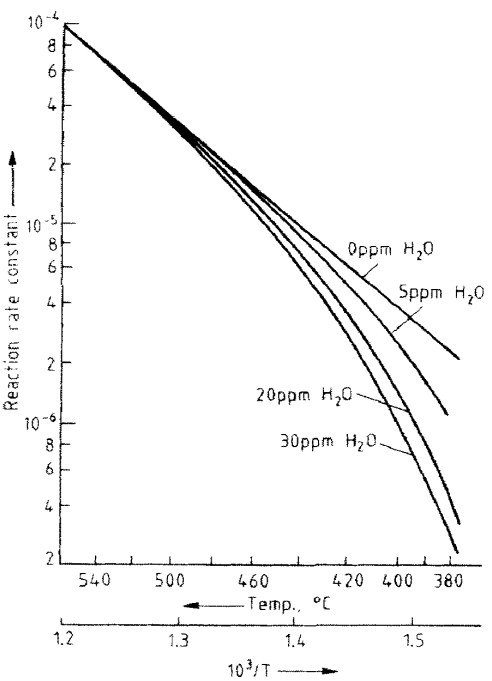


Figure 25. Reversible effect of increasing water vapor concentrations in the synthesis gas on the activity of industrial ammonia catalysts

indications that these permanent poisons exert the most detrimental effect when present as hydrogen compounds and are less harmful in higher oxidation states [381].

With regard to the sulfur bound on the catalyst surface, differences exist between the various types of ammonia catalysts, especially between those that contain alkali and alkaline earth metals and those that are free of them. Nonpromoted iron and catalysts activated only with alumina chemisorb S_2N_2 and thiophene. When treated with concentrations that lie below the equilibrium for the FeS bond, a maximum of 0.5 mg of sulfur per m^2 of inner surface or free iron surface is found; this corresponds to monomolecular coverage [382], [383]. The monolayer is also preserved on reduction with hydrogen at 620 °C, whereas FeS formed by treatment above 300 °C with high H_2S concentrations is reducible as far as the monolayer. For total poisoning, 0.16 – 0.25 mg S/m^2 is sufficient. Like oxygen, sulfur promotes recrystallization of the primary iron particle.

Under similar poisoning conditions, alkali- and alkaline earth-containing industrial catalysts adsorb more H_2S. In spite of this, however, in terms of activity, they are more stable toward the action of sulfur and are partially regenerable [383]. In a catalyst bed, most of the sulfur already has been taken up in the gas inlet layer. A catalyst sulfur content of several 100 ppm suffices to impair its activity [33].

In industrial plants, sulfur may reach the ammonia converter in various forms. In some plants, traces of H_2S and COS may not be removed in the upstream purification

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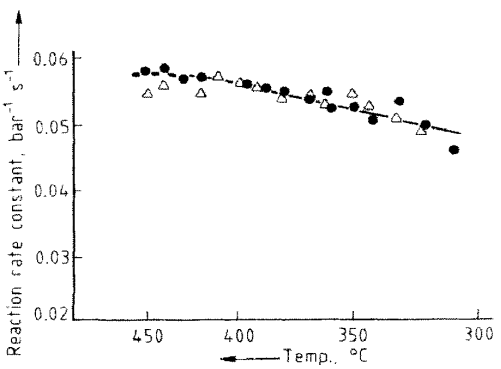


Figure 26. Activity of BASF ammonia catalyst S 6–10 in a commercial converter after 14 years of operation
• fresh catalyst; △ after 14 years operation

steps and so may enter the converter with the makeup gas. However, the sulfur contained in the compressor oil constitutes the main danger. On cracking the oil to lower molecular mass hydrocarbons, sulfur is freed as H_2S. It is therefore very important to use an oil with low sulfur content in ammonia plants, especially those still using reciprocating compressors. If after mixing with the recycle gas the make-up gas first passes through an ammonia condensation stage in which the H_2S and also to a certain extent COS are very effectively washed out by condensing ammonia, a sulfur content of the oil of 0.1 – 0.2 wt % ought to be sufficiently low. Otherwise, a value under 0.1 % is recommended [384]. In modern plants designed with centrifugal compressors and in which the sulfur content of the synthesis gas is extremely low because of very effective purification (about 0.5 – 1 μg S/m^3 (STP)), sulfur poisoning is of lesser importance than carbon monoxide and chlorine poisoning.

Chlorine compounds. The permanent poisoning effect of chlorine compounds is two orders of magnitude worse than that of oxygen compounds. Concentrations of about 0.1 ppm are viewed as the uppermost allowable limit in order not to affect adversely the life of ammonia catalysts [384]. The deactivation effect is based at least in part on the formation of alkali chlorides that are volatile at the upper synthesis temperatures.

Further information on catalyst poisoning is given in [374], [375].

3.6.2. Other Catalysts

3.6.2.1. General Aspects

For a long time efforts to improve the efficiency of industrial ammonia production concentrated on synthesis gas production, and major progress was achieved over the years. In ammonia synthesis itself considerable progress was made in converter design and recovery of the reaction enthalpie at high temperature, but there has been no substantial improvement in the catalyst since the 1920s. The standard commercial iron

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catalyst still requires relatively high pressures (usually in excess of 130 bar), high temperatures (400–500 °C) and large reactor volumes (more than 100 m^3 for a capacity of 1800 t/d) to achieve good economics, although in a few cases a pressure as low as 80 bar has been used. From the vast amount of experimental and theoretical studies of the iron catalyst one can conclude that there is only limited potential for further improvement. Substantial energy savings would require lowering the synthesis pressure considerably, down to the synthesis gas production level, say. However, to compensate for the less favorable equilibrium situation much lower operating temperatures would be necessary, because otherwise too low an ammonia concentration would result, and additional energy would be needed for recovery, thus canceling the energy saving from synthesis gas compression. To reach this goal a synthesis catalyst with a volumetric efficiency some two orders of magnitude greater than magnetite would be necessary. Process studies show an energy saving potential of about 1 GJ/t NH_3 [385].

In the search for an alternative catalyst, most metals have been tested, either as primary components or as promoters. Much of this work was performed in the early, pioneering studies in the BASF laboratories [231], [232]. Most of the studies in the following years concentrated on the magnetite system in the sense of more fundamental and general catalytic research. Rising energy costs since the mid-1960s have given a new incentive to the search for other catalyst systems with improved performance. The first development which found commercial application was a cobalt-modified magnetite catalyst introduced in 1984 by ICI. With similar kinetic characteristics its volumetric activity is about twice that of the standard iron catalyst. The only other catalyst system which exhibits a promising potential for industrial application is based on ruthenium [172]. These new efforts to find improved catalysts could use methods and knowledge of modern surface science as developed on the example of the magnetite catalyst. Structural sensitivity and nature of the nitrogen adsorption and dissociation steps could serve as guidelines [173].

For the overall performance of potential catalysts in practical application additional factors, such as number of active sites, physical form, and porosity must also be taken into account. The classical commercial iron catalyst is an unsupported catalyst. First of all iron is a cheap material and secondly by the incorporation of alumina a surface area similar to that attained in highly dispersed supported catalysts can be obtained. Of course, for an expensive material such as the platinum group metals, the use of a support material is the only viable option. The properties of the supported catalyst will be influenced by several factors [172]

- Adequate surface of the carrier to achieve a reasonable metal loading.
- Dispersion stability by using a more active support with strong interaction between the support phase and the metal precursor. Too strong an interaction may cause difficulties in the metal reducing.
- Promoter localization with respect to metal sites and support sites.
- Gas transport effects will be governed by pore size, pore distribution, and tortuosity.

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– Anion retention capability, which plays a role in the catalyst preparation by impregnation of a support with metal compound solutions.

3.6.2.2. Metals with Catalytic Potential

Materials that show significant ammonia synthesis activity can be divided into three categories according to their ability to form nitrides:

1) Platinum group metals: no stable nitrides (Ru, Os, Ir, Pt)
2) Metals forming nitrides unstable under reaction conditions (Mn, Fe, Co, Ni, Tc, Re)
3) Metals likely to be present as nitrides under synthesis conditions (groups 3–6 of the periodic table)

Of the platinum group metals only ruthenium and osmium show an activity superior to iron, though only in presence of alkali metal promoters, as may be seen from Table 20 [386].

Although osmium was the first active catalyst used by HABER in 1909 [387] in his laboratory-scale unit to demonstrate the technical viability of the high-pressure recycle process, this metal never became an industrial catalyst because of its limited availability and its dangerous properties. The interest of today therefore shifted to ruthenium. The most active ruthenium catalysts use a graphite support and alkali metal promotion, preferentially with rubidium or cesium [388], [389]. It is unlikely that the promoter is in metallic state as its high vapor pressure would probably lead to substantial losses under synthesis conditions. It is assumed that a charge transfer complex $M^+ \cdots C^-$ is formed between the metal and the graphite. A major advantage of graphite is its ability to stabilize high loadings of alkali metals. A special limitation until recently was the chemical reactivity of carbon supports. In a typical ammonia synthesis environment with high hydrogen partial pressure, the catalyst may also catalyze the methanation of carbon, which would lead to destruction of the support. Indeed, this phenomenon has been observed [390], but it can be avoided by careful heat treatment of the support above 1500 °C [391]. With this modified carbon material lifetimes of at least six years are expected [386].

The group of metals forming low-stability or unstable nitrides includes Mn, Fe, Co, Ni, Tc and Re. As in the case of iron a clear structural sensitivity was found for rhenium but the role of promoters remains the subject of discussion. There are also indications of structure sensitivity for cobalt and nickel. It was attempted to improve the activity of the classical magnetite catalyst by alloying with nickel or cobalt. The only commercial catalyst is a cobalt containing magnetite [392].

Of the group of metals forming stable nitrides, only molybdenum is of some interest. Under synthesis conditions it is present as a nitride with some ammonia formation activity and structural sensitivity [393]. Molybdenum also seems to exhibit activity in biological nitrogen fixation [394] and is synthetically active at ambient conditions in the air-sensitive GLEMSER compounds [394].

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Table 20. Ammonia synthesis activity of metals supported on carbon with potassium metal promotion (mL NH_3/mL catalyst, 573 K, 1283.13 mbar, H:N = 3:1

		Fe 0.72	Co 0.4	Ni 0.04
Mo 0.6		Ru 22.2	Rh 0.52	Pd 0
	Re 0.36	Os 5.6	Ir 0.68	Pt 0.008

The results of the intensive research in this field over the last decades demonstrate that, irrespective of the catalyst, the rate-determining step in the ammonia synthesis reaction is the dissociation of the nitrogen molecule and the catalyst effectivity is determined in the first instance by the activation energy of the dissociation reaction. The other common factor for the ammonia catalysis is the structure sensitivity of molecular nitrogen adsorption. Only if both conditions are favorable, and other factors such as hydrogen and ammonia inhibition do not play a major role, can a sufficient overall reaction rate be expected. The available data show that these conditions are fulfilled only for a limited number of metals: iron, ruthenium, and osmium. On account of its very strong ammonia inhibition rhenium is not an option. Extensive literature on non-iron catalysts is given in [172], [173]; kinetic investigations are reported in [173].

3.6.2.3. Commercial Ruthenium Catalysts

Since the early days of industrial ammonia synthesis only minor improvements have been achieved for the magnetite system: optimization of manufacturing procedures, promoter concentrations, and particle size to give somewhat higher activity and longer service life.

The most notable development for the magnetite system was the introduction of cobalt as an additional component by ICI in 1984 [395], [396]. The cobalt-enhanced catalyst formula was first used in an ammonia plant in Canada using ICI Catalco's AMV process (later also in other AMV license plants) and is also successfully applied in ICI's LCA plants in Severnside.

In 1979 BP disclosed to M.W. Kellogg a new catalyst composed of ruthenium on a graphite support [395], [397]. In October 1990, after a ten-year test program, Kellogg started the commercialization of the Kellogg Advanced Ammonia Process (KAAP) using this catalyst [397], which is claimed to be 10–20 times as active as the traditional iron catalyst. According to the patent [392] the new catalyst is prepared by subliming ruthenium-carbonyl [$Ru_3(CO)_{12}$] onto a carbon-containing support which is impregnated with rubidium nitrate. The catalyst has a considerably higher surface area than the conventional catalyst and, according to the patent example, it should contain 5 wt% Ru and 10 wt% Rb. Besides having a substantially higher volumetric activity, the promoted ruthenium catalyst works best at a lower than stoichoimetric H/N ratio of the feed gas as shown in Figure 27. It is also less susceptible to self-inhibition by NH_3 (Figure 28) and has excellent low-pressure activity. A diameter of 1.5–2.5 mm and a

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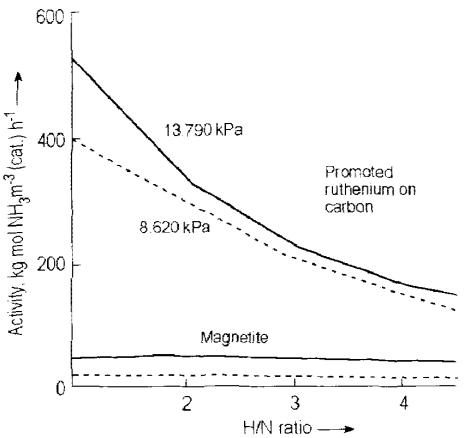


Figure 27. Effect of H/N ratio on activity of Ru and Fe_3O_4 catalysts [172]

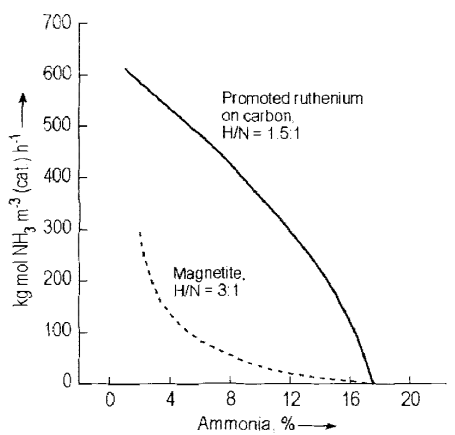


Figure 28. Ammonia inhibition of Ru and Fe_3O_4 catalysts [172]

lenght of about 6 – 7 mm are probably the dimensions of the particles of the commercial catalyst.

The potential for ruthenium to displace iron in new plants (several projects are in progress [398] of which two 1850 mtpd plants in Trinidad now have been successfully commissioned [1488]) will depend on whether the benefits of its use are sufficient to compensate the higher costs. In common with the iron catalyst it will also be poisoned by oxygen compounds. Even with some further potential improvements it seems unlikely to reach an activity level which is sufficiently high at low temperature to allow operation of the ammonia synthesis loop at the pressure level of the synthesis gas generation.

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4. Process Steps of Ammonia Production

Today the term "ammonia synthesis" is increasingly used when referring to the total ammonia production process. Synthesis conditions are no longer viewed in isolation. Of course, they are an important consideration in the total process but can be determined properly only in relation to the total plant integration (see Chapter 5). A review of ammonia production technology up to 1974 is contained in [399], and [400] gives a description of the state of the art up to 1980; the United States patent literature in the field from 1972 to 1980 is covered in [401]. More modern and comprehensive reviews of ammonia production technology can be found in [402] – [404]. The journal *Nitrogen*, published by British Sulphur, presents an update of the state of the art from time to time. A valuable information soure is also the annual AIChE Ammonia safety symposium.

The complete process of industrial ammonia production may be subdivided into the following sections:

A) Synthesis gas production
   1) Feedstock pretreatment and gas generation
   2) Carbon monoxide conversion
   3) Gas purification
B) Compression
C) Synthesis

It has been already mentioned briefly, that compared to the synthesis section itself, where of course some progress has been made in converter design and optimization of heat recovery, the more fundamental changes over the years have occurred in synthesis gas preparation and gas compression. It is therefore appropriate to discuss the various methods for the synthesis gas generation, carbon monoxide shift conversion, and gas purification in some detail. Figure 29 shows schematically the options for the process steps for ammonia production.

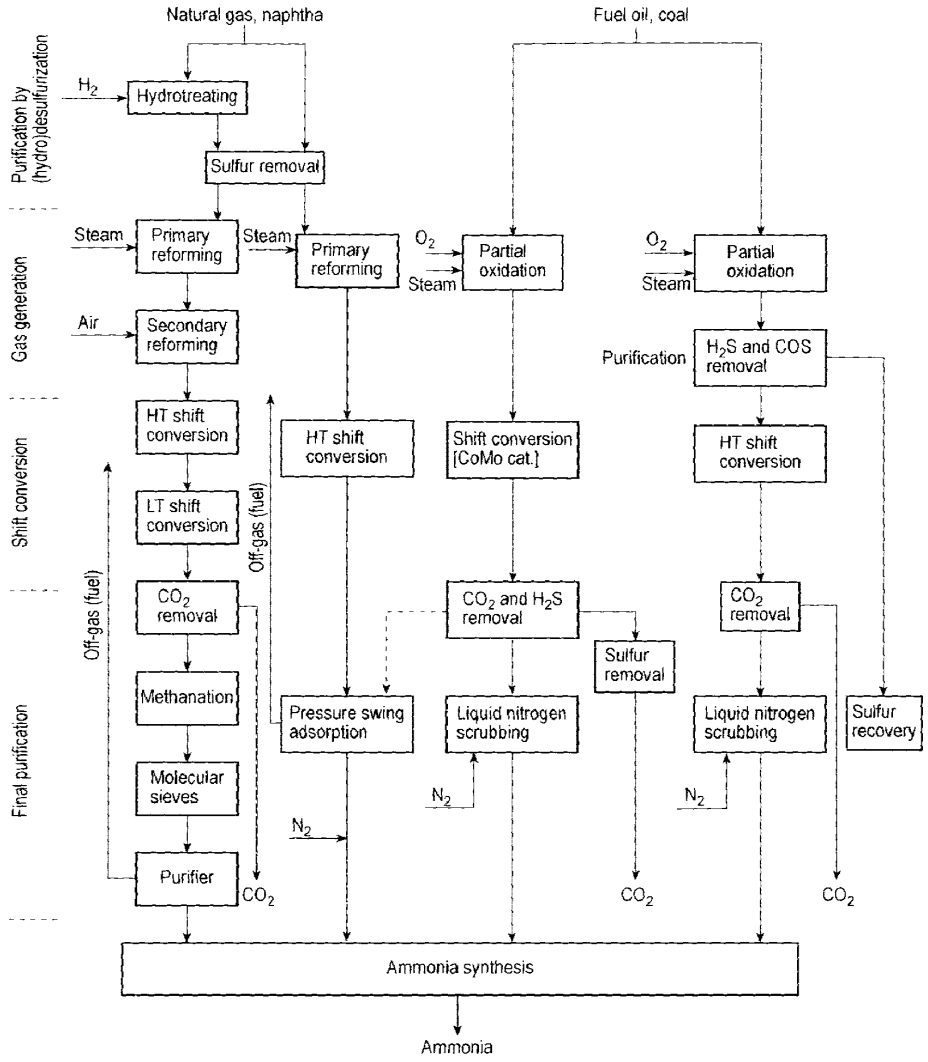
4.1. Synthesis Gas Production

The goal is preparing a pure mixture of nitrogen and hydrogen in the stoichiometric ratio of 1:3. The raw materials are water, air, and a carbon-containing reducing medium, that, for its part, may contain hydrogen (natural gas, CH_4; naphtha, CH_2; petroleum, $\approx$ CH) and nitrogen; for example, natural gas from the Slochteren field in the Netherlands contains 14% nitrogen.

Usually only the carbon-containing materials and hydrogen from other sources are regarded as raw materials in the narrow sense because of the abundance of air, which

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Figure 29. Options for generating and purifying ammonia synthesis gas



provides all of the nitrogen, and water, which generally supplies most of the hydrogen. The term feedstock is often applied to the total consumption of fossil fuel, although strictly speaking a distinction should be made between gasification feed and fuel for energy generation.

Certain raw materials for synthesis gas production that were once of primary importance currently are used only under special economic and geographical circumstances (e.g., China, where 66% of production is based on coal). These include solid

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Table 21. Feedstock distribution of world ammonia production capacity

	1962		1972		1983		1998	
	10^3t N	%	10^3t N	%	10^3t N	%	10^3t N	%
Coke oven gas and coal	2800	18	4600	9	7200	8	16500	13
Natural gas	7800	50	32100	63	66850	74	96300	77
Naphtha	2050	13	10700	21	9050	10	7300	6
Other petroleum products	2950	19	3600	7	7200	8	4400	4
Total	**15600**	**100**	**51000**	**100**	**90300**	**100**	**122500**	**100**

Table 22. Relative ammonia plant investment and relative energy requirement for 1800 t/d NH_3

	Natural gas	Naphtha	Fuel oil	Coal
Relative investment	1.0	1.15	1.5	2.5
Relative specific energy requirement (based on lower heating values)	1.0	1.1	1.3	1.7

fuels, coke oven gas, and hydrogen produced by electrolysis. Reference [405] covers coke oven gas as a feedstock for ammonia synthesis and references [406]–[409] describe producing hydrogen by water electrolysis for ammonia production. If water electrolysis is used the energy requirement amounts to about 10 000 kWh/t NH_3.

Table 21 provides an overview of the raw material sources (apart from water and air) for world ammonia capacity.

Table 21 indicates that new ammonia plants are based almost exclusively on natural gas and naphtha. This trend is also expected to continue in the near future. Naturally, the regional distribution is diverse. In North America, for example, natural gas dominates, with 95 % of capacity. In the EU, 86 % of capacity is based on natural gas and 8 % on fuel oil [410].

The capital cost and the specific energy requirement (i.e., feed and fuel, and so the manufacturing cost) largely depend on the raw material employed [411], [412]. Table 22 shows the relative capital cost and the relative energy requirement for a plant with a capacity of 1800 t/d ammonia. For the natural gas based plant the current best value of 28 GJ/t NH_3 is used.

The chemical reaction of hydrocarbons, carbon, or coke with water, oxygen, air, or any combination of these is generally referred to as gasification. It yields a gas mixture made up of CO and H_2 in various proportions along with carbon dioxide and, where air is used, some nitrogen. Any carbon containing feedstock will undergo a reaction according to Equation (35) or (36) or both simultaneously.

$$[CH_x] + H_2O \rightleftharpoons CO + H_2 + x/2\ H_2 \qquad \Delta H > 0 \tag{35}$$

$$[CH_x] + 1/2\ O_2 \rightleftharpoons CO + x/2\ H_2 \qquad \Delta H < 0 \tag{36}$$

Light hydrocarbons ranging from natural gas (methane) to naphtha (max. C_{11}) undergo reaction with steam over a catalyst according to Equation (35) which is usually

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called *steam reforming*. In the case of coal or coke, Equation (35) corresponds to the noncatalytic water gas process, which in its classical form is today only used in a number of plants in China and is otherwise only of historical interest. Corresponding to Equation (36), commonly known as *partial oxidation*, all carbon-containing feedstocks can be processed in a noncatalytic reaction with oxygen (together with some steam, which gives rise to a simultaneous reaction according to Eq. 35). An additional equilibrium reaction involved in any gasification process is the water gas shift reaction (37).

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \Delta H^0_{298} = -41\ \text{kJ/mol} \tag{37}$$

Although reaction in the right hand direction is favored by lower temperatures it is responsible for the initial carbon content of the raw synthesis gas. To maximize the hydrogen yield, this reaction is carried out in a separate step over a different catalyst at a lower temperature than the preceding gasification step (Section 4.2).

From Equation (35) it can be seen that in the steam reforming variant the proportion of hydrogen supplied by the feedstock itself increases with its hydrogen content. It attains the theoretical maximum of 66 % with methane. The hydrogen – oxygen bond energy in water is higher than the hydrogen – carbon bond energy in the hydrocarbon. The positive enthalpy per mole of hydrogen therefore decreases as the proportion of hydrogen contributed from the feedstock itself increases. Natural gas consists predominantly of methane and is therefore the most hydrogen-rich and energetically the best raw material for the steam-reforming route. In the partial-oxidation route less hydrogen is produced in the primary gasification step and the raw synthesis gas has a rather high CO content.

The raw gas composition is thus strongly influenced by the feedstock and the technology applied. But for the different feedstocks there are some constraints on the applicability of the various gas generation processes. The catalytic steam reforming technology can only be applied to light hydrocarbon feedstock (up to naphtha) but not for heavy hydrocarbons such as fuel oil or vacuum residue. These raw materials contain a substantial amount of sulfur and also minor quantities of heavy metals, which would poison the sensitive reforming catalyst. In addition cracking reactions will occur on the catalyst, depositing carbon, which not only blocks the catalyst pores but also restricts interparticle flow. Thus for heavy feedstocks the only choice is noncatalytic partial oxidation, which, however, is capable of processing any type of hydrocarbon feedstock. The various commercial coal gasification processes may also be classified as partial oxidations.

4.1.1. Steam Reforming

As the nickel-containing catalysts used in the reforming reaction are sensitive to poisons, any sulfur compounds present in the hydrocarbon feedstock have to be removed by hydrodesulfurization, generally with a combination of cobalt – molybdenum and zinc oxide catalysts [413] – [415]. (Eqs. 38, 39). In a few cases, especially with

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a higher sulfur content in the feedstock, for example, in naphtha, nickel – molybdenum catalysts may also be used for the hydrodesulfurization step. Adsorption on activated carbon is an alternative when the feed is natural gas with a rather low sulfur content.

$$R\text{–}SH + H_2 \rightarrow RH + H_2S \quad (38)$$

$$H_2S + ZnO \rightarrow ZnS + H_2O \quad (39)$$

The general overall reaction for the steam reforming of hydrocarbons can be formulated as (40):

$$C_nH_{(2n+2)} + n\,H_2O \rightleftharpoons n\,CO + (2\,n + 1)\,H_2 \quad (40)$$

or more specifically for methane (Eq. 41), usually the major constituent of natural gas, as:

$$CH_4 + H_2O \rightleftharpoons CO + 3\,H_2 \qquad \Delta\,H^0_{298} = +\,206\ \text{kJ/mol} \quad (41)$$

Simultaneous with this equilibrium, the water gas shift reaction (Eq. 37) proceeds, and when this is included we arrive at the formal overall reaction (Eq. 42)

$$CH_4 + 2\,H_2O \rightleftharpoons CO_2 + 4\,H_2 \qquad \Delta\,H^0_{298} = +\,165\ \text{kJ/mol} \quad (42)$$

To introduce nitrogen to achieve the required stoichiometric hydrogen/nitrogen ratio for ammonia synthesis, the reforming reaction is split into two sections. In the first section, the *primary reformer*, the reaction proceeds in indirectly heated tubes filled with nickel-containing reforming catalyst and is controlled to achieve a partial conversion only (in a conventional reformer usually 65 % based on methane feed, leaving around 14 mol % methane in the effluent gas, dry basis). In the following secondary reformer — a refractory-lined vessel filled with nickel catalyst — the gas is mixed with a controlled amount of air introduced through a nozzle (burner). By combustion of a quantity of the gas the temperature is raised sufficiently (to about 1200 °C) that the endothermic reforming reaction is completed with the gas adiabatically passing the catalyst layer. In this way the outlet temperature is lowered to around 1000 °C, and a residual methane content of 0.5 % or lower (dry basis) is attained in conventional plants. Nitrogen already present in the natural gas tends to cause a reduced specific air ratio in the secondary reformer and a reduced secondary reformer temperature rise. Therefore, to maintain the same methane leak, the primary reformer exit temperature must be increased.

4.1.1.1. Thermodynamics, Operation, Pressure, Steam/Carbon Ratio

The steam reforming reaction of methane is endothermic and proceeds with an increase in volume. In Figures 30 and 31 [1487] the relationship between equilibrium methane concentration (a measure for the theoretical possible conversion) and temperature, steam-to-carbon ratio S/C, and reforming pressure are plotted for the range relevant for the reaction in the primary reformer.

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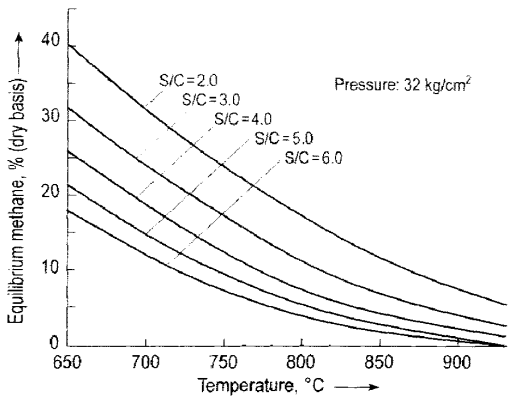


Figure 30. Methane equilibrium versus temperature at various S/C ratios

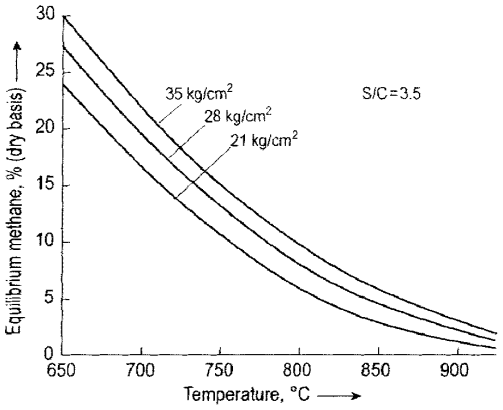


Figure 31. Methane equilibrium versus temperature at pressures

For the industrially interesting range, Equations (43–45) [416] may be used with reasonable approximation, altough they do not include a term for the small temperature dependence of the reaction enthalpy:

$$K_7 = \exp\left[\frac{-27.463}{T} + 30.707\right] \tag{43}$$

$$K_3 = \exp\left[\frac{+4.577}{T} - 4.33\right] < 600\,^{\circ}\mathrm{C} \tag{44}$$

$$K_3 = \exp\left[\frac{+4.084}{T} - 3.765\right] > 600\,^{\circ}\mathrm{C} \tag{45}$$

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A table listing the thermodynamic equilibrium methane concentration in the outlet of the primary and secondary reformer over a wide range of operating pressures, outlet temperatures and S/C ratios can be found in [417] (see also [424]).

Because natural gas is usually under elevated pressure and the reforming reaction entails an increase in volume, significant savings in compression energy can be achieved if the process is performed under elevated pressure. But thermodynamically this is unfavorable: on account of the volume increase, an increase in pressure will reduce the conversion of methane. To compensate this, higher temperatures will become necessary (limited by reformer tube material). On the other hand, higher steam-to-carbon (S/C) ratio have a beneficial effect on the equilibrium methane concentration and could to some extent mitigate the negative influence of the increased pressure, but the penalty is a higher energy consumption.

There are additional reasons for applying a higher S/C ratio. First, it prevents carbon deposition on the catalyst, which may not only increase the pressure drop but also reduce the catalyst activity. As the rate of the endothermic reforming reaction is lowerded this way, it can result in local overheating of the reformer tubes (hot bands) and premature failure of the tube walls. Second it provides necessary steam for the shift conversion (Section 4.2). Third, it reduces the risk of carburization of tube material.

In principle carbon formation may occur via the following reactions (Eqs. 46 – 48):

Boudouard reaction:	$2\,CO \leftrightharpoons C + CO_2$	$\Delta H^0_{278} = -172.5$ kJ/mol	(46)
Methane cracking:	$CH_4 \leftrightharpoons C + 2\,H_2$	$\Delta H^0_{278} = +74.9$ kJ/mol	(47)
Carbon monoxide reduction:	$CO + H_2 \leftrightharpoons C + H_2O$	$\Delta H^0_{278} = -131.4$ kJ/mol	(48)

These reactions are reversible, and there is a dynamic equilibrium between carbon formation and removal. Under typical steam reforming conditions, reactions (46) and (48) are carbon – removing, whilst reaction (47) leads to carbon formation in the upper part of the tube [503]. With naphtha as steam reformer feed, irreversible pyrolysis (as in a steam cracker for ethylene production) with the sequence naphtha → olefins → polymers → coke will occur. The mechanism of carbon formation and the determination of the risk areas in the reformer operating conditions on the basis of relevant equilibrium data are discussed in some detail in various publications [362], [363], [418] – [420].

Modern natural gas based plants with a conventional primary reformer use a S/C ratio of around 3.0, compared to values of 3.5 – 4.0 in older installations. Lowerering the S/C ratio means energy saving, and regarding the primary reforming step, the minimum ratio should be theoretically only slightly over 1.0 to avoid cracking. Catalyst experts see the practical limits at 1.5 – 1.7 for methane steam reforming [421], [1487] and 2.2 for naphtha steam reforming. But to supply sufficient steam for the shift conversion step ist has to be at least 2.0 for stoichiometric reasons. An additional safety margin is advisable in case of operational problems with the S/C ratio control and to avoid hydrocarbon formation in the HT shift reaction (a problem which will be discussed later). So in practical operation for conventional reformers (high-duty re-

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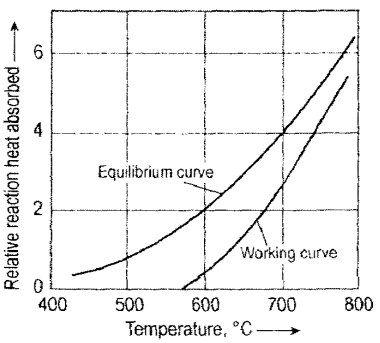


Figure 32. Equilibrium and working curves for reforming

formers) a value of about 3.0 is advisable, whereas in plants with reduced primary reforming (low-duty reformers; Section 4.1.1.6, Table 25) 2.7 – 2.8 may be sufficient.

4.1.1.2. Mechanisms and Kinetics of Steam Reforming

All steam reforming catalysts in the activated form contain metallic nickel as active component, but the composition and structure of the support and the nickel content differ considerably in the various commercial brands. Thus the theoretical picture is less uniform than for the ammonia synthesis reaction, and the number of scientific publications is much smaller. The literature on steam reforming kinetics published before 1993 is summarized by ROSTRUP – NIELSEN [362], and a more recent review is given by K. KOCHLOEFL [422]. There is a general agreement that the steam reforming reaction is first order with respect to methane, but for the other kinetic parameters the results from experimental investigations differ considerably for various catalysts and reaction conditions studied by a number of researchers.

It is rather difficult to relate data from industrial plants to laboratory experiments. To measure the intrinsic activities, a gradientless microreactor may be well suited, but to obtain kinetic data for the *extrinsic activity* of commercial-size catalyst particles useful for reformer layout, experiments in a pilot plant unit with fullsized reformer tubes are necessary. A numerical approach in which the experimental data are described by a closed analytical expression for the reaction rate is frequently used in reformer simulations. For example, it is possible to calculate the equilibrium gas composition for a given pressure and S/C ratio. Instead of plotting the change in the concentrations versus temperature, the corresponding enthalpy changes can be plotted. In this way we arrive at a equilibrium curve and a working curve, as shown in Figure 32.

As an example for an analytical expression, the formula given by MOE and GERHARD [423] is presented:

$$r = k_2 \left[K_3 p_{CH_4} p_{H_2O}^2 - p_{H_2}^4 p_{CO_2} \right] \tag{49}$$

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with

$$k_2 = \exp\left[\frac{35000}{RT} - 7.912\right] \tag{50}$$

K_3 is the equilibrium constant for reaction (42), which is the product of the equilibrium constants for reactions (41) and (37) K_{41} K_{37}. For the ratio CO_2/CO the authors assume only a slight deviation from the equilibrium and use an empirical relation without a kinetic term: $CO_2/CO = f$ (CH_4 conversion, S/C ratio, K_{37}). Other kinetic expressions may be found in [362], [418], [422]. For the reaction mechanism [422] of steam reforming of methane, the following scheme (Eqs. 51–55) was proposed:

$$CH_4 + * \rightleftharpoons CH_2{-}* + H_2 \tag{51}$$
$$CH_2{-}* + H_2O \rightleftharpoons CO{-}* + 2\,H_2 \tag{52}$$
$$CO{-}* \rightleftharpoons CO + * \tag{53}$$
$$H_2O + * \rightleftharpoons O{-}* + H_2 \tag{54}$$
$$CO + O{-}* \rightleftharpoons CO_2 \tag{55}$$

From an interpretation of the kinetic measurements, it was assumed that the surface reaction (52) should be the rate-determining step. But the validity of this mechanism is questioned by some authors [362]. Based on extensive studies using nickel/magnesium/aluminium spinel catalyst, XU and FROMENT [1489] suggested a modification of the reaction scheme. According to this, H_2O reacts with surface Ni atoms to give adsorbed oxygen and gaseous hydrogen. Methane stepwise dissociatively adsorbed on Ni surface atoms, and the radicals formed in this way react with the adsorbed oxygen to finally yield gaseous CO and H_2.

In the extrinsic reaction rate, mass transfer plays a dominant role. The combined effect of the molecular diffusion of the reactants from the bulk gas through the gas film around a catalyst particle to the geometrical surface of the particle, and to some extent the Knudsen diffusion within the catalyst pores, are the limiting factors. As the intrinsic reaction is fast, the reactants will have reacted before they travel down the lenght of the pore. The effectivity of a steam reforming catalyst, that is, how much of the catalyst particle is utilized, varies with the reaction conditions and is only about 1 % at the exit. Because of this, the apparent activity increases with decreasing particle size, and the geometrical shape of the catalyst particle also has a distinct influence (Section 4.1.1.3).

Ethane, propane, and butane, usually present in smaller concentrations in addition to methane in most natural gases, react in the steam reforming in similar way, with the overall reaction corresponding to Equation (35). With higher hydrocarbons, as contained in naphtha, the reaction is more complex. Higher paraffins in naphtha feed will be first completely cracked down in a methane-forming reaction, which proceeds between 400 and 600 °C and could be described, for example, as follows (Eq. 56):

$$C_nH_{2n+2} + (n-1)/2\,H_2O \rightarrow (3n+1)/4\,CH_4 + (n-1)/4\,CO_2 \tag{56}$$

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Table 23. Enthalpy of the naphtha/steam reaction for different reaction conditions

Temp., °C	S/C ratio	Pressure, bar	Stoichiometry	ΔH^0_{298} kJ/mol $CH_{2.2}$
450	2.0	31.5	$CH_{2.2} + H_2O \rightarrow 0.75\,CH_4 + 0.25\,CO_2 + 0.1\,H_2$	−41.7
750	3.0	28	$CH_{2.2} + 3\,H_2O$ $0.35\,CH_4 + 0.25\,CO + 0.4\,CO_2 + 1.45\,H_2 + 1.95\,H_2O$	+74.9
800	3.0	21	$CH_{2.2} + 3\,H_2O$ $0.2\,CH_4 + 0.4\,CO + 0.4\,CO_2 + 1.9\,H_2 + 1.8\,H_2O$	+102.6

Other equations, which contain CO and/or hydrogen as well, may be formulated, too. That a methanation reaction occurs is already obvious from the fact that the reaction product contains more methane than the naphtha feed and that the equilibrium conversion of the hydrocarbon in a direct reforming reaction according to equation (40) is lower than in reaction (56) at low temperature. The reaction of aromatic is principally similar but with higher risk of carbon formation.

$$C_nH_{2n+2} + n\,H_2O \rightarrow n\,CO + (2\,n+1)\,H_2 \qquad (40)$$

With rising temperature, reaction (40) becomes thermodynamically more favorable, for example, for *n*-heptane beyond about 620 °C [424]. The exothermic methanation reaction proceeds in the cooler entrance part of the reformer tubes, followed by the endothermic steam reforming reaction of the methane in the hotter part. Depending on the methane range and S/C ratio, the overall reaction of naphtha changes from exothermic (methanization) to endothermic (reforming to carbon oxides), as shown in Table 23 [425]:

The above reactions proceed also in the so-called rich-gas processes of British Gas and Lurgi/BASF, which convert naphtha with steam in autothermal reactions in a vessel filled with a special nickel-containing catalyst. It was formerly successfully used for town gas production from naphtha. This reaction may also used as pre-reformer ahead of a conventional tubular steam reforming furnace to convert higher hydrocarbons at low temperature and low S/C ratio into a methane reach gas which can than be reformed in the primary reformer with a standard methane reforming catalyst instead of an alkalized catalyst (Section 4.1.1.3.1).

For literature up to 1971, see also [426].

4.1.1.3. Reforming Catalysts

4.1.1.3.1. Primary Reformer Catalysts

In the tubular furnace of the steam reforming section, two elements are extremely important for performance; the catalyst activity and heat transfer through the walls of the reformer tubes, which strongly influence each other. Because of problems with both in the early days, catalyst makers blamed contractors for using excessive heat fluxes, which caused deterioration of the catalysts by sintering and chemical changes. For contractors and tube manufacturers, on the other hand, the culprit was the insufficient

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thermal stability of the catalyst. Of course, the reality was more complex, and there were many and diverse causes for the problems experienced with both tubes and catalysts. There have been considerable improvements in both catalysts and in tube materials and manufacturing techniques over the years, and today problems and failures in this area are more operational than technological in this origin.

The active component of the primary reformer catalyst is nickel, which is finely dispersed over the support material as crystallites produced by reduction of nickel oxide. The nickel oxide content of unreduced catalyst is between 15 and 25 %.

A good primary reforming catalyst should meet the following requirements:

it should have the desired conversion of the hydrocarbon feed at the lowest possible tube wall temperature and the lowest possible pressure drop without forming carbon; have reasonable service life without deactivation (lifetime should at least be equal to turnaround intervals); withstand extraordinary conditions during start-up and shut-down; and, if possible, have the stability to withstand in situ regeneration procedures to eliminate the effects of incidental poisoning or carbon deposition. Today this profile can be largely fulfilled by all leading catalyst producers.

Two main factors influence catalyst activity: chemical composition and surface area. But of no less importance for the performance are the heat transfer characteristics, which are governed by the size and shape of the particles.

Support materials are α-alumina, calcium aluminate, and magnesia – alumina spinel, and different procedures are used in manufacturing. In one procedure, nickel is first precipitated, usually as its hydroxide, in the presence of a suitable dispersion component. After washing, drying, and calcining the oxide, the powder is mixed with an hydraulic cement, formed into particles and subjected to the appropriate treatment to give full hydraulic bonding of the cement. The nickel oxide is thus evenly dispersed throughout the lattice structure of the cement support.

The reduction process takes longer, and there is a greater degree of shrinkage than with the other type of catalyst, based on a prefabricated support. In this preparation procedure, the support pellets are impregnated with a nickel salt solution and dried, after which they are calcined to transform the nickel salt into the oxide. The surface area of the catalyst produced in this manner depends largely on the degree of firing of the support. With increasing temperature, the surface area decreases but the mechanical stability increases. Thus there is a trade-off between activity and strength. *α-Alumina* is now the predominant support for natural gas feedstocks in North America, but is increasingly used in other parts of the world, too. *Calcium aluminate* is still used worldwide on account of its natural alkalinity, which helps to suppress carbon deposition. It is therefore preferred for the manufacture of naphtha steam reforming catalysts. Catalysts intended for dealing with higher hydrocarbons are alkalized with potash – a development first introduced by ICI [427] – to avoid carbon formation (see Section 4.1.1.1) by cracking, which is acid-catalyzed (Eq. 57).

$$C_xH_y \rightarrow x\,C + y/2\,H_2 \qquad (57)$$

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Alkalization suppresses acidic spots on the surface of the catalyst and also promotes the reactions (Section 4.1.1.1) which remove deposited carbon from the catalyst surface. It is also advisable when processing natural gas which contains C_{4+} hydrocarbons to fill the first third of the tube, where the highest heat flux occurs, with alkalized reforming catalyst.

Magnesium aluminate, the preferred support of one catalyst supplier, has a larger specific surface area. But this material must be calcined to a higher temperature during manufacture of the support particles to ensure it contains no free magnesium oxide, which would be hydrated to hydroxide at temperatures below 300 °C. This chemical change results in a volume increase, which would destroy the structure and impair the mechanical stability of the catalyst.

The various support materials have different effects on potential carbon formation. This seems to go in parallel with the Lewis/Brønsted acidity. The main commercially used catalyst supports can be ranked as follows in decreasing order of carbon forming tendency (and thus in decreasing order of the important minimum practical steam/carbon ratio): α-alumina > magnesium aluminate (spinel) > calcium aluminate > alkalized calcium aluminate [419].

Also important is the effect of the size and shape of the catalysts [428] on heat transfer and consequently performance. Unlike the most processes carried out under substantially adiabatic conditions, the endothermic steam reforming reaction in the tubes of the primary reformer has to be supplied continuously with heat as the gas passes through the catalyst. The strong dependency of the reaction rate on the surface temperature of the catalyst clearly underlines the need for efficient heat transfer over the whole length and crosssection of the catalyst. However, the catalyst material itself is a very poor conductor and does not transfer heat to any significant extent. Therefore, the main mechanism of heat transfer from the inner tube wall to the gas is convection, and its efficiency will depend on how well the gas flow is distributed in the catalyst bed. It is thus evident that the geometry of the catalyst particles is important.

To make full use of the enhanced activity attainable by increasing the internal surface area of the catalyst, the heat transfer characteristics (shape) have to be improved, too. Obviously both are strongly interrelated. If the catalyst of higher activity with an improved heat transfer characteristic is installed in a given reformer and the firing conditions are kept as before, the peak skin temperatures of the reformer tube will be reduced. If, on the other hand, the previous tube wall peak temperature is maintained, a higher throughput is possible. Figure 33 shows in a schematic manner the individual effects of surface and heat transfer characteristics.

Various catalyst shapes have been developed by the individual catalyst manufacturers and have progressively replaced Raschig rings, which themselves once displaced simple tablets. The shaped catalysts are applied especially in the high heatflux zone in the upper third of the tube; in the lower end of the tube there would be no significant difference between their performance and that of traditional sizes and shapes, apart from a certain reduction in the pressure drop. Examples are: a four-hole type (ICI

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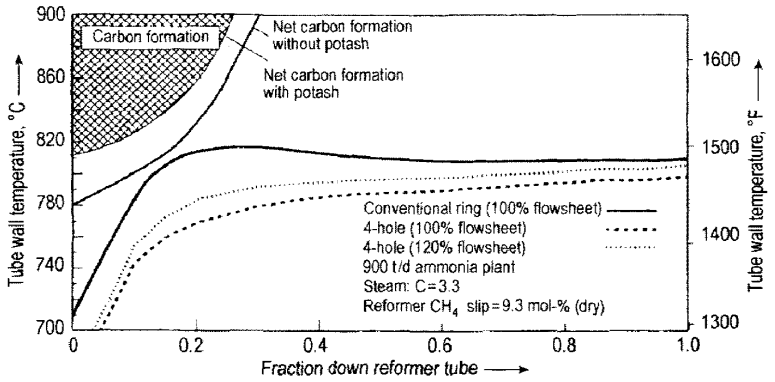


Figure 33. Shaped catalyst (ICI Katalco 4-Hole) in a top-fired primary reformer

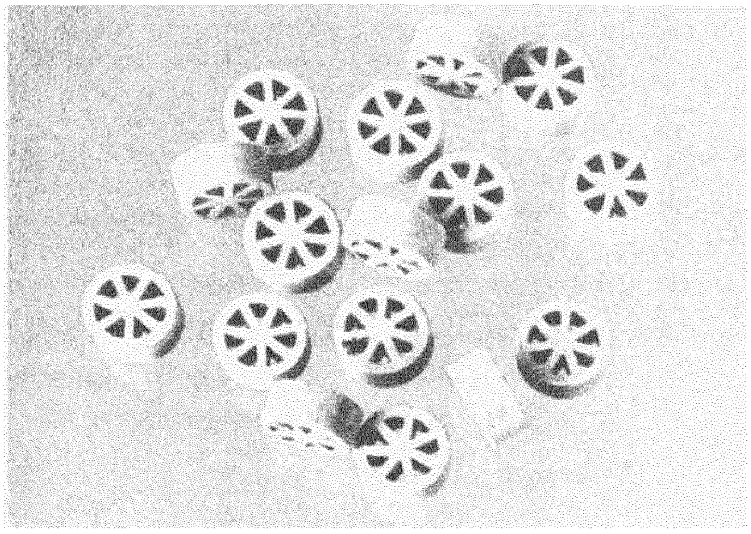


Figure 34. "Wagon Wheel" primary reforming catalyst (UCI)

Katalco), a six-shooter configuration (Topsøe), and a wagon-wheel shape (United Catalysts Inc.; Fig. 34).

Important in the catalyst loading procedure is to avoid breaking and also bridging, especially with the new forms. The latter occurs when catalysts particles, instead of packing down closely, become wedged together across the tube, leaving voids. This can lead to overheating of the reformer tubes, which may be viewed through the furnace box peep holes as hot spots or, in extreme cases, as hot bands on the tube skin. Special packing techniques have developed therefore, e.g., Unidense [429].

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Catalyst makers also succeeded in minimizing the activity reducing effect of the potassium in the alkalized catalysts [430]. Pre-reduced primary reforming catalysts are now also marketed (ICI Katalco, Topsøe) [430], and splitloading of reformer tubes with more than one type of catalyst has now become very common. The benefitial effects concern pressure drop at increased plant load, carbon formation potential, catalyst activity, catalyst cost, and desired catalyst life. For example, a reformer tube may be loaded with 15 % alkali-free catalyst in pre-reduced form (top-section), 25 % unreduced alkali-promoted (middle section) and 60 % alkali-free unreduced catalyst (bottom section).

4.1.1.3.2. Secondary Reformer Catalyst

The secondary reforming catalyst was traditionally applied in the form of Raschig rings for the bulk and solid tables for the top layer. In comparison with primary reforming catalyst, the nickel content is lower (5 – 10 % vs. 15 – 25 %). This, along with higher sintering rates due to the higher temperatures, accounts for the lower activity, which is only 5 – 10 % of that of primary reforming catalyst. For some time it was thought that there would be no advantage in using shaped catalyst in this adiabatic type of reforming and that it would probably also not be stable enough to withstand the mechanical and thermal shock of starting and stopping the process air flow. But catalyst manufacturers have meanwhile increased the mechanical stability of the shaped catalysts to such an extent that, even in a secondary reformer, advantage can be taken of the higher activity resulting from the increased geometrical surface, allowing the catalyst volume to be reduced. This provides additional space for the gas – gas mixing zone above the catalyst bed (Section 4.1.1.5) in existing plants and avoids a costly modification in case of capacity increase.

Some contractors and catalyst vendors use target bricks instead of inert balls to protect the top layer of the catalyst, while others have no protection at all. The catalyst lifetime is usually in excess of six years.

4.1.1.4. Primary Reformer

This process unit consists of a multitude of parallel tubes loaded with the nickel catalyst (Section 4.1.1.3.1) in a furnace box in which the heat needed for the reaction is transferred to the tubes by radiation. The heat is generated in burners, generally gas-fired, in the furnace box. According to the disposition of the burners, primary reformers can be classified as top-fired, side fired, terraced-wall, or, less common, bottom-fired reformers. The furnace box is connected to a convection bank in which the heat content of the flue gas is used for various process duties, e.g., preheating of the process air for the secondary reformer, preheating of steam/hydrocarbon feed, steam superheating, and preheating of combustion air. Quite a number of variables have to be considered to arrive at an effective and reliable reformer design at reasonable cost. A special consideration is the lifetime of the expensive *reformer tubes*, made of highly

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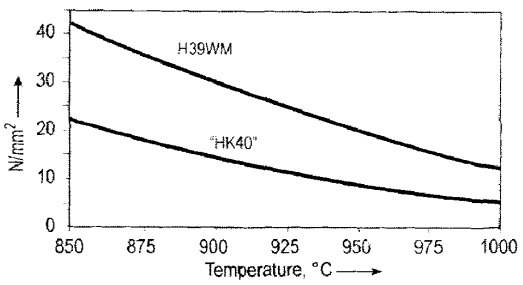


Figure 35. Mean 100 000-hour stress rupture values vs. temperature for HK 40 and micro alloy material.

alloyed chromium–nickel steel by centrifugal casting. A very important issue in this context is the *primary reformer* catalyst with respect to activity, service life, and heat transfer and pressure drop characteristics.

4.1.1.4.1. Reformer Tubes

Under the severe reaction conditions the tube material exhibits creep which finally leads to rupture. Thus, reformer tubes have limited service life. The time to rupture for a specific material depends on the tube-wall temperature and on the internal pressure. This limits the reforming pressure, which to save energy in synthesis-gas compression should be as high as possible. As the reforming reaction is endothermic and proceeds with a volume increase, the negatice effect of a pressure increase (lower conversion) has to be compensated by a higher reaction temperature and hence higher wall temperatures, but this is limited by the material. Another possibility for compensation is a higher steam surplus (steam/carbon ratio), but this is economically unfavorable. The furnace box usually accomodates 200–400 tubes (depending on plant capacity and reformer concept), 10–13 m long, with an inner diameter of 75–140 mm and a wall thickness of 11–18 mm.

The "creep rupture data" are derived from laboratory tests on material samples having a standardized geometrical form. The convenient way to express these data is to plot the stress versus the Larson–Miller parameter P:

$$P = T(\log t + K)\,1000 \tag{58}$$

Where T = material temperature, t = time to rupture, and K = a material-dependent constant.

Using these data the reformer tubes are usually designed for an expected lifetime of 100 000 h. For practical purposes plots of rupture stress versus temperature are used with the time to rupture as parameter, which in the example of Figure 35 is set as 100 000 hours lifetime.

The standard tube material for a long time was HK 40 (20 Ni/25Cr) but for replacements and new plants, HP modified (32–35Ni/23–27Cr stabilized with about 1.5% Nb) is being increasingly used on account of its superior high-temperature properties [431]. The high creep-resistance of this material is attributable to heat-stable

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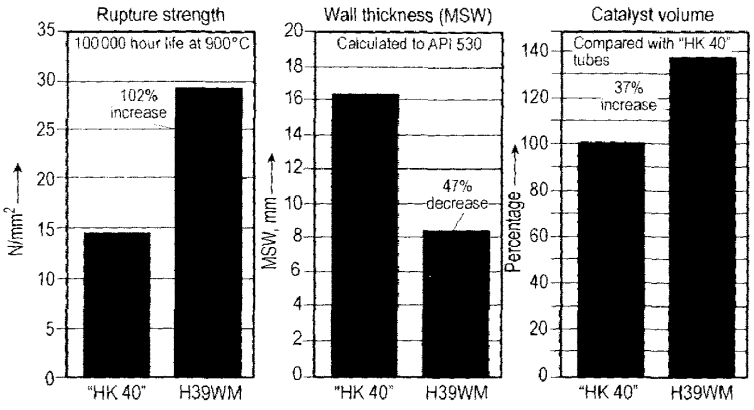


Figure 36. Benefits of Micro Alloy in reformer operation

complex chromium – niobium carbides. Generally the strength of these high-temperature alloys appears to be related to the low solubility of carbon in a highly-nickel matrix. This leads to crystallization of carbides on the grain boundaries. It is assumed that these carbides hinder the intergranular dislocations observed microscopically, which, macroscopically, translate to the well known phenomenon of creep. With HP modified, high-duty reformers with outlet pressures as high as 43 bar are in operation.

Recently a new-generation tube material has emerged, called Micro Alloy [1490] – [1493]. This contains not only niobium but also titanium and zirconium (or lanthanum), and has improved creep rupture strength still further. Table 24 shows the chemical composition of the tube materials.

The enhanced materials are equally useful in revamping older plants. Because they are inherently stronger, it is possible to retube the furnace with thinner tubes.

For the same outer diameter, the inner diameter and, therefore, the capacity of the tube can be increased. Thus more catalyst can be accomodated within a tube of a given outer diameter and, particularly when an optimized catalyst is used with improved packing and heat transfer properties, throughput is increased at (possibly) lower pressure drop than before retubing. Figure 36, demonstrates this by comparing HK 40 with Micro Alloy material.

4.1.1.4.2. Furnace Design and Layout

The layout of a primary reformer furnace is a complex task in which a number of parameters have to be well balanced. Two aspects have to be considered; the heat-consuming reaction of the hydrocarbon with the steam inside the tubes and the heat supply by radiation from the outside. The objective is to match both properly with respect to the desired conversion of the hydrocarbon at an economic steam/carbon

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Table 24. Chemical composition of reformer tube alloys

Grade	Ni	Cr	Mn	Si	Nb	Ti/Zr	Mo	C	P	S
A 698 HK 40	19–22	23–27	≤ 1.5	0.5–2.0	-	-	≤ 0.5	0.35–0.45	≤ 0.04	≤ 0.04
HP modified	32–35	23–27	≤ 1.5	≤ 1.5	≤ 1.5	-		0.35–0.45	≤ 0.03	≤ 0.03
Micro Alloy	33–37	23–27	≤ 1.5	1.5–2.0	0.7–1.5	+	≤ 0.5	0.4–0.5	≤ 0.03	≤ 0.03

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ratio and with a reasonable tube wall temperature profile. The progress of the reforming reaction along the tube, which determines the amount of heat needed at each location and the amount of radiation supplied from the outside, results in a specific tube wall temperature profile. For the purpose of determining the required creep rupture strength to achieve the selected lifetime, the peak temperature is used.

For example, general equations which define a two-dimensional heat transfer model are given in [432]. These were succesfully used in calculating, the temperature profiles of reactant temperature, outside tube wall temperature, and flue gas as a function of tube length. The progress of the reaction inside the tubes is described by selection of appropriate kinetic data for the catalyst used. As already mentioned, diagrams which give the enthalpy change of the reactants versus the feed as a function of temperature are used. These curves present the experimental data gained from a full-sized one-tube pilot plant in a useful form. They are especially suitable for the kinetics of naphtha steam reforming, which are difficult describe with closed mathematical expressions. The radiating heat flux around the tubes is not uniform around the tube circumference, and allowance has to be made in the calculations for the horizontal flux distribution. Calculations for top-fired reformers, for example, show that the outside tube rows absorb more heat than inner rows, which is compensated by allowing a higher mass flow in the outer rows. In the design the axial heat flux can be manipulated by varying the reformer configuration. The flux distribution around the individual tubes results from the furnace geometry (box dimension and row distance for example) and the ratio of tube diameter and pitch. Crucial factors in the design are also the internal heat transfer coefficient [433]–[436] and the pressure drop [437], [438].

Today contractors and licensors use sophisticated computerized mathematical models which take into account the many variables involved in the physical, chemical, geometrical and mechanical properties of the system. ICI, for example, was one of the first to develop a very versatile and effective model of the primary reformer. The program REFORM [361], [430], [439] can simulate all major types of reformers (see below): top-fired, side-fired, terraced-wall, concentric round configurations, the exchanger reformers (GHR, for example), and so on. The program is based on reaction kinetics, correlations with experimental heat transfer data, pressure drop functions, advanced furnace calculation methods, and a kinetic model of carbon formation [419], [439].

Furnace calculations are usually performed according to the method of RÖSLER [440] with numerical methods which allow a three-dimensional simulation. A furnace model in three dimensions takes into account, for example, the shielding effect by adjacent tubes, which may cause circumferential variations in the wall temperature of individual tubes. Another contributing factor to be modeled is the heat release pattern of the burner flames. Additional information on mathematical treatment of radiation is given in [441]–[443].

Usually the number, diameter, and length of the tubes are first tentatively chosen on basis of capacity and pressure drop considerations. These quantities are then optimized in an iterative procedure that adjusts all the interdependent design features. For

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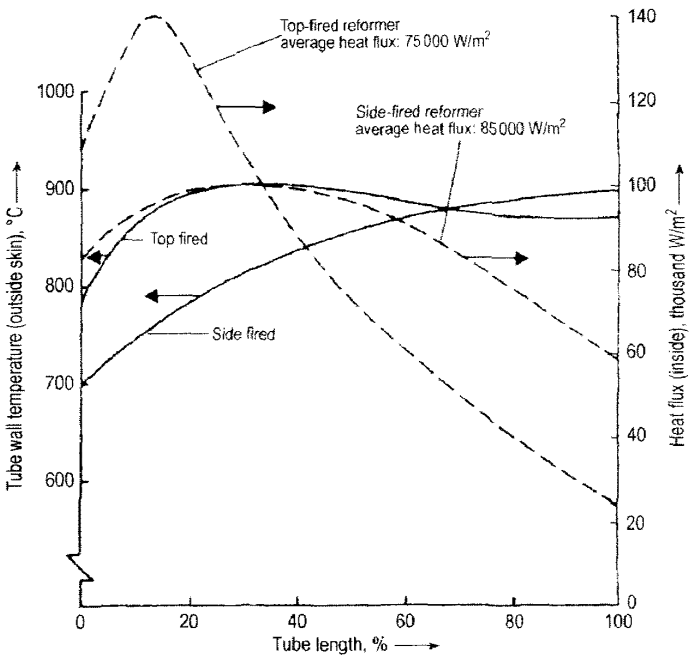


Figure 37. Tube wall temperature and heat flux profiles for top-fired and side-fired configurations.

example, in a top-fired furnace the distance between the rows has a strong influence on peak wall temperature and on the size of the furnace box and consequently on the investment cost. There is also a considerable effect of the tube pitch and tube diameter on the tube skin temperature. The same situation for heat flux was already mentioned above. Tube length is important for the radiant efficiency of the reformer box. On the other side of the optimization puzzle are the investment costs, mainly influenced by the reformer tube price and the size of the furnace box. Designing for a very high heat flux will reduce the dimensions and consequently the investment cost, but at the expense of operational reliability, whereas a more conservative furnace layout is more likely to assure a lengthy trouble-free operation. Ultimately, the design of an industrial tubular steam reformer is a compromise between economics and technical feasibility. As a rule of thumb for the interrelation of space velocity SV, average heatflux q_{av} and tube diameter d_t formula $q_{av} \cong d_t \cdot SV$ is proposed in [444].

In many modern top-fired reformers the heat flux calculated for the inner tube wall surface is around 60 000 W/m^2, although in some designs it cam be as high as 75 000 W/m^2. The maximum heat flux may be 1.4 to 2 times higher. In side-fired and terraced-wall furnaces, where the mean fluxes are generally in the range of 60 000 – 85 000 W/m^2, the difference between mean and maximum flux is much smaller, as shown in Figure 37 [444].

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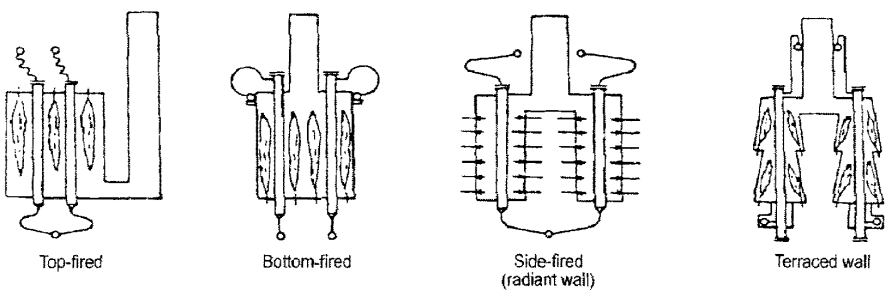


Figure 38. Primary reformer configurations.

Principally, a good design should reach the projected lifetime of 100 000 hours for the tubes, but this is only one side of the coin, the other being the actual operation of the furnace, which may not always be according to the design parameters. Influences which may shorten the service life are catalyst poisoning, loss of steam, thermal shock, overfiring in fast start-up procedures and condensation in hot tubes (e.g., water carry-over). Any loss of catalyst activity (poisoning) reduces the reaction rate and the heat absorption rate. The tube wall temperature in the affected part of the tube stabilizes at a higher level than originally designed. This leads to hot bands or hot spots, which can also result from improper catalyst loading, in which bridging of pellets leads to voids. A very important influence on actual tube life is thermal cycling, that is, how often the tubes are heated up and cooled down in combination with pressure changes. The cumulative effect of these cycles can be very damaging and leads to accelerated creep. Tubes with a thicker wall (e.g., 17 mm for 100 mm tubes) are less tolerant in this respect than those with thinner walls. The advanced tube alloys have reduced this problem to some extent. A good discussion of failure mechanisms and tube changing policy is given in [445].

4.1.1.4.3. Reformer Types, Burner Disposition, Mechanical Features

The arrangement of burnes is the criterium by which reformer designs are normally classified. The different possibilities are shown in Figure 38 [421].

Their thermal efficiency is not very different and in a top-fired furnace can be as high as 95 %. The enthalpy difference between inlet and exit, often referred to as reformer duty, is made up of the heat required to raise the temperature to the level at the tube exit and the enthalpy of the reforming reaction. In a typical tubular steam reforming furnace, about 50 % of the heat generated by combustion of fuel in the burners is transferred through the reformer tube walls and absorbed by the process gas (in a conventional ammonia plant primary reformer: 60 % for reaction, 40 % for temperature increase).

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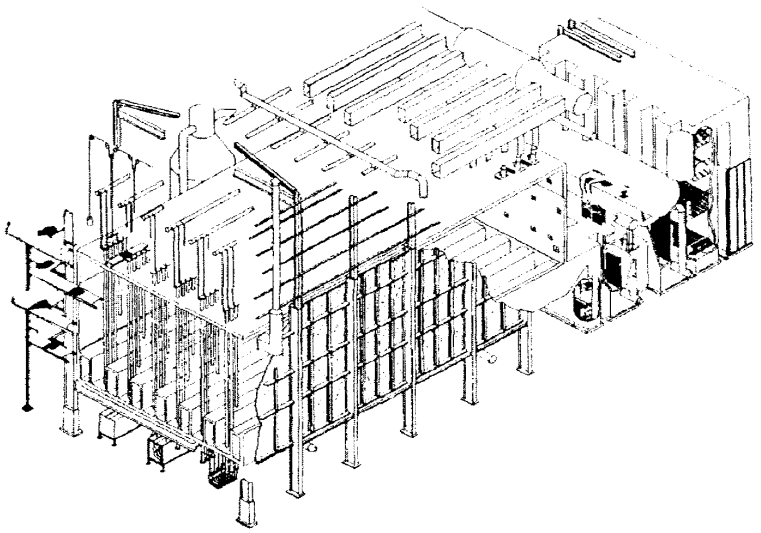


Figure 39. Example of a top-fired reformer

Top-fired reformers are preferred for large capacities. It is possible to accommodate 600 to 1000 tubes is one radiant box. Very large furnaces for methanol plants, in which there is mostly no secondary reformer and the furnace bears the whole reforming duty, have been built by various companies. Top-fired reformers in world-scale ammonia plants usually have between 300 and 400 tubes. The sytem has several advantages:

- Firing occurs only on one level, so the number of burners in relation to the number of tubes is smaller than in side-fired systems. This simplifies distribution piping for fuel gas and preheated combustion air, which is nowadays standard in all efficient plants.
- The radiation efficiency is higher than in other designs.
- The burners are located close to the "cold" inlet of the feed/steam mixture, which is where the strongest heating is needed.
- Less structural steel is needed.

However, the heat input is adjustable only to a limited degree. Figure 39 presents a sketch of a top-fired reformer [446].

In the **side-fired reformers** the burners are located in the wall, and the box accomodates one or two rows of tubes, which receive their heat mainly by radiation from the walls of the furnace box. This is claimed to provide a very uniform heat distribution, which may additionally be adjusted by control of the individual burners. The larger number of burners makes fuel and preheated combustion air distribution more complicated and more expensive. As the heigth and width of the reformer are fixed by the radiation geometry of the tubes and furnace box walls, it is only possible to

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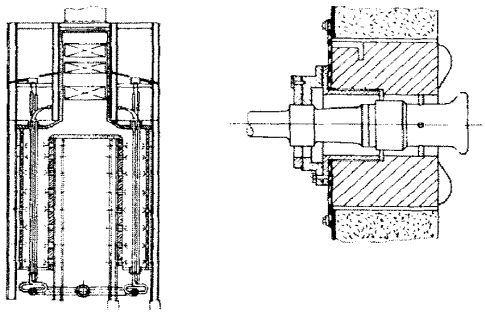


Figure 40. Example of a side-fired reformer. A) Left: Crosssection; B) Right: Radiation burner located in the side wall

extend the reformer lengthwise to accomodate more tubes. This limits it to 100 – 150 tubes, after which multiple radiant boxes becomes necessary. Therefore, this system seems to be more suited to smaller capacities or for low-severity reforming (reduced primary reformer) in a larger plant, as is the case in the Braun Purifier process or in the ICI AMV process. The maximum wall temperature is at the tube outlet, whereas the maximum heat flux is at relatively low temperature. The radiation efficiency is lower than in the top-fired system. It was mentioned [444] that the lower residence times in the flames of a side wall fired furnace could favor lower NO_x values in the flue gas. Figure 40 is an example for an side-fired reformer [426].

Bottom-fired furnaces are not very common in modern ammonia plants. They have a rather constant heat flux profile along the tube with high metal temperatures on the outlet side. Examples are the Exxon reformer and the old Chemico round furnaces.

The **terraced-wall type,** developed by Foster Wheeler may be regarded as an intermediate between the side-fired and bottom-fired tubes. The reformer has inclined walls with several terraces on which upward firing burners are installed. This unique burner positioning makes it possible to adjust the heat flux in each zone. Figure 41 is a schematic drawing of the Foster Wheeler terraced-wall furnace [426].

Apart from this principle question of choosing the reformer type, detailed mechanical design questions are important. The axial load of the weight of the tube and the catalyst has to be balanced by counterweights or spring hangers, designed to allow for the thermal expansion of the tubes. Proper design and adjustment is necessary to avoid tube bending during thermal expansion. For the connection to the feed headers flexible tube connections, commonly called "inlet pigtails", are used. For the connection to the outlet headers, contractors use different approaches. For example ICI, Jacobs (formerly Humphreys and Glasgow) and others use for their conventional furnaces a pigtail design, as shown in Figure 42.

Other designs use stiff connections between the tube outlet and the header. The *M. W. Kellogg reformer,* used in more than 140 reformers, uses the concept shown in Figure 43 [446]. The tubes of each row are welded to a horizontal header located inside the fire box between the flue gas tunnels. With equal numbers of tubes on both sides, a central riser connects the tube harp to the water-cooled transfer line on the top of the firebox. The tubes are suspended by spring hangers.

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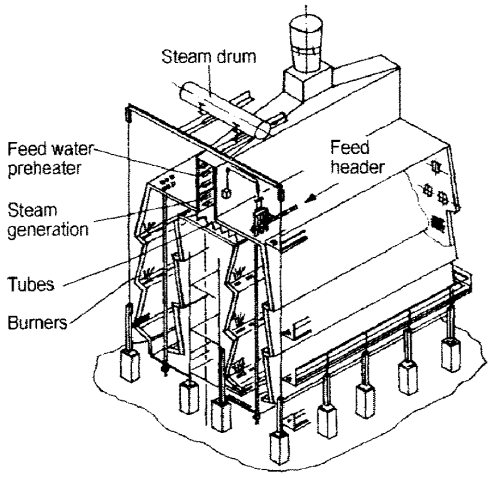
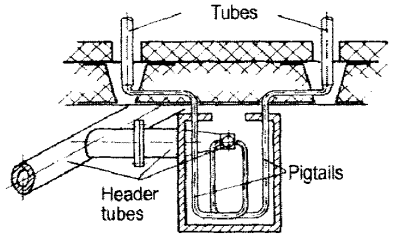


Figure 41. Example of a terraced-wall reformer (Foster Wheeler)

Figure 42. Reformer outlet pigtails [426]



In the *Uhde reformer* the tubes are rigidly connected to the header outside the fire box, as shown in Figure 44 [447]. Differences between the various outlet designs with respect to the amount of repair work (e.g., for isolation of a failed tube) are discussed in [404].

The skin temperature of lined connections, especially the transfer line between primary reformer and secondary reformer, have to be monitored to detect possible defects of the lining. In an extreme case such defects could lead to material overheating with dangerous consequences. Higher skin temperatures will also cause uncontrolled expansion stresses of these lines. A low silica content in the refractory material (and also in the reforming catalyst) is required to avoid plugging of downstream equipment by silica migration. This is especially important after the secondary reformer because of the higher process gas temperature. The refractory insulation, sometimes internally protected by a metallic shroud, is dimensioned to keep the skin temperature at 150–200 °C. With a diameter of around 1000 mm and a length of sometimes 25 m, these wall temperatures may lead to considerable expansions, which have to be mastered by appropriate flexibility of design (carefully selected fix points and bows), suspensions which allow sliding, and counterweights. For insulation of the fire box

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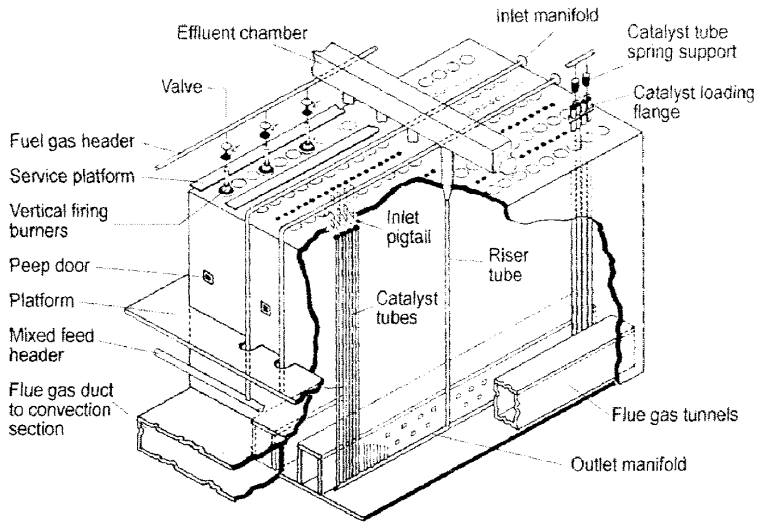


Figure 43. The Kellogg reformer

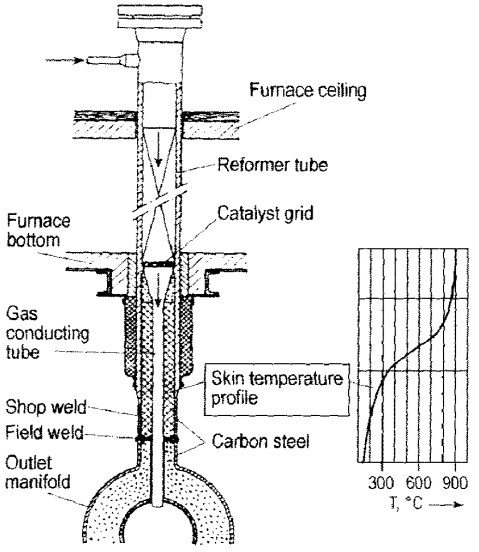


Figure 44. Reformer tube to manifold connection in the Uhde reformer

walls mostly heat-resistant bricks are used, but more recently ceramic mats are favored for this purpose as less labor is required to install them.

In top-fired reformers the hot flue gas – in most cases at a temperature of around 1000 °C – is withdrawn at the bottom of the reformer through tunnels (Figure 45) made

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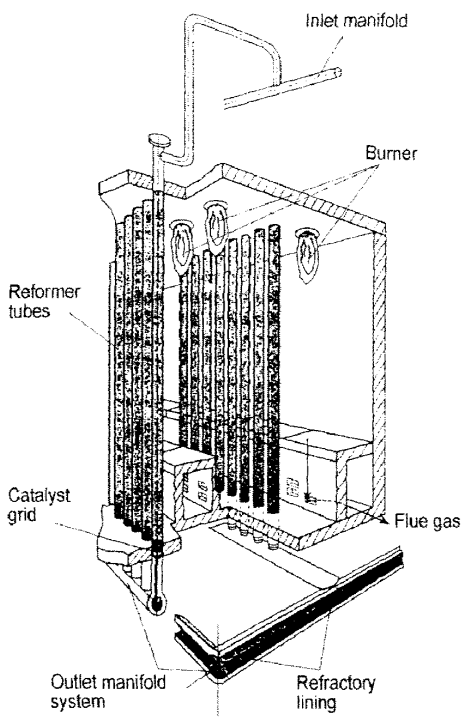


Figure 45. Example for the tunnels and transferline arrangement (Uhde reformer)

of brickwork. Proper dimensioning and positioning of the entrance openings to the tunnels is necessary to avoid an uneven flow profile in the furnace. In side-fired and terraced-wall reformers, the flue gas from the parallel radiant boxes is withdrawn at the top and fed to a common convection section.

The heat is used for the various process duties as shown in the example of Figure 46 (top-fired furnace).

4.1.1.5. Secondary Reformer

As already mentioned, in this process unit the nitrogen for ammonia synthesis is introduced and the reforming reaction is completed down to a very low methane content. Figure 47 shows the principal configuration of a secondary reformer.

Air compressed to the operating pressure is injected through a mixing device (burner) with high velocity (e.g., up to 100 m/s) into the hot effluent of the primary reformer, which is at lower velocity (around 15 m/s). The turbulence resulting from the differing velocities and densities of the gases effects the mixing process. As the process gas is above its auto-ignition temperature, ignition occurs as the two streams mix. Both

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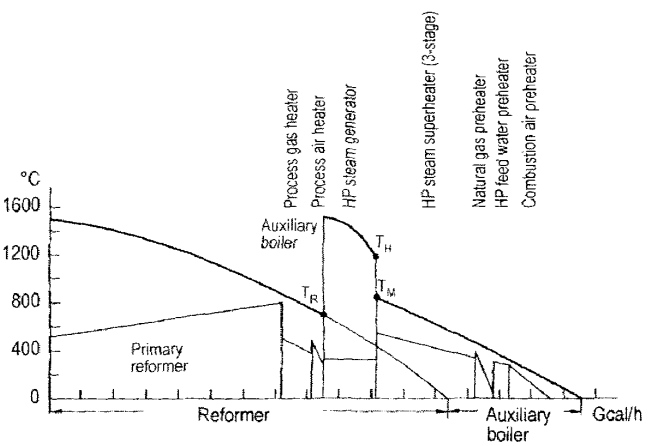


Figure 46. Example of the heat recovery in teh convection section (top-fired furnace, plant with auxiliary boiler)

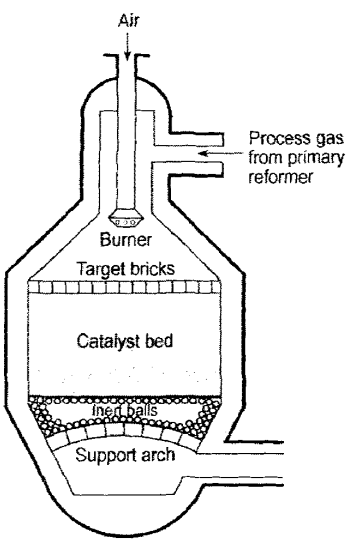


Figure 47. Typical secondary reformer [448]

the combustion section and the catalyst section determine overall performance of the reactor. In contrast to standard combustion process, fuel is in excess of the oxidant. Generally, only 20% of the process gas is burnt to heat the remaining 80% to the required temperature for the adiabatical reforming reaction on the catalyst. Essential point is to produce an evenly mixed gas stream for entry into the catalyst bed, and the combustion zone with its very high temperature should be suitably distant from the walls of the vessel; this is achieved by appropriate geometry of the burner and vessel. Catalyst activity and catalyst bed dimensions should be sufficient to attain a close approach to equilibrium.

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In the last few years, licensors and contractors [444], [448]–[454], have made substantial efforts to develop improved designs for burners and combustion chambers. Worthy of mention are especially those which could cope with the more severe conditions that arise when using higher air-preheating temperatures or oxygen-enriched air, as in some designs. Even more extreme conditions exist in secondary reformers operated with pure oxygen instead of air, which are installed in some methanol and hydrogen plants.

Sucessful simulations have been performed with computerized fluid dynamics programs (CFD), based on the fundamental Navier–Stokes equations, with appropriate volume element grids and/or a finite elemet approach, and in some cases were backed up by isothermal physical modeling (hydraulic modeling) experiments [455]. Examples for the CFD software used are FLUENT (Fluent Inc.) [450] and CFDS-FLOW3D [456] and others, usually modified by the contractor or licensor [448] to adapt them to the conditions in a secondary reformer. Discussion of simulation with CFD can be found in [444], [448], [449].

4.1.1.6. Reduced Primary Reforming

The reformer furnace and flue gas duct are the dominaring structures in every steam reforming ammonia plant and represent about 25 % of the total investment cost. For this reason some modern concepts have reduced the size of the primary reformer by shifting part of the primary reformer duty to the secondary reformer. This is achieved by introducing more air into the secondary reformer, exceeding the quantity which is needed eventually to produce a 3:1 H_2:N_2 ratio in the synthesis makeup gas, and then rejecting the surplus of nitrogen at a subsequent process stage. An example for this approach is the Brown & Roots Braun Purifier Process in which the excess of nitrogen is removed together with methane and argon in a cyrogenic condensation system, called *Purifier*, downstream of the methanator. The *ICI AMV process* uses a similar principle and passes a nonstoichiometric synthesis gas (H_2:N_2 = 2.5:1) through the loop. The surplus is rejected in the hydrogen recovery stage by using a larger than normal purge-gas flow. The reduction in size of the reforming section can be considerable as may be seen from Table 25.

An incidental benefit of reducing the primary reformer load in this way is that the NO_x emission is reduced because less firing is required, which produces a lower flue gas quantity.

Some companies (for example, Jacobs, Foster–Wheeler, and Lurgi) have gone so far as to propose bypassing some of the natural gas around the primary reformer and feeding it straight to the secondary reformer, which then operates as a quasi-autothermal reformer.

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Table 25. Primary reforming: Convential versus Reduced (low duty)

	Conventional	Reduced
Primary reformer		
Steam/carbon ratio	3.0	2.7
Exit temperature, °C	814	693
Outlet guage pressure, bar	39.5	30.1
Exit CH_4 content, mol % (dry basis)	13.2	29.4
Reforming heat duty, GJ/t NH_3	4.70	2.27
Relative catalyst volume %	100	80
Secondary reformer		
Process air inlet temperature °C	600	500
Exit temperature °C	1000	870
Exit CH_4 content, mol % (dry basis)	0.6	1.65
Ammonia plant		
Total energy consumption, GJ/NH_3	28	28

4.1.1.7. Pre-reforming

Another possibility to reduce the load of the tubular reformer is to install an upstream pre-reformer unit. This is actually an off-spring of the above-mentioned (Section 4.1.1.2) rich-gas (town gas) processes of British Gas [457], BASF/Lurgi [458] – [460], and Japan Gasoline [461]. This process has recently become the subject of renewed interest for increasing the capacity of existing natural-gas-based ammonia plants in which the primary reformer has been identified as bottleneck. Under the name pre-reforming, it is installed upstream of an existing tubular reformer [462] – [469]. The natural gas enters such a pre-reformer with a temperature of 530 °C instead of being fed to the primary reformer tubes at the same teamperature. A temperature drop of about 60 – 70 °C occurs in the catalyst bed due to the overall endothermic reaction. Medium-grade heat is used to reheat the exit gas to the correct primary reformer entrance temperature. This compensation heat may be derived from a variety of sources, including flue gas, process gas, or gas turbine exhaust. In the diagram in Figure 48 a pre-reforming arrangement is compared with a conventional configuration [470].

4.1.1.8. Heat-Exchange Reforming

The temperature of the flue gas from a traditional reformer is usually higher than 1000 °C, and the process gas at the outlet of the secondary reformer is also at around 1000 °C. From a thermodynamic point of view it is waste of exergy to use this high-level heat simply for raising steam and preheating process air for the secondary reformer. The boiling temperature in a 125 bar main boiler on the secondary reformer outlet is only 325 °C, and the process air is usually preheated in the reformer flue gas duct. A concept which completely avoids a fired primary reformer is the exchanger reformer, which with some simplification may be viewed as tubular heat exchanger with the

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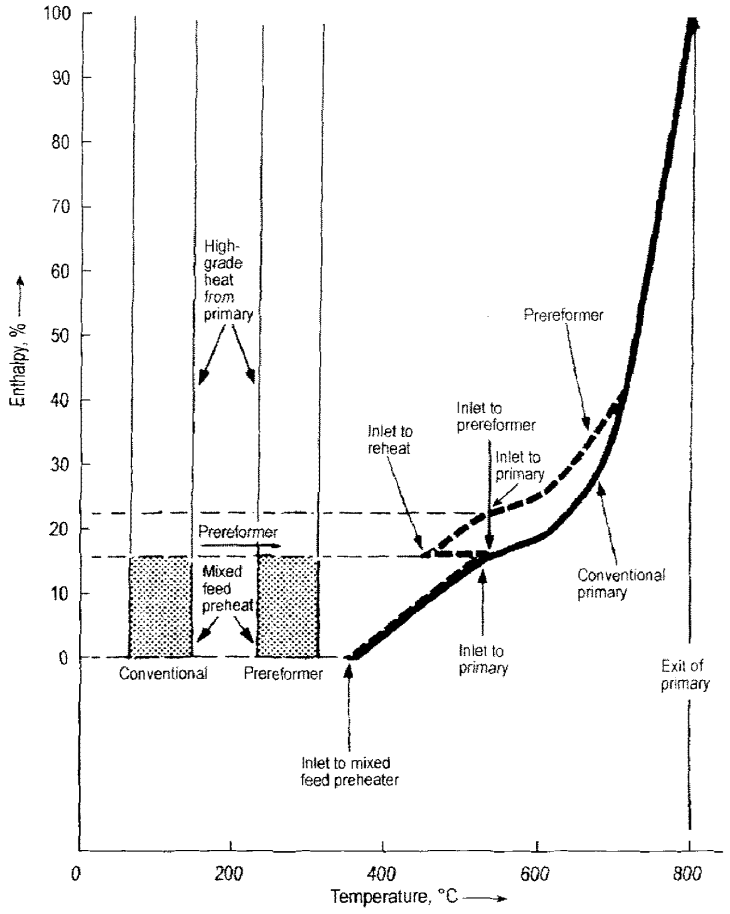


Figure 48. Pre-reforming versus conventional process configuration

catalyst inside the tubes, which are heated by the hot secondary reformer effluent flowing on the shellside.

In some designs the tubes may be open at the lower end, in which case the gas flow on the shell side consists of a mixture of the exit gases from the secondary reformer and from the reformer tubes. Commercially operating designs are the GHR of ICI [404], [471]–[474] and the KRES of M. W. Kellogg [398], [475]–[479].

In the ICI gas-heated reformer (GHR) (Figure 49) the reformer tubes consist of an outer scabbard tube with an open ended bayonet tube inside, and the annular space between the tubes is filled with the reforming catalyst. The steam/natural gas mixture enters the tubes via a double tube sheet and flows downwards through the catalyst, and the reformed gas leaves through the bayonet tubes. To enhance the heat transfer from

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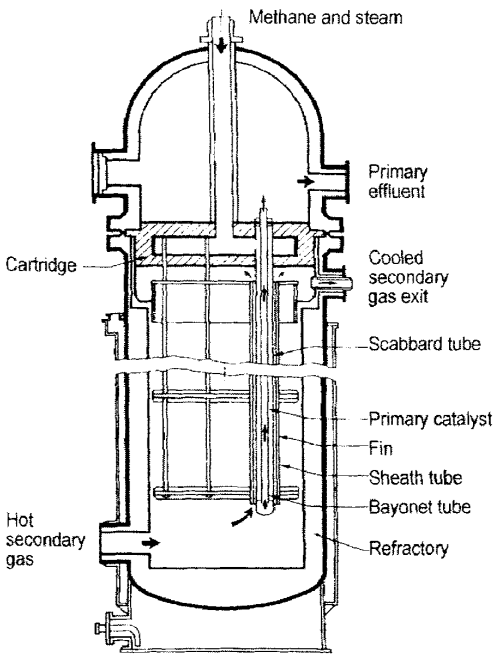


Figure 49. ICI gas-heated reformer (GHR)

the hotter secondary reformer outlet which flows on the shell side, the scabbard tubes are finned and surrounded by "sheath" tubes.

Quite recently ICI has come out with a modified design, the AGHR, with "A" standing for advanced. As shown in Figure 50, the bayonet tubes are replaced by normal tubes attached to a bottom tube sheet by a special seal that allows some expansion. In this way the delicate double tube sheet of the GHR is avoided. The seal which prevents leakage of methane-rich gas to the secondary reformer effluent flowing on the shell side has a unique design which is subject to patent applications of ICI. The AGHR will allow a single-line concept for world-scale plants whereas with the GHR several parallel units would be necessary in the case of large plants [404].

Because of the smaller size compared to a conventional fired reformer, considerable investment savings can be achieved. To close the heat balance between the exchanger reformer and secondary (autothermal) reformer, the latter has to take on a higher reforming duty, which may be achieved by using an over-stoichiometric amount of air or oxygen-enriched air. In some configurations, such as the KRES (Figure 51) concept of Kellogg, the exchanger reformer is partially bypassed, part of the feed (70 – 75 %) being fed directly into the autothermal reformer. The overall S/C ratio is 3.0 to 4.0 and the oxygen content in the enriched air is between 28 and 32 mol %. The mechanical design is relatively uncomplicated, and the pressure difference across the tube walls is only 3.4 bar (35 – 40 bar in a fired primary reformer). In contrast to the ICI GHR there is only one tube sheet and the tubes are open at the lower end, where the reformed gas

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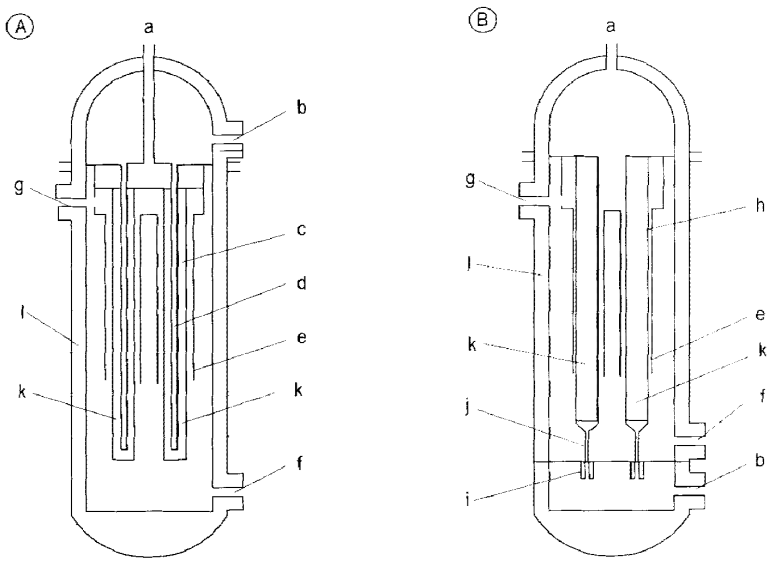


Figure 50. Comparison of GHR (A) with AGHR (B) a) Tubeside inlet; b) Tubeside outlet; c) Scabbard tube; d) Bayonet tube; e) Sheath tube; f) Shellside inlet; g) Shellside outlet; h) Catalyst tube; i) Seal; j) Tail pipe; k) Catalyst; l) Refractory lining

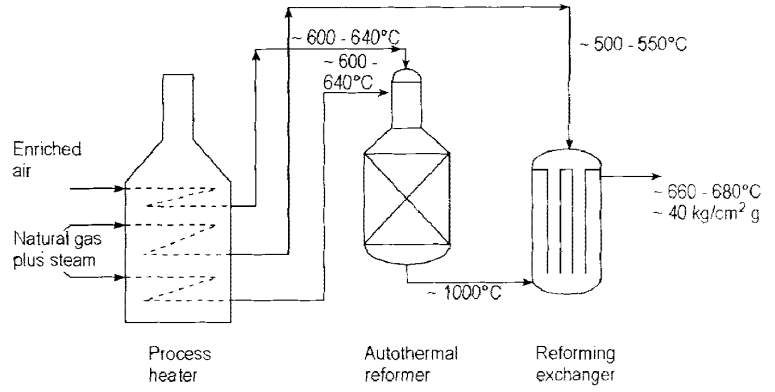


Figure 51. Kellogg reforming exchanger system (KRES) [404]

mixes with the hot effluent of the secondary reformer. The mixed gases flow upwards on the shell side, where baffles create a cross-flow to improve heat transfer. For mixing of the two gas streams, a multihole distributor is installed. Temperature and heat flux profiles for various process parameters of the KRES are shown in Figure 52.

Similar concepts are available from other licensors and contractors. Braun & Root, is offering the Tandem Reformer [480] – [483] a process developed and commercially

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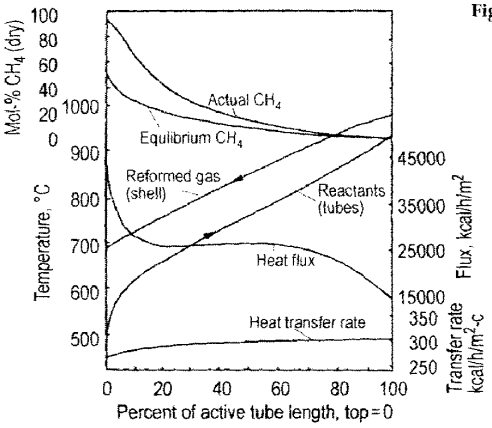


Figure 52. KRES temperature and heat flux profiles

tested in the former USSR in a hydrogen plant equivalent to a 400 t/d ammonia plant. Topsøe [404], [444], [483], [484] also has an exchanger reformer design.

A concept developed by Uhde goes a step further in this direction: exchanger reforming and subsequent noncatalytic partial oxidation, which provides the reaction heat, are accomodated in a single vessel. This combined autothermal reformer (CAR) design, shown in Figure 53, is operated at 17 bar in a demonstration unit producing 13 000 m^3/h of sythesis gas [485]–[488], [1485]. The steam/natural gas feed is passed through the reforming catalyst in the tubes, which are heated by the hot gas returning from the partial oxidation section below the tubes. The intensive mixing of the tube effluent with the oxygen or oxygen-enriched air in the partial oxidation zone (temperature about 1300 °C) is achieved by a vortex-type flow pattern. The residual methane content is governed by the amount of oxidant. For ammonia production all the feed will be passed through the reforming tubes; in other applications (methanol, oxo gas) a portion of feed can be fed directly to the oxidation chamber to attain a higher CO content.

4.1.1.9. Fully Autothermal Reforming

In the extreme case the whole reforming reaction could be performed without a tubular reformer by autothermal catalytic reforming in a design similar to a secondary reformer. In this case it would be necessary to use oxygen or oxygen-enriched air instead of air [402], [489]–[491], [1485].

Unlike the secondary reformer, which is fed with partially reformed gas, the autothermal reformer is fed directly with hydrocarbon feedstock. Because of the higher heat of reaction in the internal combustion (temperatures of 2000 °C and higher), the flow conditions, heat release characteristics and the risk of soot formation are very different from the situation in the normal secondary reformer, and special considerations in the

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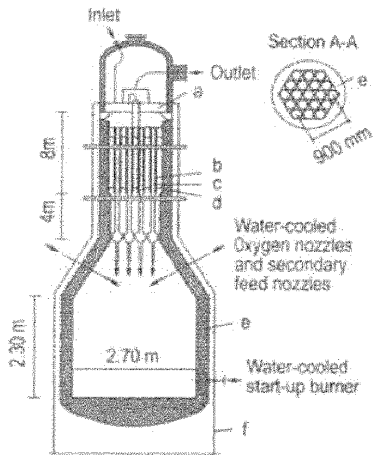


Figure 53. Uhde combined autothermal reformer (CAR)
a) Sandwich type tube sheet; b) Enveloping tube; c) Reformer tubes; d) Tube sheet; e) Refractory lining; f) Water jacket

design of burner and reactor are necessary. The burner must have excellent mixing characteristics which give a combustion zone with a turbulent diffusion flame, followed by a thermal zone in which homogeneous gas-phase reactions take place. In the following catalyst bed, a close approach to the thermodynamic equilibrium in the methane reforming reaction (Eq. 40) and the water gas shift reaction (Eq. 37) is attained. The combustion is a substoichiometric reaction with an overall oxygen/hydrocarbon ratio of 0.55 – 0.6.

Autothermal reforming of natural gas and also of naphtha at normal pressure was used in large scale in BASF in the early 1960s for the production of ammonia [492]. The catalyst beds consisted of three layers: a inert material on the top to prevent backflashing into the mixing chamber, a small intermediate layer consisting of a noble metal catalyst as starter, and a bottom layer of nickel catalyst for the reforming reaction. Two versions were in use, one of which was performed with a flame reaction in the empty space above the catalyst bed, while the other was used for naphtha. Feed and pre-mixed oxygen directly entered the catalyst bed, where the reaction was initiated in the noble catalyst layer.

4.1.1.10. Other Reforming Processes

The reaction heat in primary reforming is transferred continuously from the fire box through the tube walls to the reactants as the reaction proceeds. Running the reaction adiabatically in a bulk catalyst bed was formerly not thought to be technically feasible because in this case extremely high preheating temperatures of the steam/natural gas mixture would be necessary. But with the Regate process gas heater [493], [494] this should be possible. The Regate is similar to a steel works regenerator, exept that it operates on much shorter cycles of only 2 – 3 minutes. It is made up of refractory lined

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vessels, each loaded with a heat-retaining mass and equipped with a burner. The vessels are operated alternately between combustion phase for re-heating and a heating phase for the feed gas, in which the heat-retaining mass cools down. The hot gas line to the process has no valves, and control of gas flow is effected automatically by valves on the inlet and flue gas lines. On account of the short cycle times, the temperature drop is only 40 °C in the phase in which the feed gas is heated. So far only pilot plant experience is available.

A unique steam reforming process [495]–[497] has been developed in Japan to the pilot-plant stage. It reportedly can operate without upstream desulfurization and should be able to gasify naphtha, crude oil, and atmospheric or vacuum residues.

For additional literature on steam reforming see [402]–[404], [426], [483], [491], [494], [498]–[503]; for steam reforming of naphtha [504]–[506]; for steam reforming catalysts [404], [507]–[509]; for reformer design [404], [510], [511].

4.1.2. Partial Oxidation

4.1.2.1. Chemistry of Partial Oxidation

Hydrocarbons or coal will react with an amount of oxygen insufficient for total combustion to CO_2 according to:

$$C_nH_m + n/2\ O_2 \longrightarrow n\ CO + m/2\ H_2 \quad (59)$$

$$C + 1/2\ O_2 \longrightarrow CO \qquad \Delta H^0_{298} = -110.6\ kJ/mol \quad (60)$$

For various reasons, in practical operation some steam must always be added, the quantity depending on feedstock and process configuration, so that the following reactions proceed in parallel:

$$C_nH_m + n\ H_2O \longrightarrow n\ CO + (n + m/2)\ H_2 \quad (40a)$$

$$C + H_2O\ (g) \longrightarrow CO + H_2 \qquad \Delta H^0_{298} = +131.4\ kJ/mol \quad (61)$$

Since in some processes with coal feedstock (e.g., the Lurgi Process) the reaction according to Equation (61) may proceed to a considerable extent, they are more often referred to as coal gasification rather than as partial oxidation, but this is just a matter of definition.

The reactions of the various hydrocarbons in partial oxidation processes are shown schematically in the following equations [512]–[515]. The reaction enthalpies listed (Eqs. 62–68) are not standard enthalpies, but assume 150 °C for the reactants and 1260 °C for the reaction product [512]:

Natural gas	$CH_4 + 1/2\ O_2 \rightarrow CO + 2\ H_2$	$\Delta H_{150/1260} = +71.2$ kJ/mol	(62)
Naphtha	$=CH_2 + 1/2\ O_2 \rightarrow CO + H_2$	$\Delta H_{150/1260} = -16.7$ kJ/mol	(63)
Heavy fuel oil	$\equiv CH + 1/2\ O_2 \rightarrow CO + 1/2\ H_2$	$\Delta H_{150/1260} = -48.1$ kJ/mol	(64)
In parallel also:	$\equiv CH + H_2O \rightarrow CO_2 + \frac{3}{2} H_2$	$\Delta H_{150/1260} = +228.2$ kJ/mol	(65)

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$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O \quad \Delta H_{150/1260} = -650\ \text{kJ/mol} \quad (66)$$
$$=CH_2 + \tfrac{3}{2}\,O_2 \rightarrow CO_2 + H_2O \quad \Delta H_{150/1260} = -510.8\ \text{kJ/mol} \quad (67)$$
$$\equiv CH + O_2 \rightarrow CO_2 + \tfrac{1}{2}\,H_2 \quad \Delta H_{150/1260} = -515\ \text{kJ/mol} \quad (68)$$

The extent to which the above reactions proceed is controlled by the oxygen feed to the partial oxidation generator.

Apart from minor amounts of nitrogen and slag-forming inorganic compounds, the feedstocks in these processes are composed of four elements: C, H, O, S, which are related by the following reactions (Eqs. 69–73) (from [512], reaction enthalpies at 1500 K) in the partial oxidation generator:

$$CO + \tfrac{1}{2}\,O_2 \leftrightharpoons CO_2 \quad \Delta H_{1227} = -280.5\ \text{kJ/mol} \quad (69)$$
$$CO + H_2O \leftrightharpoons CO_2 + H_2 \quad \Delta H_{1227} = -30.1\ \text{kJ/mol} \quad (70)$$
$$CH_4 + H_2O \leftrightharpoons CO + 3\,H_2 \quad \Delta H_{1227} = +227.3\ \text{kJ/mol} \quad (71)$$
$$CH_4 + \tfrac{1}{2}\,O_2 \leftrightharpoons CO + 2\,H_2 \quad \Delta H_{1260} = -23.0\ \text{kJ/mol} \quad (72)$$
$$CH_4 + CO_2 \leftrightharpoons 2\,CO + 2\,H_2 \quad \Delta H_{1260} = +257.5\ \text{kJ/mol} \quad (73)$$

Elemental carbon may react according to Equations (74–77) (from [512], reaction enthalpies at 1500 K):

$$C + H_2O \leftrightharpoons CO + H_2 \quad \Delta H_{1227} = +135.2\ \text{kJ/mol} \quad (74)$$
$$C + CO_2 \leftrightharpoons 2\,CO \quad \Delta H_{1227} = +165.4\ \text{kJ/mol} \quad (75)$$
$$C + 2\,H_2 \leftrightharpoons CH_4 \quad \Delta H_{1227} = -92.5\ \text{kJ/mol} \quad (76)$$
$$C + \tfrac{1}{2}\,O_2 \leftrightharpoons CO \quad \Delta H_{1227} = -115.1\ \text{kJ/mol} \quad (77)$$

At 1300 °C and complete conversion of the feedstock, the complex overall reaction in the partial oxidation process is strongly exothermic for any hydrocarbon, and steam has to be added to control the reaction temperature to prevent damage of the generator refractory material. Part of this steam forms additional hydrogen (Eqs. 40 a, 61, 70); for this reason more hydrogen is formed in the partial oxidation processes than expected from Equations (62–64). The chemical nature of the feedstock has no influence on the result, as all organic structures are totally destroyed in the reaction; hence the composition depends only on the ratio of the elements C:H:O:S. An important condition for the partial oxidation process is to maintain an oxygen to carbon ratio above 1 (O/C > 1) otherwise significantly increased soot formation would occur.

At the reaction temperature of around 1300 °C a rather close approach to the equilibrium of various reactions is achieved. During cooling, the concentrations change on account of the temperature dependence of the equilibrium constants but due to rather rapid cooling rate in technical plants (quench or waste-heat boiler) the composition will become frozen at values corresponding to a temperature of about 900 °C.

Not much information is published on the kinetics of partial oxidation. The methane concentration is about 8 times higher than indicated by reaction (71), but as expected increasing pressure promotes methane formation. From a mere thermodynamical point of view no soot should be present at 1300 °C and O/C > 1. However, the raw sythesis gas contains more or less soot, depending on feedstock. Gasification of heavy oils fractions yields about 1–2 % soot, but with methane the soot content is close to zero.

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Soot-forming reactions can be the Boudouard reaction (Eq. 46) and CO reduction (Eq. 48) with hydrogen. At the reaction temperature the equilibrium is nearly completely shifted to the left-hand side; only at lower temperatures (< 1200 °C) does soot formation via these reactions become thermodynamically possible.

$$2\,CO \leftrightharpoons C + CO_2 \qquad \Delta H^0_{298} = -172{,}5\ \text{kJ/mol} \tag{46}$$

$$CO + H_2 \leftrightharpoons C + H_2O \qquad \Delta H^0_{298} = -131{,}4\ \text{kJ/mol} \tag{48}$$

Some authors assume that soot formation is only a result of thermal cracking of a portion of the hydrocarbon (Eq. 57), resulting at least partly from insufficient mixing of the reactants after the burner nozzle. Others relate it partially to the fact that Boudouard limit is reached during cooling down. Ash particles in the heavy oil fractions also seem to act as nuclei of condensation or catalysts (Ni) for soot formation [512], [513].

$$C_xH_y \rightarrow x\,C + y/2\,H_2 \tag{57}$$

In coal gasification processes (e.g., reaction with oxygen and steam countercurrently in a fixed bed or in a fluidized bed), exothermic combustion of carbon to carbon dioxide according to Equation (78):

$$C + O_2 \leftrightharpoons CO_2 \quad \Delta H^0_{298} = -393.8\ \text{kJ/mol} \tag{78}$$

followed by conversion to CO in the Boudouard reaction (Eq. 46). The carbon monoxide in turn may react with steam to produce either hydrogen and carbon dioxide (Eq. 70) or form methane and carbon dioxide (Eq. 71). The latter reaction is particularly promoted by higher gasification pressures. Carbon monoxide and hydrogen are also formed by direct endothermic carbon gasification with steam (Eq. 74). In the entrained flow processes (Texaco, Koppers–Totzek, and Shell) the reactions described overlap. The gas composition is determined by adjustment of the simultaneous equilibriums of the shift (Eq. 70), methane reforming (Eqs. 71, 73) and Boudouard reactions (Eq. 46).

4.1.2.2. Partial Oxidation of Hydrocarbons

For a long time the dominant processes were the Texaco Syngas Generation process (TSGP) and the Shell Gasification process (SGP). Quite recently Lurgi, which in the past was the leading contractor for the Shell process, has come out with an own partial oxidation process, named LurgiSVZ MPG process. Lurgi acquired technology for the MPG (multipurpose gasification) process from SVZ "Schwarze Pumpe" (Sekundärrohstoff-Verwertungszentum = secondary resource utilization center) and combined it with own developments [536].

In all three processes the reaction is performed in an empty pressure vessel lined with alumina. The reactants (oil and oxygen, along with a small amount of steam) are introduced through a nozzle at the top of the generator vessel. The nozzle consists of concentric pipes so that the reactants are fed separately and react only after mixing at the burner tip or in the space below. The temperature in the generator is between 1200

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Table 26. Feedstock and raw-gas composition in partial oxidation (Texaco process, quench, 25 bar)

	Natural gas	Naphta	Heavy fuel oil	Tar (from bit coal)
Feedstock composition				
Approximate formula	$CH_{3.71}$	$CH_{2.31}$	$CH_{1.28}$	$CH_{0.75}$
C, wt %	73.40	83.8	87.2	88.1
H, wt %	22.76	16.2	9.9	5.7
O, wt %	0.76		0.8	4.4
N, wt %	3.08		0.7	0.9
S, wt %			1.4	0.8
Ash, wt %				0.1
Raw gas composition				
H_2, mol %	61.1	51.2	45.8	38.9
CO, mol %	35.0	45.3	47.5	54.3
CO_2, mol %	2.6	2.7	5.7	5.7
N_2, mol %	1.0	0.1	0.3	0.8
H_2S, mol %			0.3	0.2
CH_4, mol %	0.3	0.7	0.5	0.1
Soot, kg 1000 m^3 (STP)	-	1.8	10	6.1
Consumption [for 1000 m^3 (STP)]				
Feedstock, kg	262	297	323	356
Oxygen, m^3 (STP)	248	239	240	243
Steam, kg		74	148	186

and 1400 °C. About 2% of the hydrocarbon feed is transformed into soot, which is removed from the gas by water scrubbing. Depending on the process configuration the gas is either cooled by quenching or in a waste-heat boiler. The processes are rather similar; they mainly differ in the nozzle design, soot removal and recirculation, and process gas cooling. The reaction pressures may be as high as 80 bar; there are no mechanical or material limitations to raising the gasification pressure further, but with respect to the overall ammonia process this might be beyond the energy optimum because of the increasing energy demand for nitrogen and oxygen compression. Nevertheless, Texaco has successfully operated a pilot plant at 160 bar in California. Maximum raw gas generation capacity of a single generator corresponds to about 1000 t/d ammonia. Over 300 plants based on Shell and Texaco technology (for ammonia and other production facilities) have been built to date [514]. World-scale ammonia plants based on partial oxidation exist in Germany, India, China, and other countries [516], [517].

Partial oxidation has practically no restrictions regarding the nature of the hydrocarbon and the sulfur content. Natural gas, refinery gases, LPG, naphtha, heavy fuel, vacuum residue, visbreaker oil, asphalt, and tar can be used as feedstock. As the investment costs for partial oxidation are higher than for steam reforming, mainly because of the cyrogenic air separation, it is usually not a choice for the lighter hydrocarbons, but heavy feedstocks from fuel oil to asphalt, when favorably priced, can be a competitive option for various locations and circumstances. In some special cases, where the primary reformer is a bottleneck for a capacity increase, a small parallel partial oxidation unit based on natural gas could be installed, if a surplus of

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Table 27. Partial oxidation of heavy fuel oil with and without CO_2 recirculation (Shell process)

	H_2O	CO_2
Generator feed		
Oil, kg	1	1
Steam, kg/kg feed	0.4	-
CO_2, kg/kg feed	-	1.2
Oxygen, m^3 (STP)	0.75	0.8
$CO+H_2$, m^3 (STP)	2.74	3.31
Raw gas (dry)		
H_2, mol %	46.1	29.3
CO, mol %	46.9	59.2
CO_2, mol %	4.3	8.8
VH_4, mol %	0.4	0.4
N_2 + Ar, mol %	1.4	1.5
H_2S + COS, mol %	0.9	0.8
Soot, H_2, wt % based on feed oil	2.6	2.6

oxygen is available at the production site. This possibility is in competition with other solutions, e.g., a parallel autothermal reformer (Section 4.1.1.9), or an UHDE CAR unit (Section 4.1.1.8). For processes other than ammonia production which require a sythesis gas with a high carbon monoxide content (methanol, oxo synthesis, production of carbon monoxide), partial oxidation can sometimes also be an economic possibility. How the gas composition can vary with the feedstock analysis may be seen from Table 26 [512], [518]. Increasing carbon content of the feedstock leads to higher CO concentrations in the raw gas. With recirculation of carbon dioxide to the gasifier, the CO content can be increased even further, as shown in Table 27 [512], [519]. Other parameters of influence are oxygen purity, operating pressure, and amount of steam added for reaction moderation.

Shell Gasification Process (SGP) [514], [520]–[523]. Preheated oxygen and the heavy oil fraction are introduced through a nozzle into an empty reactor vessel which is lined with high-alumina brickwork. The pressure shell is equipped with a special system to monitor the skin temperature for early detection of defects in the generator lining. Oil enters through the central tube of the burner nozzle. A high pressure drop of up to 80 bar is necessary to ensure sufficient atomization by the oxygen, which is fed through the annulus between the oil gun and the outer case of the burner nozzle. Steam is added as moderator for the reaction and to assist the atomization. The generator temperature is between 1200 and 1400 °C. The raw gas contains soot and ash. A waste heat boiler capable of producing 100-bar steam cools the gas down to about 340 °C. Figure 54 is a simplified flow sheet of the SGP [514].

After this the soot is removed from the product gas in two stages. About 95 % is removed by direct water-spray (quench type), the remainder by countercurrent water-scrubbing in a packed column. Older units used a gas-oil fraction to extract the carbon from the aqueous soot suspension. The pebbles formed in this operation were separated with vibrating sieves and either re-mixed with the generator feed or separately

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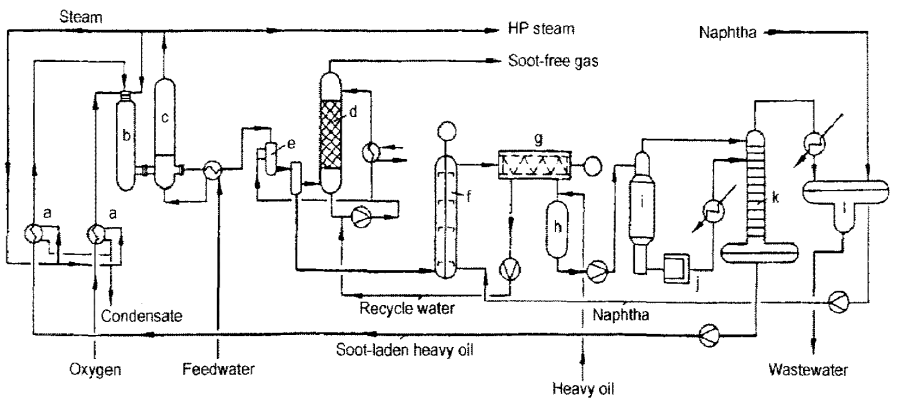


Figure 54. The Shell gasification process (SGP)
a) Preheater, b) Reactor, c) Waste heat boiler, d) Scrubber, e) Quench, f) Extractor, g) Vibrating screen, h) Flash tank, i) Soot-oil tank, j) Homogenizer, k) Naphtha stripper, l) Naphtha recycle tank

burnt in a steam boiler. A further development substituted the gas oil by naphtha, which on account of its high price was distilled off and recycled to the extraction stage before feeding the oil/pebble mixture to the generator. As a total recycle of the soot-free water would lead to ash built up in the soot-removal cycle, some wastewater run-down is necessary, which for environmental reasons requires nowadays an effective cleaning procedure [524] – [527]. Of special concern thereby is the removal of the heavy metals like nickel and vanadium. Stripping, floculation, chemicals addition and filtering operations were applied in a rather elaborate sequence. More recently, especially when using heavy feeds like visbreaker oil another technique for soot handling and water clean-up was developed. The carbon-water slurry is filtered off and the moist filter cake is subjected to a controlled oxidation in a multiple-hearth furnace. A vanadium concentrate (about 75 % V_2O_5) is obtained. The treatment of the run-down water is as described. From 1200 mtpd ammonia plant running on visbreaker oil, about 200 tons of vanadium can be recovered for metallurgical use [522]. Table 28 gives an example for the gas composition of an SGP plant (waste heat boiler) with an operating pressure of 55 bar.

Further information on the SGP is found in [528] – [531].

Texaco Syngas Generation Process (TSGP) [512] – [514], [518], [532] – [535], [537] – [542]. The burner nozzle is water cooled, but in contrast to the Shell Process oxygen is fed through the center pipe and oil through the outer annulus. This process, too, uses steam as moderator; the soot content in the raw gas is 1 – 2 % based on feed. The cooling of raw gas (about 1400 °C) is effected either by direct quenching with water from the soot water cycle or by a waste heat boiler (Section 4.6) as shown in Figure 55 [532].

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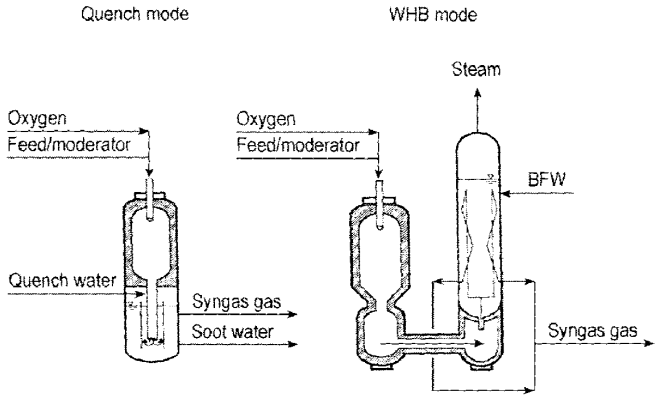


Figure 55. Raw gas cooling in the Texaco Syngas Generation Process

Table 28. Example of Shell gasification at 55 bar [513]

Heavy fuel oil, wt%		Oxygen, mol%		Raw gas (dry), mol%	
C	84.6			CO	46.3
				CO_2	4.7
				CH_4	0.5
H	11.3			H_2	46.3
S	3.5			H_2S	0.8
N	0.4	N_2	2.0	N_2	0.6
		Ar	3.0	Ar	0.8
O	0.13	O_2	95.0		
Ash	0.07				

With the Texaco process the quench mode is preferred for ammonia production as it offers some advantage by providing directly the major part of the steam needed in the subsequent carbon monoxide shift conversion. As can be seen in Figure 56 the quench is followed by two-step sootscrubbing, consisting of a venturi-scrubber and a subsequent packed column for countercurrent scrubbing. The soot can be extracted from the water with naphtha, because of its more lipophilic surface properties. The soot–naphtha suspension is separated in a settler from the nearly carbon-free "grey-water", which is recycled to the quench and scrubbing section. The soot–naphtha phase is mixed with feed oil, after which the naphtha is distilled of in a stripping column and returned to the soot-extraction step.

To prevent accumulation of ash and slag in the water circuit, some water is discharged continuously. In a combined chemical and physical treatment sulfides, cyanides and suspended solids (ash) are removed. A concentrated sludge has to be filtered off and disposed of. The run-off water from the filters is stripped of ammonia and after pH-adjustment sent to a biological treatment unit. Uhde [532] has developed an alternative route for soot treatment in which the soot is filtered off and subjected to combustion, and the filtered water is recycled to the quench and scrubbing circuits. Let down water is treated as described above. This soot treatment technique avoids not

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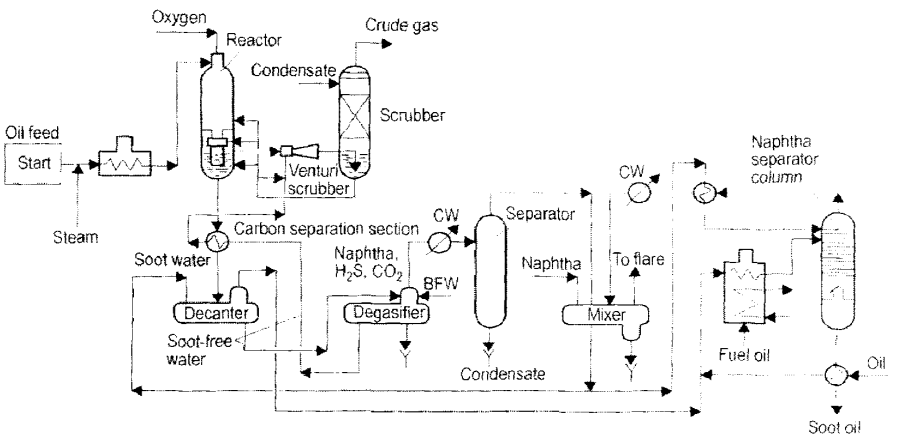


Figure 56. Soot removal in the Texaco Process

only the energy consuming and costly naphtha extraction step but also has advantages when processing oils with high vanadium content.

A typical gas composition (dry basis, mol%) produced from heavy fuel oil at 88 bar (quench type) [513] is CO 48.3, H_2 44.6, CO_2 4.6, CH_4 0.5, N_2 0.6, Ar 0.8 (introduced with the oxygen), H_2S 0.6, COS 300 ppm. (Feedstock (wt%): C 85.7, H 10.73, S 2.65, N+ash 0.6, O 0.32: oxygen purity 95.0 mol%).

A recent development is the Uhde [532] three-stream burner with an adjustable tip. A portion of the of oxygen enters through the center nozzle, the remainder through the outer annulus, the oil is fed through the inner annulus. The center oxygen nozzle also accommodates the preheat burner. This combi-burner concept avoids the change from preheat burner to process burner in the start-up phase, a cumbersome procedure necessary when using the traditional two-stream Texaco burner. As tested in a demonstration plant the carbon conversion could be increased to better than 99.6 %, which means a reduction soot formation by a factor better than 5.

LurgiSVZ MPG Process [536]. The process is offered in two versions which differ in synthesis gas cooling: quench or boiler mode. Burner and reactor are essentially the same for both versions. For ammonia, the quench mode ist preferred because the quenchend synthesis gas saturated with water has the right temperature level to be fed directly to a dirty shift catalyst. Gasification pressure can be as high as 100 bar. The special burner design (multiple nozzle concept) is the main reason for high feedstock flexibility, it also accepts different non-mixible feeds without choking and can even handle slurries with particles in the mm-range. The oxidant (O_2, enriched air) is mixed with steam as moderator prior to feeding it to the burner. Burner and reactor are tuned

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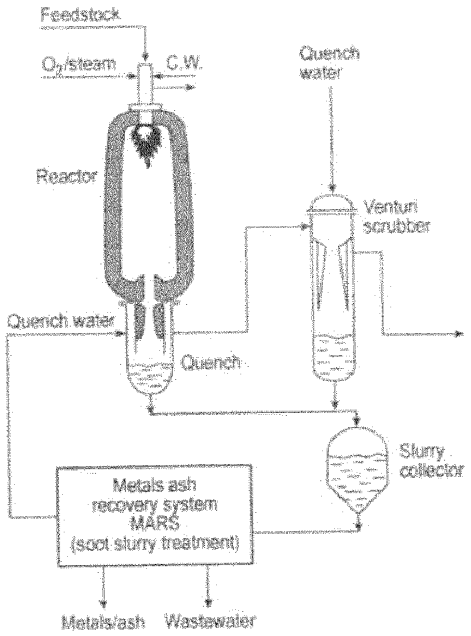


Figure 57. LurgiSVZ MPG (quench version)

by fluid dynamic simulation for optimum performance. The burner management system includes a sophisticated safeguarding system as well as a logic for fully automatic start-up.

For the quench cooling, water from the soot removal section ist injected radially into a quench ring. At the bottom of the separator part, soot slurry mixed with ash (in case of low-ash feed) is withdrawn. When processing high ash feedstock, molten slag is formed which flows down the refractory wall into the quench where it is blast-cooled into glassy spheres (1 – 2 mm in diameter), which collect at the quench separator bottom and are drawn off via a slag lock-hopper. Figure 57 shows the MPG quench version.

The raw gas from the partial oxidation contains soot, about 0.8 wt% of the hydrocarbon feed. Soot particles together with ash are removed mainly in the venturi scrubber downstream of the quench. The soot slurry from quench and venturi is sent to the metals ash recovery system (MARS) Figure 58. First the soot slurry is flashed to atmospheric pressure and then filtered, leaving a filter cake with about 80 % residual moisture. The filter cake is subjected to a controlled combustion in a multiple hearth furnace. Under the conditions applied, a metal oxide concentrate containing 75 wt% of vanadium, together with some nickel and iron, is obtained which can be sold to metal reclaimers. The MARS ist practically autothermal as the heat of combustion is sufficient to evaporate the moisture of the filter cake.

The filter water from the MARS is recycled to quench and venturi. Surplus of water, formed the gasification step has to be rejected. It is fed to a stripper to remove traces of

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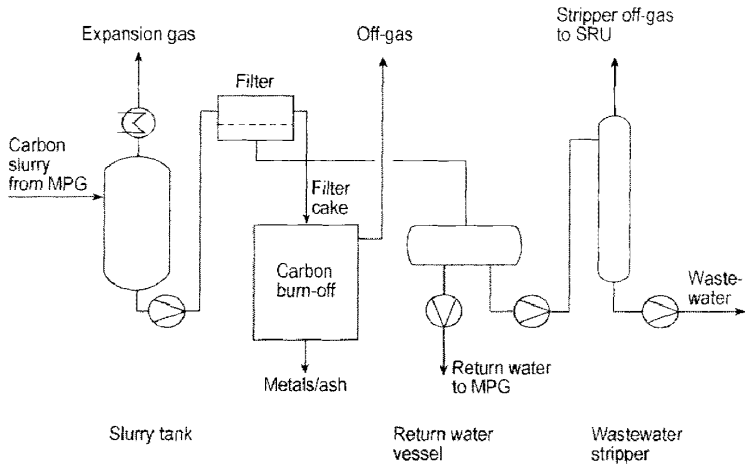


Figure 58. Metals ash recovery sytem in the LurgiSVZ process

ammonia, hydrogen cyanide and hydrogen sulfide, with the off-gas sent to a Claus unit with tailgas treatment. After this the stripped water which still contains traces of NH_3, HCN and H_2S and metals ist subjected to a flocculation and sedimentation procedure and finally purified in a biological wastewater treatment unit.

Ash and soot removal in the waste heat boiler version ist slightly different, the MARS is identical.

4.1.2.3. Partial Oxidation of Coal (Coal Gasification Processes)

As in any gasification of coal the exothermic reaction of carbon with oxygen to CO (60) and CO_2 (Eq. 78) and the endothermic reaction with water (Eq. 61) run in parallel in different extent it seems to be often a mere semantic question whether to classify a process as a partial oxidation or to use just the more general expression of coal gasification. Bouduard equilibrium (Eq. 46), water gas shift equilibrium (Eq. 37) and methane formation equilibrium (Eq. 71) are additional determinants

$$C + 1/2\ O_2 \rightleftharpoons CO \qquad \Delta H^0_{298} = -110.6\ \text{kJ/mol} \qquad (60)$$

$$C + O_2 \rightleftharpoons CO_2 \qquad \Delta H^0_{298} = -393.8\ \text{kJ/mol} \qquad (78)$$

$$C + H_2O(g) \rightleftharpoons CO + H_2 \qquad \Delta H^0_{298} = +131.4\ \text{kJ/mol} \qquad (61)$$

Historically the water gas process was used for ammonia production. Coke was reacted intermittently with air and steam in a fixed bed. The heat provided by the exothermic reaction of coal and air in the "blow phase" is stored in the fixed bed and provides the heat needed for the endothermic reaction of carbon with steam in the "run

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Table 29. Coal gasification processes in commercial operation. Suitable feedstocks

	Pressure, bar	Temp., * °C	Anthracite	Bituminous coal	Lignite	Ash > 30 %
Lurgi (dry)	20–100	300–600	+/++	+/++	++	yes
British Gas/ Lurgi	20–70	450	+/++	++	-/+	no
Winkler/HTW	1–10	1050	+	+	++	yes
Koppers/Totzek		1800	+	++	++	no
Shell	20–40	1500	+	++	++	no
Texaco	20–40	1350	+	++	-	no
Dow	10–20	1000–1450	+	++	-	no

* At gasifier outlet.

phase" (Chapter 2). This old atmospheric pressure process is still used with some improvements in number of smaller ammonia plants (30 000–80 000 t/year) in China but elsewhere no longer in operation [543].

Coal gasification processes [544]–[547] in commercial operation are shown in Table 29 [545].

So far only the Koppers–Totzek, Texaco and Lurgi gasifiers, and probably the Winkler process in some smaller installations, have been used in ammonia plants, but the successful demonstration of the Shell process in other applications make it a potential candidate for ammonia production, too. Additional processes in different stages of technical development are the HTW and the Dow process. Information on the status and the development in the gasification of coal can be obtained from [541], [545], [548]–[554].

The **Koppers–Totzek Process** [555]–[560] used in several ammonia plants in China, India, and South Africa, operates practically at atmospheric pressure. Figure 59 is a simplified sketch of the gasifier.

Dry coal dust is fed to the two (sometimes four) burners of the gasifier. Oxygen, together with a small amount of steam, is introduced immediately at the head of the burners, and the mixture enters the reaction zone with high velocity. Core flame temperature may be as high as 2000 °C. The residence time is less than 1 s and the gas leaving the top of the reactor vessel is at 1500–1600 °C. The hot gas is cooled in a waste-heat boiler, followed by a water scrubber to remove carbon and ash traces from the raw gas and to effect further cooling. The soot water suspension is fed to a settler, and water and carbon slurry are separately recycled to the process. Liquid slag is withdrawn from the reactor bottom. Any surplus of water has to be cleaned prior to discharge. The combustion chamber has a refractory lining and, in addition, a water jacket for cooling. The process can handle bituminous coal and lignite, the maximum gas capacity of one generator is about 50 000 m^3/h. Typical gas composition (mol%) is CO_2 8–12, CO 59–62, H_2 26–29.

To overcome the disadvantage of atmospheric pressure operation, a version was developed capable of operating at 25–30 bar. This **PRENFLOW** (pressurized entrained flow) process [561], [562] is being tested in a 48 t/d pilot plant.

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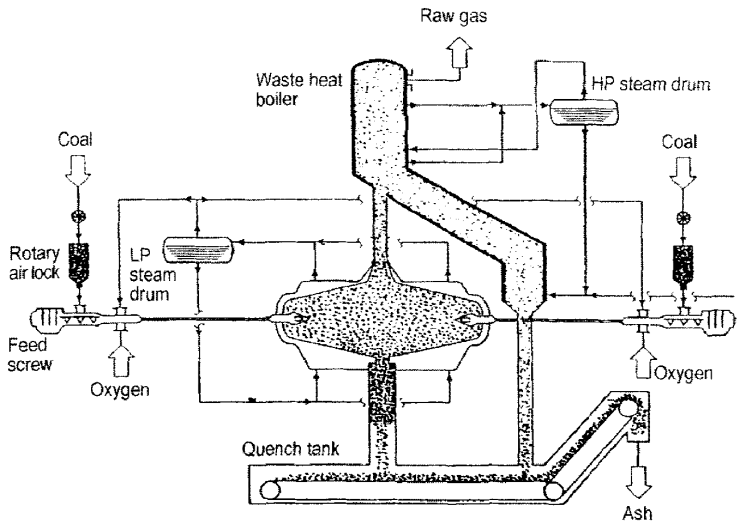


Figure 59. Koppers–Totzeck gasifier

A new concept of a atmospheric pressure gasification that has been presented recently [563] is the **Advanced Coal Gasification Process (ACGP)**, developed by AECI Engineering, Kynoch Ltd, and Babcock Wilson. Similar to the Koppers–Totzek, it is an entrained flow process. Pulverized coal and oxygen are injected near the base of the gasifier through eight burners by a proprietary feed technique that applies a special pump capable of injecting the coal dust directly instead of using a lock-hopper screw device as in the traditional Koppers–Totzek process. The gasifier is a slender column with a square cross section, which is lined with highly heat resistant material in the combustion area. The upper part is made of finned tubes which are welded together and have a watercirculation by thermosyphon action. So far no commercial installation has been constructed but it is claimed that one unit is capable to produce the ammonia synthesis gas for 750 t/d of ammonia The developers believe that the low investment costs resulting from the rather simple mechanical design could economically off-set the energetic disadvantage of the pressure-less gasification.

The **Texaco Coal Gasification Process** [545], [564]–[571] is rather similar to the Texaco partial oxidation process for heavy hydrocarbons. An aqueous slurry containing 60–70% coal is fed by reciprocating pumps to the generator at a pressure of 20–40 bar. For ammonia and hydrogen production, quench cooling is applied, whereas for CO-rich synthesis gas (e.g., methanol, oxo-procces) the waste heat boiler version is recommended. Waste-heat boiler, quencher, and carbon scrubber are especially adapted to deal with the ash and slag introduced with the bituminous coal feed. Carbon is removed from the soot water in a settler system, the slurry is recycled to the process.

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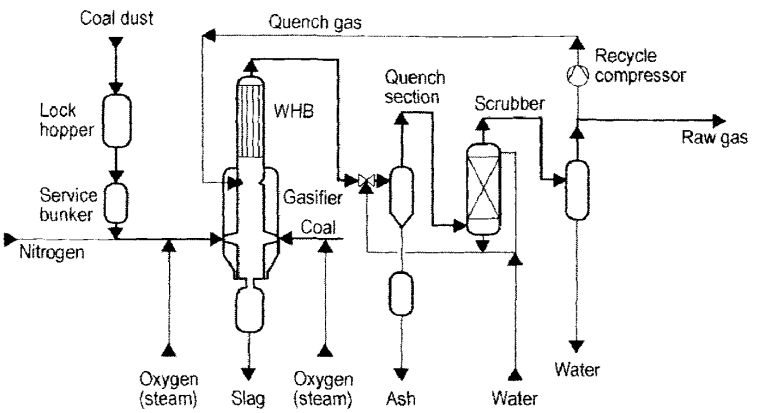


Figure 60. Shell coal gasification process (SCGP)

In its coal gasification process [545], [572]–[577] **Shell** has completely departed from the concept of its process for partial oxidation of heavy hydrocarbons. With reversed flow pattern in the gasifier (from bottom to top), dry coal dust is introduced via lock hoppers into the reactor vessel operating at 20–40 bar. The reactor vessel is refractory-lined and scrubbing with water in a venturi jet and a packed column is used to remove the particulates from the raw gas. Much development was dedicated to the liquid-slag withdrawal system and the nitrogen-aided coal-feeding system. A scheme of the process is presented in Figure 60 [545].

The **Lurgi Dry Gasifier** [545], [578]–[584] performs the reaction in a moving bed, usually operating at 25–30 bar. Figure 61 shows the principle of this gasifier. Crushed coal with a particle size of 4–40 mm enters the top of the gasifier through a lock hopper and is evenly distributed over the cross section of the coal bed surface by a distribution disk equipped with scraper arms. Ash with only 1% of residual carbon is removed at the bottom of the gasifier by a revolving grid with slots through which steam and oxygen are introduced. The temperature in the lower section of the bed is around 1000 °C, and at the top where the raw gas exits about 600 °C. As a result of this lower temperature the raw gas has an increased content of impurities such as tars, phenols, and some higher hydrocarbons. In addition the methane content is relatively high (up to 10–15%), so that purification and conditioning of the raw gas is a rather elaborate task [547]. The process actually can use any sort of coal and can handle ash contents higher than 30%. The **British Gas/Lurgi Slagging Gasifier** [545], [580], [585] operates without a grate with withdrawal of the liquid slag.

The classic **Winkler gasifier**, which operates at atmospheric pressure, is today still in use in some smaller plants (e.g., in China). In a further development **(HTW process)** by Rheinbraun it has been tested in a demonstration plant with lignite at 10 bar [586], [587].

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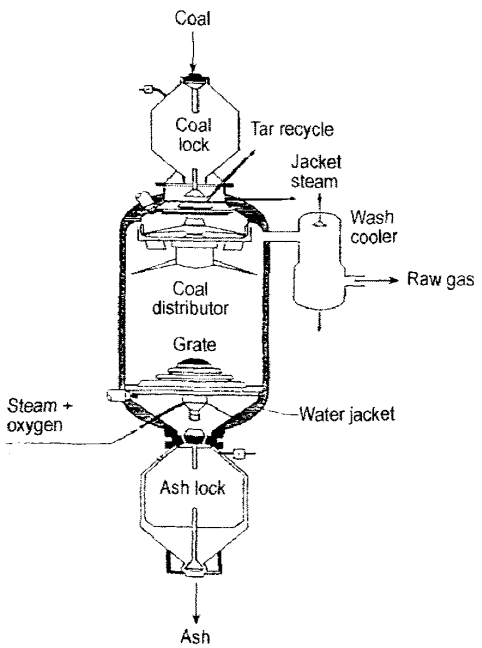


Figure 61. Lurgi dry bottom gasifier

4.1.3. Alternative Routes for Supply of Synthetic Gas

Hydrogen-containing byproduct gases or waste gases from other processes (examples are given in Table 30) can principally be used for ammonia production. The methods for recovering pure hydrogen from these gases are largely identical with those described in the Sections 4.2 and 4.3. In addition cryogenic processes such as condensation or methane wash may be applied [588]. In the past, ammonia plants based on coke-oven gas had some importance, but their present share of world capacity is lower than 3 %, and other byproduct gases contribute less than 0.5 %.

Ammonia plants based on **water electrolysis** for hydrogen production contribute less than 0.5 % to world production and are a very uneconomic option. One metric ton of ammonia requires theoretically 1976 m^3 H_2 (STP). As conventional alkaline water electrolysis has an electric energy consumption of 4.6 MWh/1000 m^3 H_2 (STP) [589], the hydrogen supply for the ammonia plant corresponds to 9.1 MW [589]. With the theoretical heat equivalent of 3600 kJ/kWh (hydroelectric power supply assumed) the hydrogen production for 1 t NH_3 consumes 32.7 GJ. When generating the electric power from fossil feedstocks a conversion factor of 10 900 kJ/kWh has to be used to give a figure of 99 GJ, which is more than three times the total energy consumption of a modern natural-gas-based ammonia plant. In addition to the above-mentioned

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Table 30. Examples of hydrogen-rich gases [588]

	Pressure, bar	% H_2	% CO
Refinery sector			
Catalytic reformer	18 – 20	70 – 90	
Hydrocracker HP vents	42 – 140	70 – 90	
Hydrotreater vents	14 – 56	65 – 85	
Chemical and other industry			
Ethylene off-gas	10	90 – 95	
Acetylen off-gas	10	50 – 55	27
Styrene off-gas	18 – 32	80 – 90	
Coke oven gas	0.5	60 – 64	5

figures, energy for air separation to yield the stoichiometric nitrogen requirement (about 80 kWh/t NH_3) and for compression is required (about 700 kWh/t NH_3). Application of pressure (6 – 200 bar) has no significant influence on the power consumption of the electrolysis. The total energy needed for electrochemical decomposition of water decreases only slightly with increasing temperature, but the reversible part of energy requirement (ΔF), which has to be supplied as electric energy, decreases considerably (3 kWh /m^3 (STP) at 800 – 900 °C) H_2 [590], which means that an increasing amount of the total energy could be supplied as heat, but this definitely would not improve the competiveness. High-temperature electrolysis is still in the development stage.

In addition the investment cost for conventional water electrolysis is rather high, about 1 000 DM/kW_{el} in 1989. This would give a total investment for a world-size plant capacity 1 200 t/d of ammonia, which is about 2.5 times the value of a natural-gas-based steam reforming ammonia plant [590].

4.2. Carbon Monoxide Shift Conversion

As ammonia synthesis needs only nitrogen and hydrogen, all carbon oxides must be removed from the raw synthesis gas of the gasification process. Depending on feedstock and process technology, this gas contains 10 – 50 % carbon monoxide and also varying amounts of carbon dioxide. In the water gas shift reaction, traditionally known as carbon monoxide shift conversion, the carbon monoxide serves as reducing agent for water to yield hydrogen and carbon dioxide. In this way not only is the carbon monoxide converted to readily removable carbon dioxide but also additional hydrogen is produced:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H^0_{298} = -41.2 \text{ kJ/mol} \tag{37}$$

As no volume change is associated with this reaction, it is practically independent of pressure, but as an exothermic process, it is favored by lower temperatures, which shift the equilibrium to the right-hand side. Even with a low excess of steam in the gas, the equilibrium concentrations of CO are low; for example, 0.2 vol % at 220 °C and

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0.12 vol % at 200 °C for a steam/gas ratio of 0.4. The temperature dependence of the equilibrium constant K_p as defined by Equation (79) is given in the Equation (80) [591].

$$K_p = f_{CO_2} f_{H_2} / f_{CO} f_{H_2O} \quad (79)$$

$$1/K_p = \exp 13.148 - 5639.5/T - 1.077 \ln T - 5.44 \times 10^{-4} - 1.125 \times 10^{-7} T^2 + 49170/T^2 \quad (80)$$

The variation of the heat of reaction may be calculated with following formula [592]:

$$\Delta H = -47.617 + 1.302 \times 10^{-2} T - 0.126 \times 10^{-5} T^2 + 0.791 \times 10^{3} T^{-1} \text{ kJ/mol} \quad (81)$$

To keep the temperature low the heat of reaction must be removed in an appropriate way, and to achieve a sufficient reaction rate effective catalysts have to be applied. The process is therefore performed in steps, with intermediate heat removal between the individual catalyst beds, in which the reaction runs adiabatically. Recently, quasi-isothermal reactors have been developed in which cooling tubes run though the catalyst layers.

As the process configuration and catalysts are to some extent different for steam reforming and partial oxidation, they are treated separately here.

4.2.1. Shift Conversion in Steam Reforming Plants

In the traditional plant concept, the gas from the secondary reformer, cooled by recovering the waste heat for raising and superheating steam, enters the high-temperature shift (HTS) reactor loaded with an iron – chromium catalyst at 320 – 350 °C. After a temperature increase of around 50 – 70 °C (depending on initial CO concentration) and with a residual CO content of around 3 % the gas is then cooled to 200 – 210 °C for the low-temperature shift (LTS), which is carried out on a copper – zinc – alumina catalyst in a downstream reaction vessel and achieves a carbon monoxide concentration of 0.1 – 0.3 vol %.

4.2.1.1. High-Temperature Shift Conversion (HTS)

4.2.1.1.1. High-Temperature Shift Catalyst

In the unreduced state the HTS catalyst is iron(III) oxide (Fe_2O_3) containing additionally 5 – 10 % chromic oxide (Cr_2O_3). During operation, it is reduced more or less stoichiometrically to the composition of magnetite (Fe_3O_4) [593] – [595]. The catalyst is active in the temperature range of 300 – 500 °C. Steam surplus is not only necessary for thermodynamic reasons but also to suppress undesirable side reactions. Decreasing the steam surplus lowers the oxygen to carbon ratio in the HTS to such an extent that the

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atmosphere can reduce magnetite partially to metallic iron. In addition the Boudouard reaction can occur under these conditions. The resulting carbon is deposited within the catalyst particles causing their disintegration, and iron carbides will be formed, which are effective Fischer – Tropsch catalysts that lead to the formation of some methane and higher hydrocarbons [404], [596], [597]. The minimum steam surplus depends on the CO/CO_2 ratio, lower values allowing lower steam surplus. Thus in conventional plant operation at 32 – 35 bar with CO/CO_2 of 1.65 – 2.13, an S/C ratio in the primary reformer of around 3.0 seemed to be the minimum with respect to the HT shift, whereas for concepts with reduced primary reforming and a CO/CO_2 ratio of 1.2 (the Braun process, for example) an S/C ratio of 2.8 was sufficient. Newly introduced HTS catalysts with additional copper promotion (e.g. 3 %) suppress this side reaction [598] and are therefore less sensitive to lower steam-to-gas ratios. The presence of MgO and ZnO should also effect some reduction of methane formation [599] – [602]. A review of catalyst research, surface science investigations and relevant literature is given in [603]. The function of Cr_2O_3 is mainly to prevent the sintering of the iron oxide, which leads to a reduction of surface area. But attempts to substitute Cr by Ce or Zr [604] – [607] (because in commercial Fe/Cr catalysts a minor amount of the chromium is still present as Cr^{6+} [603]) resulted in a lower activity of these Cr-free catalysts.

In the production of the HTS catalyst, mixed iron(III)hydroxide and chromium(III)-hydroxide are precipitated from an aqueous solution of ferrous sulfate and chromic acid by addition of sodium hydroxide solution while agitating with air to perform the oxidation of Fe^{II} to Fe^{III} and injecting steam for temperature adjustment. The oxide slurry is washed in alternating agitating and settler operations (to achieve a very low residual sulfur content). The washed hydroxides are spray-dried and the resulting powder is granulated with an additive which serves as lubricant and binder and than pressed into tablets of the required size 6 × 6 mm, 9 × 5 m, 9 × 9 mm are standard, but other dimensions are possible, too). Some manufactures use iron nitrate instead of iron sulfate as raw material. The BET surface area of commercial Fe – Cr HT shift catalysts is between 30 and 80 m^2/g, depending on Cr_2O_3 content and calcining temperature [608]. The space velocities in commercial HT reactors are today approximately 3500 – 4500 h^{-1}.

The classical HTS iron catalyst is resistant against sulfur compounds, but this is of greater importance in partial oxidation processes and less for the practically sulfur-free steam reforming gas.

4.2.1.1.2. Reaction Mechanism and Kinetics

The reaction kinetics were studied by many researchers with sometimes different or contradictory results. Reviews are found in [592], [602], [603], [609]. A reason for this is that often diffusional effects were not eliminated, and therefore no real intrinsic reaction rates were obtained [610], [611]. In industrial practice equations are required for dimensioning reaction vessels and catalyst. The mathematical expressions used for this purpose are for the most part not based on theoretical assumptions and research

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results; they are rather just a quantitative modeling of laboratory measurements and can usually be extrapolated only to a limited extent beyond the range of the measurement conditions. Correlation with measurements in industrial units and allowance for activity decline with operating time and inclusions of safety margins led to useful mathematical expressions for design purposes. An early example is a rate equation given by LAUPICHLER [612], but its accuracy was not very satisfactory. A better approach to reality is achieved by an expression developed by MOE [631]. Another equation was developed on the basis of a theoretical assumption of a stepwise reaction on the catalyst surface, assuming the reaction of CO to be rate-determining and equilibrium conditions for the other steps involved. Assuming that the relevant equilibrium constants are very small and that there are no diffusional limitations, an equation of the following form can be derived (82) [609]:

$$r = kP\,[\mathrm{CO}]\left[1 - \frac{[\mathrm{CO_2}]\,[\mathrm{H_2}]}{K_\mathrm{p}\,[\mathrm{CO}]\,[\mathrm{H_2O}]}\right] \tag{82}$$

To make allowance for mass transport restrictions, the equation can be modified by including a term containing the diffusion coefficient of CO. For operating pressures between 10 and 50 bar, when the reaction rate is controlled by bulk diffusion, Equation (83) can be applied:

$$r = k_\mathrm{H} P^{1/2}\,[\mathrm{CO}]\left[1 - \frac{[\mathrm{CO_2}]\,[H_2]}{K_p\,[\mathrm{CO}]\,[\mathrm{H_2O}]}\right] \tag{83}$$

The same equation was derived empirically from the experimental observations, indicating that the forward rate with respect to CO is first order and with respect to water zero order and that the forward reaction rate is proportional to the square root of the total pressure between 10 and 50 bar ($p^{0.60}$ for 1 – 10 bar; some authors report a maximum reaction rate between 11 and 30 bar [613], [614]). BOHLBRO [613] proposed a power law type rate expression (Eq. 84) which fitted well his experimental data covering a wide range of conditions, diffusion-free and diffusion-controlled, atmospheric and elevated pressure, with commercial catalysts of various particle sizes.

$$r = k\,(p_\mathrm{CO})^l\,(p_{\mathrm{H_2O}})^m\,(p_{\mathrm{CO_2}})^n\,(p_{\mathrm{H_2}})^q\,(1-\beta) \tag{84}$$
$$\beta = p_{\mathrm{CO_2}}\,p_{\mathrm{H_2}}/K\;p_\mathrm{CO}\,p_{\mathrm{H_2O}}$$

Virtual activation energies of 114.6 to 59.8 kJ/mol were found, depending on catalyst particle size. CHINCHEN [612] found for the intrinsic reaction measured on an ICI catalyst the real activation energy to be 129.4 kJ/mol.

Two reaction mechanisms were proposed [602]: a) the catalyst acts as a simple adsorbent on which the reactants react on the surface (Langmuir – Hinshelwood type); b) the active catalyst sites are successively oxidized and reduced by the adsorbed reactants (Rideal – Eley type). Evaluation of the vast amount of experimental material leads to the conclusion that the HT shift (and also the LT shift) proceeds via mechanism (b), which schematically may be formulated as shown in Figure 62.

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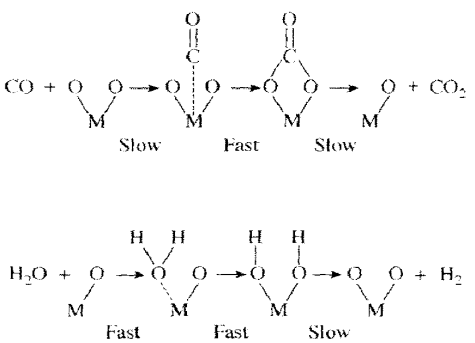


Figure 62. Oxidation–reduction mechanism of the HT shift conversion

To calculate the amount of catalyst for a particular case, mass and heat balance have to be considered; they can be described by two differential equations: one gives the differential CO conversion for a differential mass of catalyst, and the other the associated differential temperature increase. As analytical integration is not possible, numerical methods have to be used for which today a number of computer programs are available with which the calculations can be performed on a powerful PC in the case of shift conversion. Thus the elaborate stepwise and graphical evaluation by hand [592], [609] is history. For the reaction rate r in these equations one of the kinetic expressions discussed above (for example, Eq. 83) together with the function of the temperature dependence of the rate constant has to be used.

Following practical rules of thumb [592] are useful for choosing the operation conditions: Equilibrium approach should be 10 – 20 °C at a converter outlet temperature of $\leq$ 450 °C; maximum catalyst temperature should not exceed 550 °C; adiabatic temperature rise for 1 % CO (wet basis) converted: 10.6 °C at 500 °C, 11.0 °C at 400 °C, 11.6 °C at 225 °C; inlet temperatures for HTS below 330 °C are uneconomical.

4.2.1.2. Low-Temperature Shift Conversion (LTS)

The classical iron–chromium catalyst exhibits a sufficient activity only above temperatures of 320 – 360 °C. The introduction of the new copper–zinc based low-temperature shift catalyst in 1963 [615], made it possible to take advantage of the lower equilibrium CO concentrations at temperatures around 200 °C, shown for various steam/gas ratios in Figure 63. As can be seen from the diagram, a rather low CO concentration even at very low steam/gas ratios should be attainable with a sufficiently active LTS catalyst. In combination with methanation (Section 4.3.2.1.) it was possible to replace the energy consuming copper liquid scrubbing stage, which was used in old plants to remove the comparatively high residual CO content (around 3 %) after the HTS.

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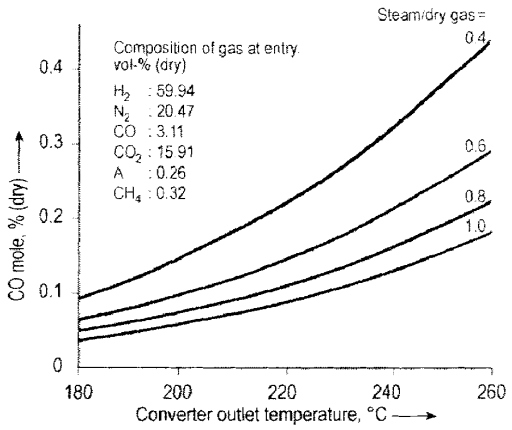


Figure 63. Equilibrium CO concentrations in LTS

4.2.1.2.1. Low-Temperature Shift Catalyst

The LTS catalyst, supplied in pellets like the HTS catalyst, consists of 40–55% copper oxide, 20–30% zinc oxide, the balance being alumina. The catalyst properties are influenced far more by the formulation and manufacturing procedure [616] than by its chemical composition. It makes a great difference whether the individually prepared components are just mixed physically as oxides or are incorporated by co-precipitation. The latter procedure assures a rather fine distribution of the copper oxide crystals, which are well separated from each other by zinc oxide and even smaller alumina crystals. This retards sintering of the copper cristallites in the reduced catalyst during prolonged operation [617], [618]. The co-precipitation step of the catalyst manufacturing sequence has to be very carefully controlled with respect to temperature, pH, and agitation to achieve the desired result. Commercial pellet sizes range from 6.4 × 3.2 mm to 3.5 × 3 mm; the surface area is around 60–120 m^2/g, and the pore volume 0.35–0.45 ml/g.

The copper oxide is reduced in situ with hydrogen and a carrier gas (usually nitrogen) to form the fine copper crystallites of about 10^{-6} cm on which the activity depends.

Sulfur, usually present as H_2S, has to be below 0.1 ppm, but even with such low concentrations, the catalyst is slowly poisoned. The ZnO adsorbs the sulfur and it finally transforms into bulk ZnS. When the ZnO is exhausted in a given layer of the catalyst, the H_2S causes deactivation of the copper by sintering. The poisoning process moves through the catalyst as a relatively sharp front and can be seen in the change of the catalyst temperature profile over time [619], [620] (Figure 64).

The LTS catalyst is protected by a guard bed, formerly loaded with ZnO, but nowadays usually with LTS catalyst [621]. Changing the guard bed more frequently prolongs the service life of the main LTS catalyst bed. Without a guard bed the lifetime is normally 2–4 years, depending on gas quality. With an upstream guard bed,

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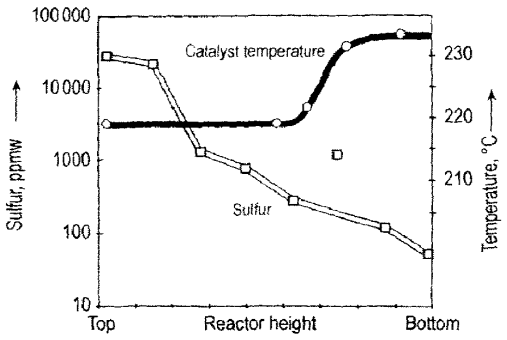


Figure 64. Sulfur and temperature profile for used LTS catalyst

changed at appropriate intervals the life time of the main bed can be extended to 6 – 10 years [499]. Traces of chlorine compounds [622], which may be introduced with the natural gas or more often with the process air to the secondary reformer, may also deactivate the LTS catalyst by accelerating the sintering of the copper particles. Unlike sulfur poisoning, chlorine is more diffusely distributed over the whole catalyst bed by migration as volatile zinc and copper chlorides. A chlorine guard catalyst for installation upstream of the LTS is offered by catalyst vendors.

As chemical composition and formulation of the LTS catalyst are very similar to methanol production catalysts, small quantities of methanol are formed and found in the process condensate after cooling the LTS effluent. In a consecutive reaction, amines (mainly methylamine) are formed from the methanol and traces of ammonia originating from the secondary reformer and the HTS. These pollutants are removed from the process condensate by steam stripping and ion exchange. Byproduct formation is higher with fresh catalyst and declines with operating time. New catalyst types with increased activity and higher selectivity have reduced the problem. The tendency for methanol formation increases with decreasing steam/gas ratio [623].

4.2.1.2.2. Reaction Mechanism and Kinetics

Compared to the HT shift reaction fewer publications exists on the reaction kinetics of LT shift reaction. Studies made before 1979 may be found in [602]. A rather simple power law (Eq. 85), for example [624] fitted well measurements between 200 and 250 °C, but the weak point is that the exponents are temperature dependent. An expression of the Langmuir – Hinshelwood-type, published in [625], includes additionally the influence of H_2 and CO_2 concentration on the reaction rate.

$$r = k\,(p_{CO})^{l}\,(p_{H_2O})^{m};$$
$$200\ °C:\ l = 0.45,\ m = 0.07;\ 250\ °C:\ l = 1.07,\ m = 0.55 \qquad (85)$$

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A more complex formula (Eq. 86), used for evaluation of catalyst volume, is described in [592]:

$$\frac{d(G[CO_2])}{dV} = \frac{A}{T} \frac{k_l [CO] [H_2O]^{1/2} (1 - K/K_p)}{1/p + k_a [CO] + k_b [CO_2]} \tag{86}$$

k_l, k_a, k_b temperature dependent functions, G g mols/sec wet gas, V catalyst volume, A constant, $K = (CO_2)(H_2)/(CO)(H_2O)$, K_p equilibrium constant, P total pressure.

For comparison of the activity of commercial shift catalysts, sometimes the so-called K_w *value* is found in the literature. This term, introduced by K. ATWOOD is defined for shift reactions as follows [626]:

$$K_w = SV_w \log[(CO_{in} - CO_{eq})/(CO_{out} - CO_{eq})] \tag{86a}$$

The index w refers to wet gas.

For the LT shift an oxidation reduction mechanism has been discussed which is similar to that proposed for the HT shift, but this concept is not unquestioned and the presently available experimental material provides no convincing evidence.

4.2.1.3. Intermediate-Temperature Shift (ITS)

A relatively new process concept is the intermediate temperature shift [627], [628], which performs the reaction in a single step. The catalyst is based on a copper–zinc–alumina formulation and optimized for operating in a wider temperature range (200–350 °C) than the standard LTS catalyst (190–275 °C). The reaction heat can be removed by use of a tube-cooled reactor raising steam or heating water for gas saturation to supply process steam in the reforming section (Linde LAC, ICI Catalco LCA). In a new plant using the spiral-wound Linde reactor [629], a methane slip of only 0.7 mol% (dry basis) is achieved. Further purification is performed by PSA. Generally the shift conversion reactors have an axial gas flow pattern, but recently radial gas flow configurations have been chosen in some instances. The lower gas velocities result in reduced pressure drop, which saves compression energy and allows the use of smaller catalyst tablets (3 × 3 mm or 2 × 2 mm), which because of the higher activity can achieve a lower CO leakage. In a 1000 t/d plant without hydrogen recovery the ammonia production would be increased by 10 t/d. Ammonia Casale has patented radial flow designs for both HTS and LTS. In a recent revamp the pressure drop was reduced from 0.55 to 0.35 bar in the HTS and from 0.55 to 0.22 in the LTS. The CO leakage from the LTS could lowered to 0.11% from 0.25% [628].

Additional literature on shift conversion in steam reforming plants can be found in [402], [404], [498], [499], [630]–[638].

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In some ammonia process schemes operating without a secondary reformer and applying pressure swing adsorption (PSA) for further purification (KTI PARC), only a HTS is used.

4.2.2. Shift Conversion in Partial Oxidation Plants

The raw synthesis gases from partial oxidation of heavy hydrocarbons and coal differ mainly in two aspects from that produced from light hydrocarbons by steam reforming. First, depending on the feedstock composition, the gas may contain a rather high amount of sulfur compounds (mainly H_2S with smaller quantities of COS); second, the CO content is much higher, in some cases in excess of 50 %. The sulfur compounds (Section 4.3.1.4) can be removed ahead of the shift conversion to give a sulfur-free gas suitable for the classical iron HTS catalyst. In another process variant the sulfur compounds are removed after shift conversion at lower concentration because of dilution by CO_2. The standard iron catalyst can tolerate only a limited amount of sulfur compounds. With a sulfur concentration in the feed >100 ppm sulfur will be stored as iron sulfide (Eq. 87):

$$Fe_3O_4 + 3\,H_2S + H_2 \rightleftharpoons 3\,FeS + 4\,H_2O \qquad (87)$$

FeS also catalyzes the shift reaction, but its activity is only half that of Fe_3O_4 [592] – [594]. In principle the catalyst can tolerate up to 500 or 1000 ppm H_2S, but with a considerable loss of mechanical strength, which is additionally affected by other contaminants in the gas, such as soot and traces of formic acid. For this reason the *so-called dirty shift catalyst* is used in this case, which was originally introduced by BASF [639]. This cobalt – molybdenum – alumina catalyst [603], [630], [640] – [644] is present under reaction conditions in sulfidized form and requires for its performance a sulfur content in the gas in excess of 1 g S/m^3. Reaction temperatures are between 230 and 500 °C. COS is not hydrolyzed on dirty shift catalysts, but may be removed in the subsequent sour-gas removal stage using the Rectisol process. Separate hydrolysis on alumina based catalysts is possible at temperatures below 200 °C [603].

In later developments aditionally potassium carbonate promotion of the dirty shift catalysts was introduced [645], [646] which increased the activity at low temperatures to achieve CO values sufficiently low to use a methanation step after CO_2 removal. But according to [647] it is also possible to achieve such low CO concentrations with nonalkalized dirty shift catalyst as shown in Figure 65.

The vertical lines represent different sulfur concentrations together with the temperatures at which the catalyst begins to lose sulfur to the gas. In the example of Figure 65, the gas must have a sulfur content higher than 550 ppm to keep the catalyst in the sulfided state at the outlet of the first bed.

Equations to describe reaction rate measurements on dirty shift catalyst are given in [648], [649].

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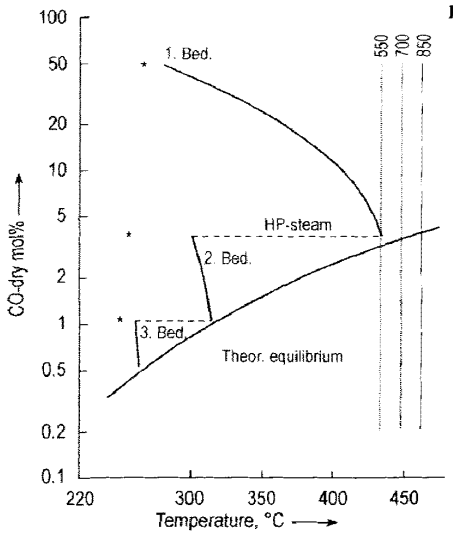


Figure 65. Dirty shift conversion on BASF catalyst K 8-11

Irrespective of the catalyst type used, the high initial carbon monoxide concentrations mean that the reaction must generally be performed in steps, with intermediate cooling. But it has also been reported that the CO content can be reduced from 50 to 0.8 % in a single step in a large hydrogen plant by using a quasi-isothermal reactor (e.g., the Linde spiral-wound reactor).

4.3. Gas Purification

In further purification, carbon dioxide, residual carbon monoxide, and sulfur compounds (only present in the synthesis gas from partial oxidation) have to be removed as they are not only a useless ballast but above all poisons for the ammonia synthesis catalyst.

The raw synthesis gas produced by steam reforming of natural gas and light hydrocarbon feedstocks is free of sulfur. Any sulfur contained in the feedstock has to be removed of upstream of gasification to avoid poisoning of the sensitive reforming catalysts. This is usually performed by hydrodesulfurization and adsorption of the H_2S by ZnO. As this is an essential part of the steam reforming process, it was already treated in Section 4.1.1.

In partial oxidation processes there is no prior treatment of the feedstock and the total sulfur contained in the coal or hydrocarbon feed is converted in the gasification to H_2S and a smaller amount of COS. As H_2S is soluble in the same solvents which can be used for CO_2 removal, selective absorption and/or desorption is a special problem

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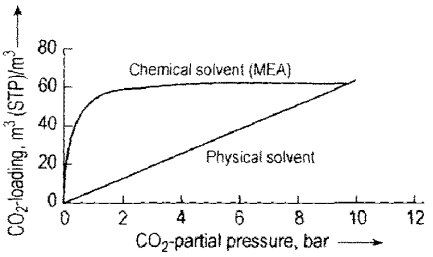


Figure 66. CO_2 loading characteristics of various solvents

encountered in partial oxidation of sulfur containing feedstocks. Therefore removal of the sour gases, as CO_2 and H_2S are frequently called, and the subsequent recovery of sulfur will be treated in a separate section.

4.3.1. CO_2 Removal

The standard method is to scrub the CO_2-containing synthesis gas under pressure with a solvent capable of dissolving carbon dioxide in sufficient quantity and at sufficient rate, usually in countercurrent in a column equipped with trays or packings. The CO_2-laden solvent is flashed, often in steps, to around atmospheric pressure, and the spent scrubbing liquid is subsequently heated and regenerated in a stripping column before being recycled to the pressurized absorption column. In the early days of ammonia production water, often river water, served as solvent in a once-through process without regeneration and recycling.

Today a variety of solvents are used and they can be categorized as physical or chemical solvents. In the physical solvents the carbon dioxide dissolves without forming a chemical compound, and this allows recovery simply by flashing. In the chemical solvents the carbon dioxide becomes fixed as a chemical compound, which needs heat for its decomposition. At low carbon dioxide partial pressures, the chemical solvents absorb substantially more carbon dioxide than the physical solvents; at higher partial pressures the physical solvents (according to Henry's law, the loading is approximately proportional to the CO_2 partial pressure) have a higher loading capacity than the chemical solvents, for which the solubility approaches a saturation value. Figure 66 shows the loading characteristic for various solvents.

Chemical solvents are best suited to scrubbing gases that have a relative low CO_2 partial pressure, whereas the physical solvents are more suitable for higher CO_2 contents in the raw gas. As both sour gases, CO_2 and H_2S, have good solubility in the applied solvents, special process configurations are required for partial oxidation gases to recover separately a pure CO_2 fraction and an H_2S-rich fraction suitable for sulfur disposal.

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Chemical solvents are aqueous solutions of potassium carbonate or alkanolamines containing additional activators to enhance mass transfer and, in some cases, inhibitors to limit or prevent corrosion processes. Primary and secondary amines, for example, monoethanolamine (MEA) and diethanolamine (DEA), exhibit a high mass-transfer rate for carbon dioxide but have a high energy demand for regeneration. For this reason tertiary amines are commonly used today, for example, methyldiethanolamine together with an activator. Triethanolamine does not achieve the required final CO_2 concentration, and in the few cases where it was used it was followed by additional scrubbing with monoethanolamine (MEA). The **solvents with physical absorption** characteristics are various poly-glycol ether mixtures, *N*-methyl pyrrolidone, methanol, propylene carbonate, and sulfolan with additives. Table 31 (from [650], supplemented and modified) lists the various solvents and their properties.

Over the years considerable progress has been achieved in improving the efficiency of the carbon dioxide removal systems. The first generation of single-train steam reforming ammonia plants used MEA and consumed about 5.8 GJ/t NH_3, which was about 41 % of the total energy consumption. Table 32 demonstrates the progress made in energy consumption.

The first progress was made by addition of corrosion inhibitors (e.g., Amine Guard introduced by Union Carbide) [651] – [655], which allow a higher loading of the solvent. The energy consumption of the modern systems, as shown in the last two lines of Table 32 depends largely on process configuration and required final purity, which may range from 50 to 1000 ppm in the purified gas. There is also a trade-off between energy consumption and investment costs.

4.3.1.1. Process Configuration

Usually packed towers are used for absorption and regeneration. Column diameters and height of the packings in connection with the required circulation rate of the solvent and the heat needed for regeneration can be varied over a considerable range to meet the process conditions of the individual ammonia plant. Packed height requirement is calculated according to the concept of height of transfer units and number of transfer units using mass-transfer rate expressions and absorption equlibrium data from laboratory and pilot plant measurements with the relevant type of packing material (geometry). Heat effects associated with the gas absorption have to be considered, too, and will complicate the calculation. As flooding represents the maximum capacity condition for a packed column it is used as design basis for the column cross section. In addition the pressure drop has to be evaluated. Standard procedures and data on packing characteristics are found in [656]. Compared to the widely used Pall rings newer packing forms such as Cascade mini rings, Metal Intalox, Tellerettes and others, are more effective and will allow to reduce absorber dimensions. Ceramic packings are no longer used in newer plants because they can loose their mechanical strength after some time of operation as the result of being leached by the solvent.

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Table 31. Solvents used for CO_2 removal

	Chemical absorption processes			Physical absorption processes				
	Alkanolamine processes		Hot poptash processes	Selexol	Fluor solvent	Purisol	Rectisol	Sulfinol D
	MEA	aMDEA	Selexol	Fluor solvent	Purisol	Rectisol	Sulfinol D	
CO_2 p.press. inlet	low mod	mod high	mod high	mod high	high	high	high	high
CO_2 outlet, ppm	50	50 (any)	< 500	< 1000	1%	< 1000	< 10	< 1000?
Corrosion inhibitor	yes	no	yes	no	no	no	no	no
Solovent losses	yes	no	no	no	no	no	yes	yes
Absorber temp. °C	40–60	60–70	90	−5	−3	amb.	< −30	25–85
Hot regeneration	yes	small amount	yes	no	no	no	no	yes
Dew point raw gas	sat'd	sat'd	sat'd	−5	−3	−5	−5	10
Solution reclaimer	yes	no	no	no	no	no	no	yes
Regeneration gas	no	no	no	air	air	N_2	no	no

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Table 32. Heat requirements for regeneration in CO_2 removal systems [404], [651]

Process	Heat requirement, kJ/mol CO_2
MEA (without Amine Guard)	209
MEA (with Amine Guard III)	116
Benfield hot potash (1-stage)[a]	88
BASF aMEAD process (1-stage)[a]	73
Benfield LoHeat	28–35
BASF aMEAD process (2-stage)[b]	28–30

[a] Single-stage regeneration. [b] Two-stage regeneration.

Another risk is breakage which may occur in plant upsets. For example rapid depressurization could lift the packing. For this reason the material of modern packings is either steel (often stainless steel because of potential erosion/corrosion) or polypropylene. In some processes the variation of the promoter concentration may be a variable in the optimization puzzle, too.

The number and pressure level of the intermediate flashing stages are determined by tolerable synthesis gas losses and the CO_2 specification. In most cases a higher or lower proportion of the CO_2-laden solution is regenerated simply by flashing, and only a fraction of the total solvent circulation is regenerated by stripping. With increasing chemical character of the solvent the stripping duty increases, and in the old MEA CO_2-removal systems all CO_2 had to be recovered in this way, needing a high consumption of low pressure steam.

The flashed solvent, containing a CO_2 load corresponding to the CO_2 partial pressure (semi-lean solution), is returned to first stage of the scrubber; the stripped lean solution is fed to the top of the second stage and its residual CO_2 content determines the achievable purity in the treated gas.

An important issue is the proper design of the distributors for the solvent and an adequate liquid holdup in the pump sump to balance fluctuation in the liquid flow sometimes caused by foaming. Foaming may require addition of suitable antifoaming agents. To reduce the mechanical energy demand the laden solution is depressurized over a hydraulic turbine mounted on the pump shaft. In processes which need addition of inhibitors to prevent corrosion, careful control of inhibitor concentration is required.

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4.3.1.2. Chemical Absorption Systems

4.3.1.2.1. Hot Potash Systems

The commercial hot potash systems differ in the type of activator used to increase the reaction rate between the CO_2 and the solvent. The activators enhance mass transfer and thus influence not only the regeneration energy demand (circulation rate of the solvent) but also the equipment dimensions. The following activators are used: in Benfield [657]–[660] and Carsol [661], [662] processes ethanolamines; in the Giammarco Vetrocoke process glycine (originally arsenic oxide) [663]–[666]; in the Catacarb system [667], [668] amine borate; in the Exxon Flexsorb HP process [669], [670] a sterically hindered amine; in the Carbosolvan process [671], [672] sulfosolvan B. New activators named ACT-1 (UOP) [673], [674] and LRS-10 [675], [676] (British Gas) have been introduced recently. All hot potash systems need corrosion inhibitors the concentration of which must carefully to be monitored.

Benfield LoHeat System (UOP) [677]. The high thermal efficiency of this two-stage adsorption process using lean and semi-lean solvent is achieved by recompression of the flash steam with an injector or a mechanical vapor compressor. UOP has also developed a number of other process configurations [404], [669], [678]–[680]. The diethanolamine promoter enhances the mass transfer by carbamate formation (Eqs. 88–90) [681]:

$$R_2NH + CO_2 \rightleftharpoons R_2NCOOH \quad (88)$$

$$R_2NCOOH + K_2CO_3 + H_2O \rightleftharpoons 2\,KHCO_3 + R_2NH \quad (89)$$

Overall reaction:

$$K_2CO_3 + CO_2 + H_2O \rightleftharpoons 2\,KHCO_3 \quad (90)$$

Optimum CO_2 absorption is achieved if the concentration of K_2CO_3 is about twice of the concentration of $KHCO_3$. UOP defines a so-called conversion factor $F_c = 1 - \{[K_2CO_3]/([K_2CO_3] + 0.69\,[KHCO_3])\}$ which should be 0.25–0.30. The $KHCO_3$ content should be kept under control for another reason: it is less soluble than K_2CO_3 and could precipitate if the concentration becomes too high. Precipitated bicarbonate peels off the passivation layer, and problems may arise by formation of a slurry composed of bicarbonate, vanadium, and iron. Normally the vanadium of the corrosion inhibitor oxidizes the iron on the metal's surface ($V^{5+} + Fe^{2+} \rightleftharpoons V^{4+} + Fe^{3+}$). The resultant Fe_3O_4 produces a tight, coherent film on the steel surface, thus preventing any corrosion as long as it remains intact. Figure 67 is a simplified flowsheet of the Benfield LoHeat CO_2 removal process [404].

Recently UOP has introduced a new activator, called ACT-1 [673] which is claimed to reduce CO_2 levels in the absorber exit gas in existing plants and should reduce the solvent circulation rate as well. For new installations the enhanced mass transfer achieved with the new activator translates into smaller towers and therefore to investment capital savings. The activator is an amine compound, but speculations on its nature are still going on.

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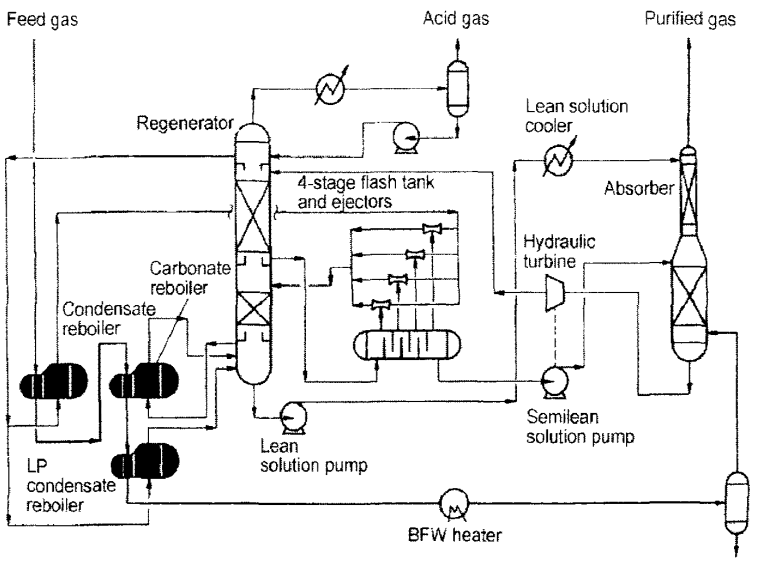


Figure 67. Benfield LoHeat CO_2 removal process.

Catacarb Process [667], [681], [682]. This process was introduced about 30 years ago. A modified potassium salt solution is used, containing various stable and non toxic catalysts and corrosion inhibitors. The process is very versatile and allows the process and mechanical configuration to be tailored to a wide range of CO_2 partial pressures. Figure 68 showes a Catacarb single-stage low heat design.

Giammarco–Vetrocoke process [663]–[666], [681], [683]. This process was developed in the 1950s and is suitable for carbon dioxide absorption as well as for treating hydrogen sulfide gases. Among the several tested and used activators arsenic trioxide proved to be the most efficient (an increase of efficiency a the factor of 10–12 compared to non promoted potash). It also acted as a corrosion inhibitor. Arsenic-promoted Giammarco–Vetrocoke systems were used in quite a number of ammonia plants. Because of its toxicity and for environmental reasons the arsenic was later replaced by glycine in a concentation of 30–50 g/L with vanadium compounds added as corrosion inhibitor. A two-stage process with intermediate flash and lean and semi-lean solution circle is normally used.

LRS 10 of British Gas [675], [676], [681]. This new activator combination for hot potash systems was commercially introduced in 1988 and since then used in 30 plants which include ammonia, LNG, hydrogen and vinyl acetate. A corrosion inhibitor is still used in the absorption solution.

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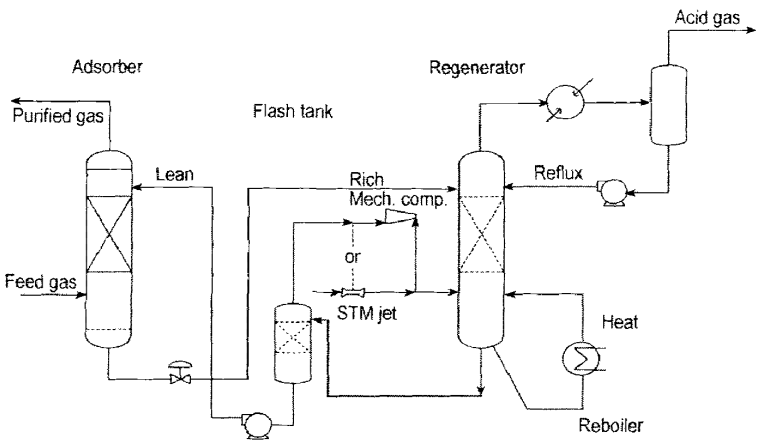


Figure 68. Catacarb single stage low heat design.

Exxon's Flexsorb process [669], [670] uses a sterically hindered amine as an effective promoter of a hot potash system. A lower energy requirement and less solution makeup than in other processes are claimed. So far it has been successfully used in several large plants.

Other hot potash processes offered are the **Carbosolvan process** [671] and the **SPIC process** [681].

4.3.1.2.2. Ethanolamine-Based Systems

MEA Process. Some organic compounds of the group of ethanolamines with the general formula $R_nN(C_2H_5OH)_{3-n}$ where R is H or an aliphatic group, have been successfully used as aqueous solutions in CO_2-removal systems. Very important was for a long time monoethanolamine (MEA), which was introduced in 1943 for the purification of ammonia synthesis gas. It actually was the first solvent to substitute water scrubbing and it remained for a long time, until the less energy consuming MDEA and hot potash processes were developed. In fact practically all of the 600 to 1000 t/d single-train ammonia plants used this solvent for CO_2 removal. The chief merits of MEA was that a rather low residual carbon dioxide content in the treated gas could be achieved in a very simple and inexpensive process configuration, but admittedly at the expense of very high energy consumption in form of low-level steam for solvent regeneration. But energy (natural gas consumption) was not a matter of concern in those days. The basic disadvantage of the system was that the carbamate formed in the absorption solution (depending on CO_2 loading and MEA concentration in water) is extremely corrosive. On account of this corrosion problem, in early MEA units it was not possible to use MEA solution containing more than 20 %. Union Carbide intro-

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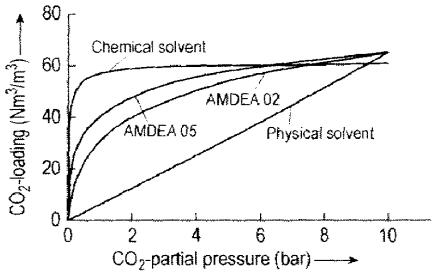


Figure 69. CO_2-loading capacity of various solvents

duced a corrosion inhibitor, named *Amine Guard* by which dramatically reduced corrosion and the MEA concentration could be raised to 30%, resulting in higher CO_2 loading of the solvent. As can be drawn from Table 32, the energy saving achieved thereby was considerable. Today there are worldwide quite a number of MEA units still in operation, which are increasingly being revamped to more efficient processes, e.g. aMDEA. For new installations the MEA technology has become obsolete.

A leading process today is the **BASF Activated MDEA process (aMDEA).** [684] – [690]. The process uses an aqueous solution of the tertiary amine methyldiethanolamine (MDEA) with a special amine activator. No corrosion inhibitors are necessary, and unlike MEA no solvent degradation is observed, so recovery installations are not required. Owing to the low vapor pressure of MDEA and the activator, there are no losses of the active solvent components. The carbon dioxide binds much less strongly to MDEA than to MEA, and the solvent character is more like a hybrid between a strong chemical and a purely physical solvent. On account of the relative weak binding forces, a substantial amount of carbon dioxide can be recovered simply by flashing to low pressure, and only a small amount has to be recovered by stripping. The process is very versatile: increasing the activator concentration shifts the character of the solvent more to the chemical side and vice versa, as illustrated by Figure 69. For example, highly activated MDEA 06 has a more chemical solvent behavior with high efficiency in absorption, but a more energy intensive regeneration, ideal for low-investment configurations and best suited revamps in which only the solvent is swapped. On the other hand, weakly promoted MDEA 01, with moderate adsorption efficiency and low energy requirement, is an excellent choice for purification of natural gas with high CO_2 partial pressure.

The possible process configurations include a wide rage of two- and single-stage designs, the latter allowing old MEA units to be revamped [689], [691] – [693] simply by swapping the solvent without changing the process equipment. Figure 70 gives a standard two-stage configuration normally used in modern low-energy ammonia plants. Table 33 gives examples of aMDEA process options.

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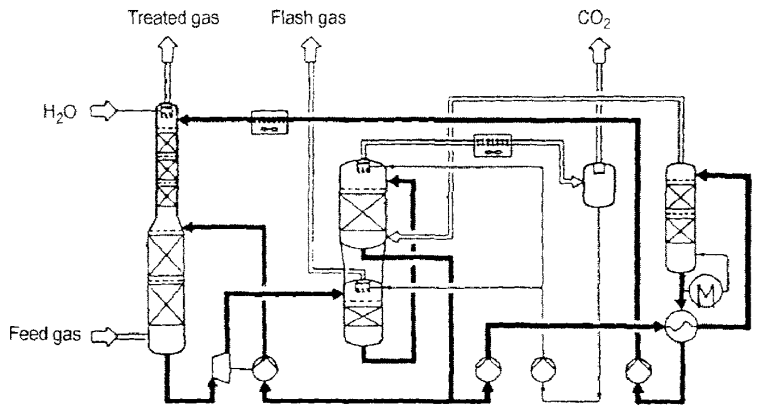


Figure 70. BASF aMDEA Process (Standard two-stage configuration)

Table 33. Examples of aMDEA process options in steam reforming ammonia plants:

	aMDEA 02 (two-stage)	aMDEA 03 (two-stage)	aMDEA 03 (one-stage)
Feed gas	100	100	100
CO_2 in feed, vol%	18	18	18
CO_2 in lean gas, vol%	0.1	0.1	0.1
Solvent circulation	102	100	43
(lean/semi-lean)	(12/88)	(12/88)	-
Packing height	180	100	52
(lean/semi-lean)	(47/53)	52/48	-
Reboiler duty	98	100	250
Specific energy, MJ/kmol CO_2	28.5	28	73

4.3.1.3. Physical Absorption Solvents

Selexol Process (UOP) [667], [694]–[703]. This process, originally developed by Allied Chemical and now marketed by UOP, uses polyethylene glycol dimethyl ether as solvent, which is stable, noncorrosive, not very volatile, but has a rather high capacity to absorb water. For this reason a relatively dry raw gas (dew point –5 °C) is required, which is achieved by chilling. The solvent is also suited for application in partial oxidation processes, as the solubility of H_2S is 8 times higher than that of CO_2, which allows the recovery of a pure CO_2 fraction and also a fraction rich in H_2S for producing elemental sulfur in a Claus plant, which will be described in more detail in the following section. To achieve a high CO_2 recovery rate, which is important when ammonia is to be converted to the maximum possible extent to urea, a 3-stage flash is used as shown in Figure 71. In the first step the solution is depressurized to an intermediate pressure to flash the less soluble gases. To minimize the CO_2 loss the flash gases are recompressed and recycled to the absorption column. The next flash drum is at about atmospheric pressure in which the medium-pressure solvent is flashed and more than 70% of the CO_2 is released. Then follows a vacuum flash in a third vessel,

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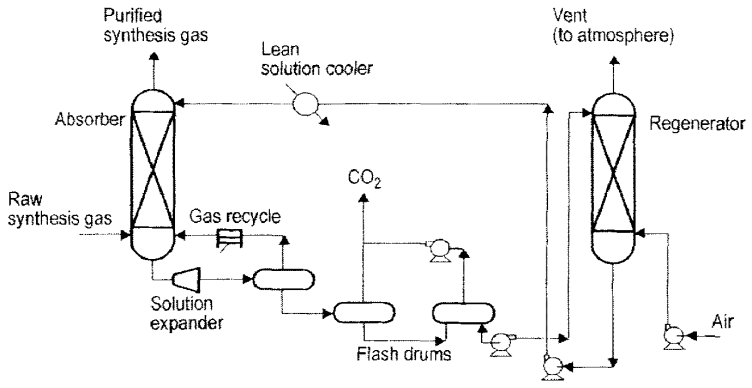


Figure 71. Selexol R. physical CO_2 absorption process (steam reforming gas)

after which the last traces of CO_2 are stripped out with air in a packed column. To avoid any loss of carbon – besides the small amount which goes with the lean gas to the methanation – the stripping air may be added to the process air of the secondary reformer. Practically no heat is required for regeneration, but for comparison with processes requiring regeneration heat, the mechanical power needed should be included.

The **Sepasolv MPE process (BASF)** [667], [685] is similar and uses polyethylene glycol methyl isopropyl ether. No commercial plants are in operation so far.

The **Fluor Solvent Process** [704]–[706], [708] is based on propylene carbonate, which has good chemical stability when used with sulfur-free gases, but is less suited for sulfur-containing gases in partial oxidation plants. The process configuration used for ammonia plants is similar to that of the Selexol plant, using several flash stages, and final air or nitrogen stripping for CO_2 recovery and solvent regeneration. Only a few commercial installations are known.

The physical solvents *methanol* (Rectisol process), *sulfolane* (Sulfinol Process) and *N-methylpyrrolidone* (Purisol) are preferentially used in the treatment of partial oxidation gases and will be described separately in the following section.

4.3.1.4. Sour Gas Removal in Partial Oxidation Processes

Raw synthesis gas produced by partial oxidation has a carbon dioxide partial pressure between 10 and 30 bar, depending mainly on feedstock and gasification pressure. In the lower half of this partial pressure range chemical solvents based on tertiary amines (e.g., MDEA) might be suitable in some cases, but at higher values physical solvents become increasingly preferable. In addition the presence of sulfur compounds, mainly H_2S along with a minor quantity of COS, introduces some complications for CO_2 removal from partial oxidation gases. Since the sour gases are both

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soluble in the solvents and a separate recovery in the regeneration stage is only partially possible (only pure CO_2 can be obtained along with a CO_2 fraction more or less rich in H_2S), two principal plant flow sheets are possible. In one, a first scrubbing stage, which removes the sulfur compounds, is positioned upstream of the shift conversion. The second stage, removing pure CO_2, is located downstream of the shift reactors. This concept reduces the effort required to receive a highly concentrated H_2S fraction suitable for further processing in a **Claus** plant [709], [710] or a sulfuric acid plant. For systems which can not produce a CO_2 fraction with a H_2S concentration suitable for these gas-phase oxidations alternatively a liquid oxidation of the H_2S, e.g., the Stratford – Holmes process, could be applied for sulfur recovery. In another arrangement, which removes the sour gases after shift conversion and has to operate over dirty shift catalyst (see Section 4.2.2), the H_2S is diluted by a large amount of CO_2. This makes it even more difficult to design the regeneration step for producing a H_2S-rich fraction for downstream processing and a pure CO_2 fraction for urea or other uses.

The **Rectisol process** [667], [707], [711] – [715] seems to be the prime choice in partial oxidation plants. The process, invented by Lurgi and developed further by Linde, operates with chilled methanol, a cheap and readily available solvent, in which carbon dioxide, hydrogen sulfide and carbonyl sulfide (COS) are readily soluble at low operating temperatures of below – 30 °C. The Henry absorption coefficient for H_2S is about six times higher than for CO_2.

The Rectisol process is very versatile and allows a number of different configurations. When used with the Shell partial oxidation process (Figure 54) a first scrubbing stage, which removes the sulfur compounds — and the of course the relatively low CO_2 content — from the gas is positioned upstream of the shift conversion. The second stage, removing the high amount of carbon dioxide formed in the shift conversion, is located downstream of the shift reactors. A different arrangement, used in the quench version of the Texaco partial oxidation process, has both seperation steps after the shift conversion, as shown in Figure 72.

After separation of the surplus steam as process condensate, the shifted gas is cooled in an ammonia chiller followed by additional condensate separation. The gas then passes the hydrogen sulfide absorber, where it is scrubbed with sulfur-free methanol pre-laden with CO_2. Next it enters the carbon dioxide absorber, where its carbon dioxide content is removed in different sections: in the top section, through which it passes last, it is washed with practically pure methanol from the hot regeneration stage. Additional sections use flash-regenerated methanol, and interstage cooling is provided to remove the absorption heat. Hydrogen sulfide enrichment in the hot regeneration stage is achieved by a special design involving a combination of flashing and reabsorption.

The applicability of the **Selexol process** for partial oxidation gases [568] was already mentioned. With high H_2S concentrations in the raw synthesis gas a H_2S rich fraction can be separated and fed to a Claus plant for production of elemental sulfur. At lower H_2S concentrations a liquid-phase oxidation has to be applied. As shown in the example of Figure 73, two H_2S-containing CO_2 streams are treated in separate

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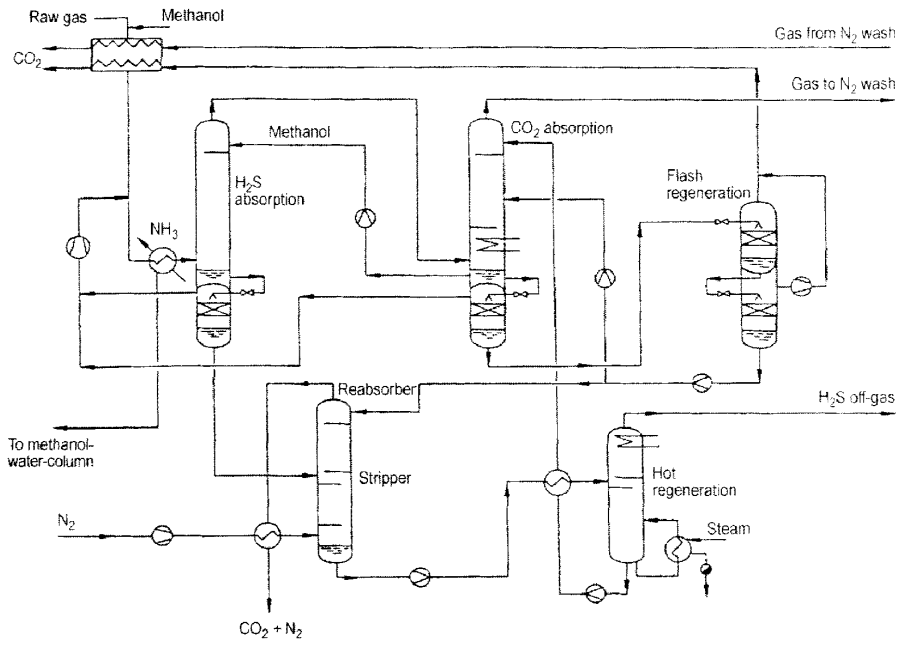


Figure 72. Rectisol sour gas removal used in Texaco Gasification process (quench type)

Stratford-Holmes liquid-phase oxidizers [716] which have a common regeneration to yield solid sulfur, which is filtered off. A COS hydrolysis stage has to be installed upstream of the sour gas scrubbing unit as Selexol does not remove this sulfur compound. The Stratford system uses a solution of vanadium salts in a higher oxidation state, which will oxidize the hydrogen sulfide to elemental sulfur. The carbon dioxide stream from low-pressure flashing contains, for example 0.8 % H_2S and is purified down to 5 ppmv followed by a zinc oxide absorption to bring the content down to 0.1 ppmv, suitable for downstream processing (e.g., urea production). The other fraction from vacuum flashing and the stripper has a H_2S concentration of 4 % (the example is based on a Texaco coal gasification gas). The tail gas from this oxidizer contains less than 160 ppmv H_2S and a smaller amount of COS as the hydrolysis step cannot remove it completely. The reduced vanadium salts are re-oxidized with air.

The **Lurgi Purisol process** [663], [717], [718], [726] uses *N*-methylpyrrolidone (NMP) as solvent and can be operated at ambient temperature or, with inclusion of a refrigeration unit, at temperatures down to −15 °C. The H_2S/CO_2 selectivity is superior to Selexol, permitting the production of a rich Claus gas with about 50 % H_2S even at relatively low concentration of hydrogen sulfide in the raw gas. The solubility of COS is only 20 % of that of H_2S, but it is largely hydrolyzed by the NMP. Preferred operating pressure is 45 to 85 bar. The process can, of course, be

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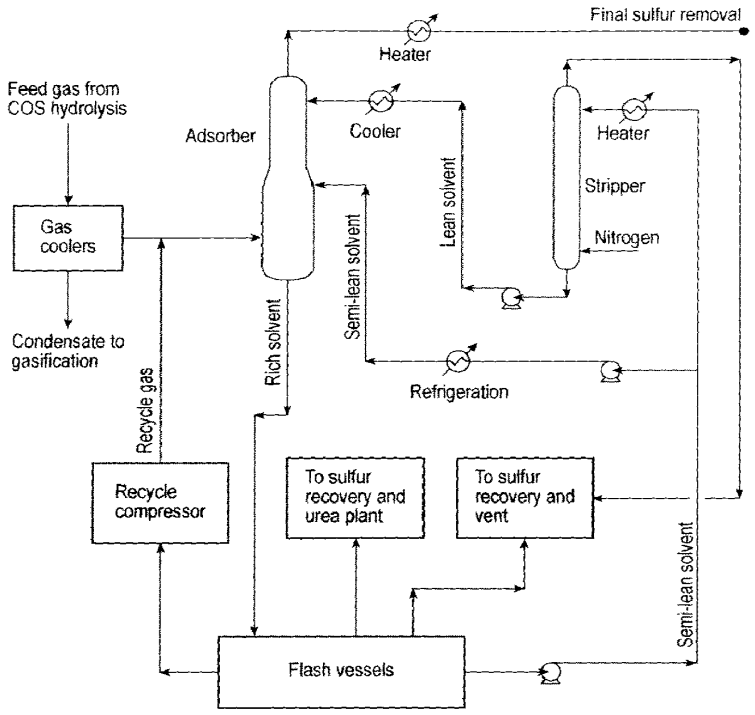


Figure 73. Selexol acid gas removal (partial oxidation gas)

applied in steam reforming plants, too, but in this case the raw gas (25 – 30 bar) is compressed after the LT shift to higher pressure before being fed to the Purisol absorber. Similar to Selexol, vacuum flashing and air stripping are used for solvent regeneration to achieve values below 1000 ppm CO_2 in the lean gas.

The **Sulfinol process** [719] – [722] cannot strictly be classified as a physical solvent process, as the solvent is a mixture of sulfolane (tetrahydrothiophene 1,1-dioxide), DIPA (diisopropanolamine), and water in a ratio of about 45 : 40 : 10. Sulfolane is a true physical solvent, whereas the DIPA is a chemically acting component. To achieve a higher CO_2/H_2S selectivity, DIPA may be substituted by MDEA (methyldiethanolamine) in the M-Sulfinol process. In partial oxidation process a concept with two separate Sulfinol units is preferred: the first ahead of the shift conversion (gas composition for example CO_2 5.4 vol %, H_2S 0.5 vol %), and the second one for recovery of sulfur-free CO_2after the shift conversion (feed gas for example CO_2 33 vol %, H_2S 0 vol %).

Surveys and additonal literature on the CO_2-removal processes are found in [723] – [734]; a theoretical analysis is given in [734].

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4.3.2. Final Purification

After bulk removal of the carbon oxides has been accomplished by shift reaction and CO_2 removal, the typical synthesis gas in steam reforming ammonia plants still contains 0.2 – 0.5 vol % CO and 0.005 – 0.2 vol % CO_2. In partial oxidations the residual CO content after the shift conversion is usually higher, around 1.5 – 2.5 %. These compounds and any water present have to be removed down to a very low ppm level, as all oxygen-containing substances are poisons for the ammonia synthesis catalyst [735].

4.3.2.1. Methanation

Copper liquor scrubbing [737], for carbon monoxide removal, commonly employed in early plants has become obsolete and is now operated in only a few installations. Not only does it have a high energy demand, but it is also environmentally undesirable because of copper-containing wastewater. The choice today is methanation, which is by far the simplest method to reduce the concentrations of the carbon oxides well below 10 ppm and is widely used in steam reforming plants. It is actually the reverse reaction of steam reforming of methane:

$$CO + 3\,H_2 \rightleftharpoons CH_4 + H_2O\,(g) \quad \Delta H^0_{298} = -206\ \text{kJ/mol} \tag{91}$$

and

$$CO_2 + 4\,H_2 \rightleftharpoons CH_4 + 2\,H_2O\ (g) \quad \Delta H = -165\ \text{kJ/mol} \tag{92}$$

The advantages of simplicity and low cost more than outweigh the disadvantages of hydrogen consumption and production of additional inerts in the makeup gas to the synthesis loop.

The reaction is carried out over a supported nickel catalyst at a pressure of 25 – 35 bar in this section of the steam reforming plant and at a temperature of 250 – 350 °C. The required catalyst volume is relatively small. Under conditions where the reaction is limited by the intrinsic reaction rate, methanation activity is directly related to the nickel metal surface area formed on catalyst reduction. The function of the support is to provide a matrix on which the nickel crystallites can be finely dispersed and which also prevents sintering during prolonged operation. To achieve optimum size of the crystallites, in commercial methanation catalysts the nickel is normally incorporated by co-precipitation rather than by impregnation. To achieve a good balance between reducibility and sintering resistance, additional promoters are used. Nickel content is usually between 20 and 40 % [738]. Precious metals, especially ruthenium, have excellent methanation activity at very low temperatures (150 – 175 °C), but under conditions used in steam reforming plants they are no more effective than the standard nickel catalysts. Measurements showed that the methanation of CO_2 is slower than that of CO. A kinetic relation is given in Equation (93):

$$SV = \frac{k_{CO}\,P^{0.5}}{\log_{10}(CO_{in}/CO_{out})} \approx \frac{C\,k_{CO}\,P^{0.5}}{\log_{10}(CO_{2in}/CO_{2out})} \tag{93}$$

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SV = space velocity, h^{-1}, P = pressure in psi absolute, k_{CO} = reaction rate for CO, C = constant ≈ 0.5.

If a breakthrough of carbon monoxide from the low-temperature shift or carbon dioxide from the absorption system occurs, the intensely exothermic methanation reaction can reach temperatures exceeding 500 °C very quickly [739]. For example, 1 % CO_2 breakthrough leads to an adiabatic temperature rise of 60 °C; 1 % CO increases the temperature by 74 °C [738]. Controls should be installed and other security measures taken to avoid these high temperatures because the catalyst may be damaged or the maximum allowable operating temperature of the pressure vessel wall exceeded. Catalysts containing nickel must not be exposed to gases containing CO at temperatures below 200 °C because of the risk of nickel carbonyl formation. $Ni(CO)_4$ is an extreme toxic substance, stable at low temperatures. Nitrogen blanketing of the methanator is advised in shut down operations [736].

Methanation as final purification for the raw gas from partial oxidation was proposed by Topsøe [739]. In this case the shift conversion is carried out in two stages with a special sulfur-tolerant shift catalyst followed by removal of hydrogen sulfide and carbon dioxide in an acid gas removal unit. Because of the potential danger of a sulfur break-through causing poisoning, the normal copper – zinc – alumina catalyst is usually not applied, which is surprising as the same risk exists in partial oxidation based methanol plants for the similarly composed methanol catalyst.

4.3.2.2. Selectoxo Process

The Selectoxo process (Engelhard) reduces the hydrogen consumption of the methanation system, as well as the inert gas content of the purified synthesis gas fed to the synthesis loop. After low-temperature shift conversion, the cooled raw gas is mixed with the stoichiometric quantity of air or oxygen needed to convert the carbon monoxide to carbon dioxide. The mixture is then passed through a precious-metal catalyst at 40 – 135 °C to accomplish this selective oxidation [740] – [743]. The carbon dioxide formed by the Selectoxo reaction adds only slightly to the load on the downstream carbon dioxide absorption system.

4.3.2.3. Methanolation

Methanolation [744], [745] has been proposed for partially replacing methanation. It converts the residual carbon oxides to methanol, preferably at higher pressure in an intermediate stage of synthesis gas compression. Methanol is removed from the gas by water scrubbing. The methanol may be recycled to the steam reformer feed or recovered as product. As full conversion of the carbon oxides is not achieved, a clean up methanation unit must follow the methanolation section.

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4.3.2.4. Dryers

It is energetically advantageous to add the purified synthesis gas at a point in the synthesis loop where it can flow directly to the synthesis converter (see Section 4.5.1). For this reason water and traces of carbon dioxide must be removed from the makeup gas downstream of methanation. This is accomplished by passing the makeup gas through molecular sieve adsorbers, which can be positioned on the suction side or in an intermediate-pressure stage of the synthesis gas compressor.

4.3.2.5. Cyrogenic Methods

4.3.2.5.1. Braun Purifier Process

Cyrogenic methods are usually used for final purification of partial oxidation gases, but may be also incorporated in steam reforming plants. A prominent example for the application in a steam reforming concept is the Braun Purifier process [746]–[753].

The purifier is a cryogenic unit placed downstream of the methanator and its duty is to remove the nitrogen surplus introduced by the excess of air used in the secondary reformer of the Braun ammonia process (Sections 4.1.1.6 and 5.1.4.2). Additionally the inert level in the synthesis loop is reduced through this unit because methane is completely and argon is partially removed from the makeup gas. Another advantage of the process is that it separates the front-end and the synthesis loop, permitting the H/N ratio in the synthesis loop to be set independent of the secondary reformer. The purifier is a relatively simple unit composed of feed/effluent exchanger, a rectifier column with an integrated condenser and turbo-expander. At −185 °C methane and argon are washed out. The cooling energy is supplied by expansion of the raw gas over the turbo-expander (pressure loss about 2 bar) and expanding the removed waste gas to the pressure level of the reformer fuel.

4.3.2.5.2. Liquid Nitrogen Wash

Normally, for the partial oxidation processes, only a high-temperature shift conversion is used. This results in a carbon monoxide content of the gas after shift conversion of 3 vol% or sometimes somewhat higher. Liquid nitrogen wash [754]–[756] delivers a gas to the synthesis loop that is free of all impurities, including inert gases and is also the means for adding some or all of the nitrogen required for synthesis.

The nitrogen is liquefied in a refrigeration cycle by compression, cooling, and expansion. It flows to the top of a wash column, where it countercurrently contacts precooled synthesis gas from which most of the methane and hydrocarbons have been condensed. All of the cold equipment is installed in an insulated "cold box." The wash column temperature is about −190 °C. Liquid nitrogen wash systems are in operation at pressures up to 8 MPa corresponding to the highest gasification pressures. Careful surveillance of the inlet gases is required. As water and carbon dioxide in the inlet gas

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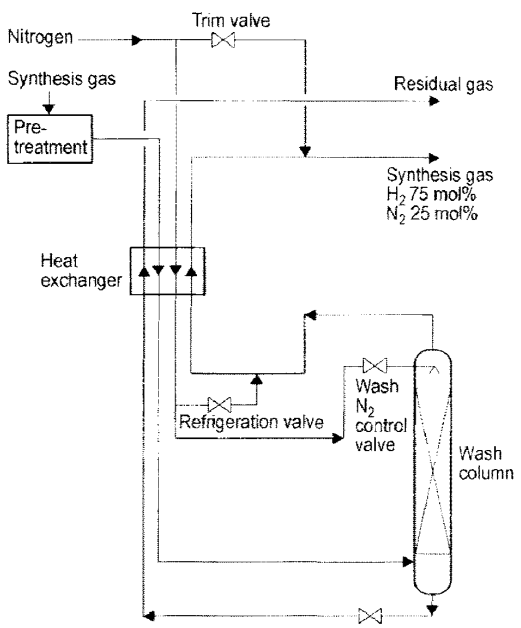


Figure 74: Liquid nitrogen wash

will freeze, causing operating difficulties, removal of these impurities down to a very low level is required. Traces of nitric oxide (NO) may react with olefinic hydrocarbons, causing explosions [757], [758].

Normally, an air separation plant is installed in conjunction with liquid nitrogen wash for economy in operation. In modern plants, the air separation and the nitrogen wash frequently are closely integrated with one another so that economies can be realized in the refrigeration system. Figure 74 is a simplified flow diagram of a liquid nitrogen wash.

4.3.2.6. Pressure Swing Adsorption

This process is actually more than a process just for final purification. It can be used to replace the LT shift conversion, carbon dioxide removal, methanation, and even the secondary reformer as well [404], [728], [759]–[762]. It uses molecular sieves as adsorbents in a series of vessels operated in a staggered cyclic mode changing between an adsorption phase and various stages of regeneration. The regeneration of the loaded adsorbent is achieved by stepwise depressurization and by using the gas from this operation to flush other adsorbers at a different pressure level in the regeneration cycle. The hydrogen recovery may be as high as 90 % depending on the number of adsorbers in one line, which may be as high as 10. Very high purity can be obtained, with about 50 ppm argon and less than 10 ppm of other impurities.

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The process scheme for the ammonia plant may consist of production of pure hydrogen followed by separate addition of pure nitrogen from an air separation unit [763] – [765]. In a special version the nitrogen can be added in the PSA unit itself to increase hydrogen recovery [766] – [769]. In some processes it may also remove the excess nitrogen introduced with the process air fed to the secondary reformer, e.g. the LCA Process of ICI (Section 5.1.4.3). Since this technology has proven its reliability in rather large hydrogen plants for refineries it is now also used for world-scale ammonia plants, e.g., the Linde LAC process (Section 5.1.4.4).

4.4. Compression

4.4.1. Reciprocating Compressors

Up to the mid-1960s reciprocating compressors were used to compress the synthesis gas to the level of the synthesis loop, which was around 300 bar in the majority of the plants at that time. Higher pressures were used in a few installations, for example, in Claude and Casale units. Prior to about 1950 gas generation processes and shift conversion operated at essentially atmospheric pressure. The gas was first compressed to the level of the CO_2 removal section (usually 25 bar) and afterwards to around 300 bar for final purification (at that time usually copper liquor scrubbing) and synthesis. Reciprocating compressors with as many as seven stages in linear arrangement with intermediate cooling were used, whereby the CO_2 removal section was usually installed between the 3rd and 4th stages. Machines with a suction volume up to 15 000 m^3 (STP) for the first stage were not uncommon. Huge flywheels were designed as the rotors of synchronous motors (ca. 125 rpm) with two crankshafts on both sides connected over crossheads with the piston rod for the horizontally arranged stages. In some instances gas engines were used as drivers.

The rapid technical progress in the hydrocarbon based technologies of steam reforming and partial oxidation made it possible to generate the synthesis gas at a pressure level sufficient for the CO_2 removal operation. As gasification proceeds with a considerable volume increase and feedstocks such as natural gas are usually already available under pressure at battery limits, considerable savings in compression energy are achieved in this way.

Along with the introduction of pressure gasification, horizontally balanced compressors in which the cylinders are in parallel configuration on both sides of a common crankshaft became the preferred design. In these machines a good dynamic balance can readily be achieved, higher speeds are possible and also the use of asynchronous motors is possible. The low height of the arrangement has less severe requirements for foundations, allows simpler piping connections and facilitates maintenance. When gas engine drivers (two-stroke type) were used instead of electric motors, some designs applied a common crankshaft for the piston rods of the gas machine cylinders and

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compressor cylinders. In a very few cases steam turbines with special speed reduction gears have been used. In smaller plants, the various compression services, e.g., natural gas, process air, and synthesis gas compression, were apportioned among the crankshaft throws in such a manner that a single compressor can perform all compression duties [770]. Further information on reciprocating compressors is given in [771] – [774].

4.4.2. Centrifugal Compressors

One of the most important features of the energy integrated single-stream steam reforming ammonia plant pioneered by M. W. Kellogg in 1963 was the use of centrifugal compressors for the compression duties of synthesis gas and recycle, process air, and refrigeration. From this time onwards application of centrifugal compressors became standard practice in most ammonia plants irrespective of the synthesis gas generation technology. The fundamental advantage of these machines are low investment (single machines even for very large capacities) and maintenance cost, less frequent shutdowns for preventive maintenance, and high reliability (low failure rate) [775]. In most cases the centrifugal compressors in ammonia plants are directly driven by steam turbines. This avoids the losses associated with generation and transmission of electric power. For this reason the overall efficiency of a plant with steam-driven centrifugal compressors is superior, although the centrifugal compressors are inherently less efficient than reciprocating units. A further advantage is that centrifugal compressors require only a fraction of the space needed for reciprocating compressors.

Manufacturing capabilities limit the minimum possible passage width (today about 2.8 mm) at the outer circumference of a centrifugal compressor impeller and this imposes a limit on the minimum effective gas volume leaving the last impeller. Unless the total volumetric gas flow has a reasonable relationship to the passage width of the last impeller and the pressure ratio, excessive pressure losses would occur within the passage and in the diffusers between the impellers, rendering the machine extremely ineffective. The first single-train ammonia plants with a capacity of 550 – 600 t/d had to lower the synthesis pressure to 145 – 150 bar to meet the required minimum gas flow condition. Today, with improved manufacturing techniques, the minimum gas flow from the last wheel is 350 m^3 for synthesis gas with a molecular mass of about 9 and an efficiency of around 75 %. This corresponds to a capacity of 400 t/d at 145 bar. As newer synthesis catalysts allow a pressure of 80 bar in the synthesis loop (ICI's LCA Process, Kellogg's KAAP) a centrifugal compressor could be used down to 220 t/d. Of course, for today's world-scale capacities of 1200 – 1800 t/d these technical limitations have no influence on the synthesis pressure, which even for plants with 1800 t/d is between 155 and 190 bar [402], [404], [776] – [778].

The tensile strength of the steels normally used to manufacture the compressor impellers allow a maximum wheel tip speed of about 330 m/s, which limits the pressure increase attainable by each impeller. A pressure increase, for example, from

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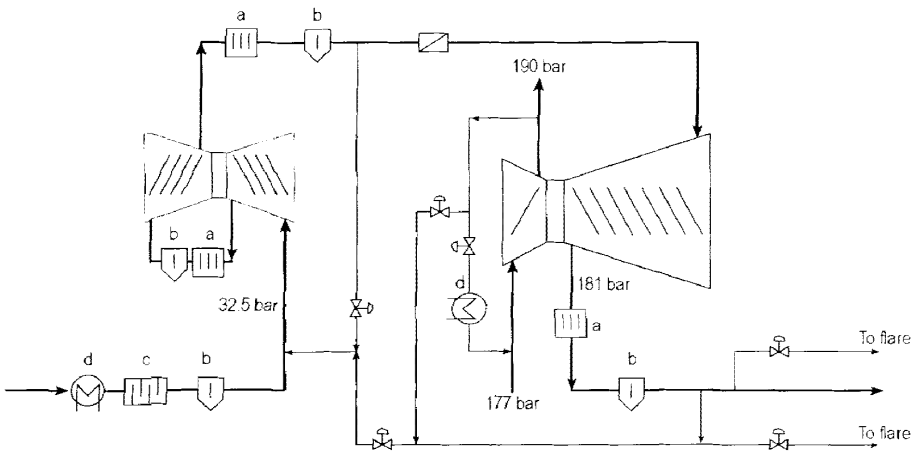


Figure 75. Centrifugal compressor for make-up and recycle gas compression of an ammonia plant (courtesy of Uhde)
a) Air cooler; b) Separator; c) Silencer; d) Water cooler

25 to 200 bar would require 18 – 20 impellers. However, a compressor shaft must have sufficient rigidity to avoid excessive vibration, and this limits the possible length such that a compressor shaft cannot accommodate more than eight or nine impellers. It is therefore necessary to arrange several compressor casings in series, with compression ratios from 1.8 to 3.2.

To overcome the pressure drop (5 – 20 bar) in the synthesis loop re-compression of the recycle gas is required. In practically all modern ammonia plants, the shaft of the final casing also bears the impeller for the compression of the recycle gas. Depending on synthesis configuration, mixing of make-up gas and recycle can be performed inside the casing or outside (three or four-nozzle arrangement; Fig. 77).

In older plants which used a reciprocating compressor for the recycle, a recycle cylinder was often mounted together with the other cylinders on the reciprocating frame. Sometimes special rotary compressors, so-called mole pumps were also used, with the unique feature that compressor and electric driver were completely enclosed in a common high-pressure shell. In old Casale plants, the makeup gas was introduced into the high pressure recycle loop and acted as the driving fluid of an injector which compressed the recycle gas.

Today modern plant concepts for world-scale capacity plants tend to limit the number of compressor casings to two. Figure 75 shows an example of the synthesis gas compressor of a large ammonia plant.

Geared or metal diaphragm couplings are used to connect the shafts of the individual casings (two in Figure 75). These flexible couplings prevent possible compressor damage resulting from slight misalignment and shaft displacement.

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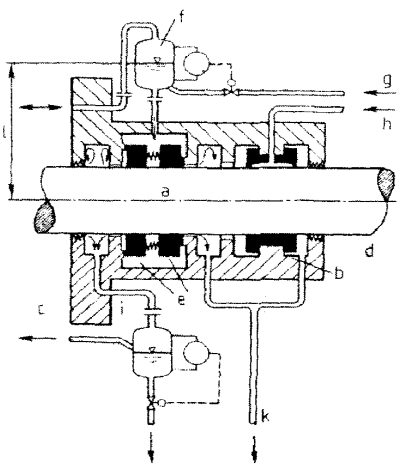


Figure 76. Liquid film shaft seal with cylindrical bushing for a high-pressure centrifugal compressor
a) Shaft; b) Bearing; c) Pressure side; d) Ambient side; e) Floating seal rings; f) Seal oil surge vessel; g) Seal oil; h) Lube oil; i) Drain to gas – oil separator; k) Drain to lube oil tank; l) Elevation for seal oil head

Sealing of the rotating shaft against the atmosphere is an important and demanding task. The high pressures and the high rotational speeds involved do not allow mechanical contact shaft seals. Usually, liquid-film shaft seals with cylindrical bushings (floating rings) are applied [779]. In this concept, an oil film between the shaft and a floating ring, capable of rotation, provides the actual sealing. The floating ring is usually sealed to the compressor casing by O-rings. Seal oil flows between both halves of the floating ring. Part of the oil returns to the reservoir, while the remainder flows against the gas pressure into a small chamber from which, together with a small quantity of gas, it is withdrawn through a reduction valve. Figure 76 is a schematic diagram of a liquid film shaft seal.

The seal oil pressure in the floating ring cavity must always be slightly higher than the gas pressure within the casing which is provided by static height difference of the oil level in the elevated oil buffer vessel. In this way normally no oil should enter into the synthesis gas. As the labyrinth section on the pressure side is connected with the suction side through an equalizing line, it is necessary to seal the compressor shaft towards the atmosphere only at suction pressure level.

Often, seal oil supply is combined with the lubricating oil system, with oil reservoir, filters and (in part) pumps in common.

Bearings. The high rotational speeds and the relatively large masses of the compressor rotors place high demands on the performance of the bearings. This is especially true for the thrust bearings, which must withstand high thrust forces. The minimum clearances necessary at the labyrinths and the impellers allow practically zero wear. Any wear resulting in friction could lead instantly to severe damage. For these reasons, in addition to measuring bearing temperatures, the axial position of the rotor and the radial vibrational deflections are continuously monitored by sensors. An increased vibrational amplitude is often an early indication of mechanical faults, such as rotor imbalance, bearing damage, occurrence of friction, or misalignment.

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Dry (oil-less) gas seals represent an interesting concept for centrifugal compressors. Development dates back to 1969 and the first commercial application was in a natural-gas compressor in 1973. Since then they have been widely used in off-shore service [780]–[782]. Only recently have they gained acceptance in the ammonia industry, where several compressors for synthesis gas and refrigeration duty equipped with dry seals have been successfully placed in service. Nitrogen is used as an inert fluid for the seal, which is achieved at the radial interface of rotating and stationary rings. During operation the seal is not completely tight; some of the seal gas flows back to the suction side to be re-compressed, and a small amount from the suction side may go to the atmospheric side and is sent to the flare on account of its content of combustibles. During stops, when the shaft is not rotating, the seal ring is pressed tight against the seat by means of a spring and the differential gas pressure. Dry gas seals in combination with oil-lubricated bearings (dry/wet) have the advantage that a much smaller oil system is required and that there is no contact between oil and gas, which eliminates an emission source.

Magnetic Bearings. A new development, already in commercial service, but so far not used in ammonia plants, is magnetic bearings [780], [783]. Magnetic bearings promise a wider temperature range, are less prone to wear, are less prone to developing vibrations due to imbalance and require less maintenance. A combination of magnetic bearings and dry seals (dry/dry) could totally eliminate the oil system.

Integrated geared centrifugal compressors developed by DEMAG and GHH are a new development which might become of interest for plants of smaller capacity operating at lower pressure. The driver (e.g., a steam turbine) drives a common gear to which the individual compression stages are connected. Each stage has a single impeller which runs with very high speed, for example, 25 000 rpm or higher. Compressors with three or four stages are in operation, for example, a methanol synthesis compressor for 75 000 m^3/h and a pressure of 75 bar. It is likely that this concept can be extended to a final pressure of 120 bar with ammonia synthesis gas.

Compressor control is achieved basically by controlling the rotational speed of the driver, in modern plants often with the help of a distributed control system (DCS). If the volumetric flows through the machine at start-up or during reduced load operation deviate too far from the design values, it is necessary to re-circulate gas through individual stages or through the whole machine. Otherwise the compressor can enter a state of pulsating flow, called surge, which could cause damage. Anti-surge control (minimum by-pass control, kickback control) is designed to prevent this condition, as well as to minimize the incidence and degree of uneconomical re-circulation. A point of discussion is sometimes the minimum load at which the compressor can run without kickback, which means without loss of efficiency. Usually a load of 75 % is possible, and with special impeller design, the value may be lowered to 70 % but with a slight sacrifice of full-load efficiency.

Other compression duties in the plants, such as process air in steam reforming plants and air, and oxygen, and nitrogen compression in partial oxidation plants, are

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also performed by centrifugal compressors. Also for the ammonia compression in the refrigeration section centrifugal compressors are normally in service. In some cases screw compressors have been used for this duty on account of their good efficiency and load flexibility, which is of interest in plants where the ammonia product is split between direct users at the site and cold storage in changing ratios.

Criteria for compressor selection and economic comparisons are discussed in [784] – [792]. Additional information is given in [793] – [806]. Operational problems, mechanical failures, repair and maintenance are described in a number of papers presented at the annual AIChE Ammonia Safety Symposia.

4.4.3. Compressor Drivers

Steam turbines. In modern plants the centrifugal synthesis gas compressors, including recycle, are almost exclusively driven by a steam turbines. These are generally extraction turbines with a condensing section. Steam is extracted at suitable pressure levels (e.g. 45 – 55 bar) to provide, for example, the process steam in steam reforming plants, and for other drivers, e.g., air compressor, ammonia compressor, boiler feed water pumps, and blowers.

As failures and breakdowns of these large rotary machines could lead to long and expensive repairs and to a corresponding loss of production it is advisable to keep the essential spare parts, for example, spare rotors, in stock. In older steam turbines, sometimes blade failures occurred, but this is no longer a problem due to improved blade design and shroud bands, which are standard today.

Gas turbines have also been used as drivers for compressors in ammonia plants. The exhaust may be used for steam production, for preheating duties, or as combustion air in the primary reformer [804], [807] – [811].

4.5. Ammonia Synthesis

Under the conditions practical for an industrial process ammonia formation from hydrogen and nitrogen (Eq. 94)

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3 \quad \Delta H = -92.44\ \text{kJ/mol} \tag{94}$$

is limited by the unfavorable position of the thermodynamic equilibrium, so that only partial conversion of the synthesis gas (25 – 35 %) can be attained on its passage through the catalyst. Ammonia is separated from the unreacted gas by condensation, which requires relatively low temperatures for reasonable efficiency. The unconverted gas is supplemented with fresh synthesis gas and recycled to the converter. The concentration of the inert gases (methane and argon) in the synthesis loop is controlled by withdrawing a small continuous purge gas stream. These basic features together

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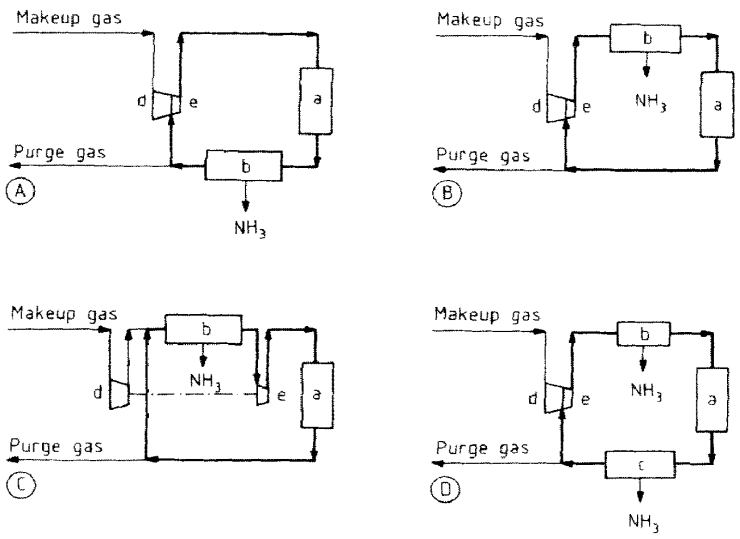


Figure 77. Schematic flow diagrams of typical ammonia synthesis loops
A) Synthesis loop for pure and dry makeup gas; B) Product recovery after recycle compression; C) Product recovery before recycle compression (four-nozzle compressor design); D) Two stages of product condensation
a) Ammonia converter with heat exchangers; b) Ammonia recovery by chilling and condensation; c) Ammonia recovery by condensation at ambient temperature; d) Synthesis gas compressor; e) Recycle compressor

with the properties of the synthesis catalyst and mechanical restrictions govern the design of the ammonia synthesis converter and the layout of the synthesis loop. Evaluation criteria are energy consumption, investment and reliability.

4.5.1. Synthesis Loop Configurations

A number of different configurations are possible for the synthesis loop. They can be classified according to the location of ammonia condensation and the point at which the makeup gas is introduced. Figure 77 shows the principal possibilities.

If the makeup gas is absolutely free of catalyst poisons, such as water and carbon dioxide (for example, after molecular sieve drying or liquid nitrogen wash), it can be fed directly to the synthesis converter (Fig. 77 A). After the gas leaves the synthesis converter, ammonia is condensed by cooling and the recycle gas is referred to the recycle compressor. This represents the most favorable arrangement from a minimum energy point of view. It results in the lowest ammonia content at the entrance to the converter and the highest ammonia concentration for condensation.

When the makeup gas contains water or carbon dioxide, advantage is taken of the fact that these materials are absorbed completely by condensing ammonia. This requires the condensation stage to be located partially or wholly between the makeup gas supply point and the converter. This arrangement has the disadvantage that the

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ammonia concentration for condensation is reduced by dilution with the makeup gas. Also, at equal condensing temperature, a higher ammonia concentration exists at the inlet to the converter. Figure 92 B shows the simplest such configuration. An additional drawback of this arrangement is that all the ammonia produced must be compressed with the recycle gas in the recycle compressor.

The scheme shown in Figure 92 C, the frequently used "four-nozzle compressor", avoids this waste of energy. With this arrangement, recycle compression follows directly after condensing and separating the ammonia. In this configuration, it is possible to cool the recycle gas using cooling water or air immediately before admixing the makeup gas (i.e., before diluting the recycle gas) and thereby to reduce the energy expenditure for refrigerated cooling.

Splitting the cooling step for ammonia condensation also offers advantages when the recycle gas is compressed together with the makeup gas. This applies especially at synthesis pressures above about 25 MPa (250 bar). At these pressures, a greater portion of the ammonia formed can be liquefied by cooling with cooling water or air (see Fig. 92 D).

When ammonia-containing recycle gas and carbon dioxide containing makeup gas mix together under certain conditions of concentration and temperature, precipitation of solid ammonium carbamate can result.

In recent years, also as a retrofit in existing plants, molecular sieve drying of makeup gas has increasingly been applied in order to realize the energy-saving arrangement of the synthesis loop corresponding to Figure 92 A.

4.5.2. Formation of Ammonia in the Converter

The central part of the synthesis system is the converter, in which the conversion of synthesis gas to ammonia takes place. Converter performance is determined by the reaction rate, which depends on the operating variables. The effect of these parameters is discussed briefly in the following (see also Section 4.5.7).

With increasing pressure, ammonia formation increases (Fig. 78). This results not only from the more favorable equilibrium situation for the reaction, but also from the effect on the reaction rate itself. In industrial practice, there are plants that operate at about 8 MPa (80 bar), but there are also those that operate at more than 40 MPa (400 bar). Today, plants are built mainly for synthesis pressures of 150–250 bar. Typical operating parameters for modern synthesis loops with different pressures are listed in Table 34.

Converter performance decreases with increasing inert gas content (Fig. 79). The usual range is 0–15 vol%. For a secondary loop based on purge gas, it can be 30% or more (see Section 4.5.6).

Converter performance also diminishes (Fig. 80) with increasing oxygen content of the synthesis gas. Today, a level of 10 ppm in the makeup gas, corresponding to about 3 ppm in the converter inlet gas, is usually, not exceeded (see also Section 3.6.1.5).

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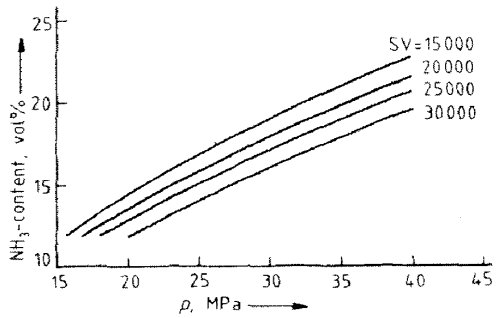


Figure 78. Performance for a four-bed quench converter as a function of operating pressure with space velocity (per hour) as parameter; 10% inerts in the inlet synthesis gas

Table 34. Typical operating parameters for modern synthesis loops at 140 and 220 bar (1000 t/d NH_3) [402, p. 226]

Parameters	Inlet pressure, bar	
	140	220
Inlet flow, Nm^3/h	500 000	407 000
Inlet NH_3 conc., mol%	4.1	3.8
Outlet NH_3 conc., mol%	17.1	19.9
Inlet inert conc., mol%	8.0	12.0
NH_3 separator temperature, °C	−5	−5
Relative catalyst volume	1	0.6

In contrast to the above-mentioned variables, the dependence of the converter performance on the H_2/N_2 ratio shows a true maximum (Fig. 81). The optimum conversion at high space velocity [SV = m^3 (STP) gas $h^{-1} \cdot m^{-3}$ catalyst] lies close to an H_2/N_2 ratio of 2 and approaches 3 at low space velocities. The reason is that equilibrium plays a greater role at low space velocities and has a maximum at a ratio of 3, except for small corrections [33] with regard to the behavior of real gases. Usually, the ratio is adjusted to 3, because in most plants, conversions near equilibrium are attained.

In practice, space velocities vary from about 12 000 h^{-1} at about 15 MPa (150 bar) to about 35 000 h^{-1} at about 80 MPa (800 bar). Usually, with increasing space velocity, the ammonia concentration in the effluent synthesis gas from a given converter does indeed go down (Figs. 78, 79, 81). However, the operating point normally chosen means that the increase in gas flow rate more than compensates for the reduced ammonia concentration. Thus, a still higher ammonia production rate is achieved. Plant operation often takes advantage of these phenomena. For example, this characteristic can be used to maintain ammonia production rate when the synthesis catalyst ages and its activity declines. Increasing converter flow rate and declining synthesis catalyst activity can reach a point, even with careful control, where the reaction "blows out" and production ceases. This occurs when the heat of reaction is no longer sufficient to provide the temperatures necessary for operation of the feed–effluent heat exchanger. The heat exchanger then fails to heat the cold converter feed gas to the required reaction "ignition" temperature. Achieving maximum ammonia production requires operating in the neighborhood of this "blow out" point, in turn requiring very

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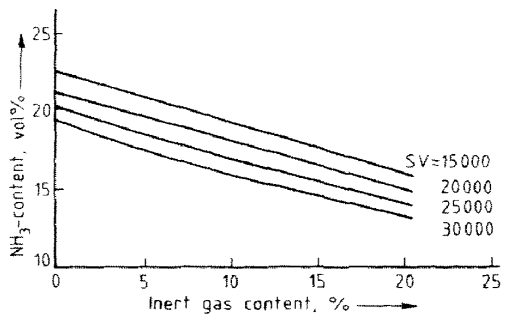


Figure 79. Performance of a converter as a function of inlet inert gas (CH_4 and Ar) content with space velocity (per hour) as parameter, inlet NH_3 content is 3.5 %; 30 MPa pressure; catalyst particle size is 6 – 10 mm

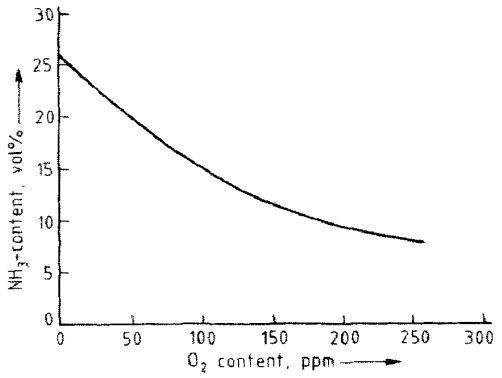


Figure 80. Performance of a converter as a function of oxygen content (all oxygen-containing impurities) in the inlet synthesis gas

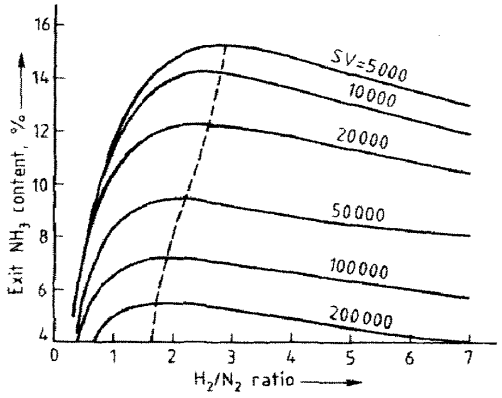


Figure 81. Ammonia conversion as a function of hydrogen/nitrogen ratios in the inlet synthesis gas with space velocity (per hour) as parameter; 9.7 MPa pressure [811]

careful control [812] – [814]. If the synthesis converter is to be operated in this region, then it is advisable to oversize the converter feed – effluent heat exchanger system to attain a higher degree of control stability.

Converter Design. Design of ammonia synthesis reactors is not just the calculation of the required catalyst volume; other parameters have to be considered, too, and for

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some of them optimum values have to be found. This raises the question of the definition of optimum. In the early days with more strict material and fabrication-related limitations the converters were usually designed for minimum high-pressure volume, and this meant maximum use of the catalyst. Today the objective is to optimize the heat recovery (at the highest possible level) and to minimize the investment for the total synthesis loop.

The ammonia converter is a demanding engineering and chemical engineering task. To calculate the parameters for the design, including dimensions and number of catalyst beds, temperature profiles, gas compositions, and pressure drop, a suitable mathematical model is required.

Two differential equations describe mathematically the steady-state behavior of the reactor section of a converter. The first models the concentration – position relationship for transformation of the reactants to products, i.e., the reaction kinetic equation (Section 3.5). The second handles the temperature – position behavior of the reacting synthesis gas, the catalyst, and the vessel internals. The form of the latter is characteristic of the type of converter. The temperature profile depends not only on the rate of reaction heat evolution but also on the method and nature of the system for removing heat from the catalyst bed or beds. Additional equations describe the behavior of the separate feed – effluent heat exchanger system [815] – [819]. General information on converter calculations are given in [183], [818] – [820]. Computer programs and applications can be found in [821] – [825]. For a discussion of modeling of different converter types, see [815] – [819], [825], [826]. Models for multibed quench converters are described in [825] – [832]. Tubular reactors are treated in [833] – [840]. The individual effects of the operational parameters are evaluated in [33], [253], [840].

The reaction temperature profile is of particular importance because the reaction rate responds vigorously to temperature changes. Figure 82 plots lines of constant reaction rate illustrating its dependence on temperature and ammonia concentration in the reacting synthesis gas. The line for zero reaction rate corresponds to the temperature – concentration dependence of the chemical equilibrium. From Figure 82 it is apparent that there is a definite temperature at which the rate of reaction reaches a maximum for any given ammonia concentration. Curve (a) represents the temperature – concentration locus of maximum reaction rates. To maintain maximum reaction rate, the temperature must decrease as ammonia concentration increases.

If the objective in design or operation were optimizing catalyst utilization, then Figure 82 shows that the converter temperature – composition profile should follow curve (a), which corresponds to maximum reaction rate at all points. It is also obvious that in reality this "ideal" temperature – concentration profile cannot be achieved. For example, a synthesis gas with about 3 % ammonia concentration entering the converter cannot be heated to the "ideal" temperature by heat exchange because the very high temperature required does not exist in the converter system. To reach the "ideal" temperature, the first portion of the catalyst must initially operate adiabatically. Consideration of the service life of the catalyst requires that this maximum initial temperature not exceed that recommended by the manufacturer, usually 530 °C (cf. Section

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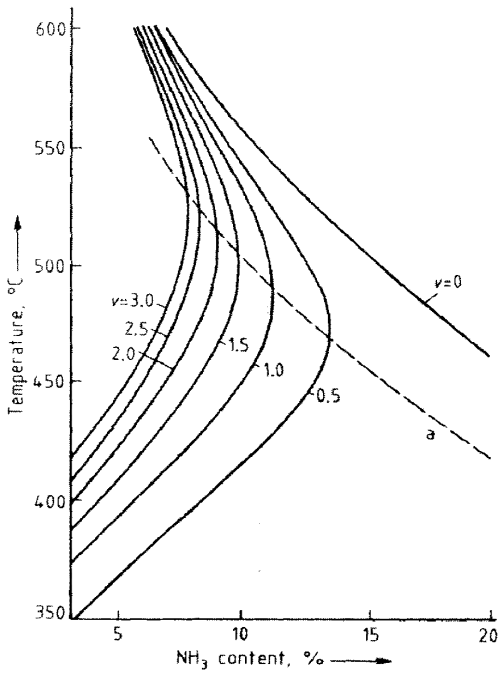


Figure 82. Nitrogen reaction rate r in m^3 $NH_3/(m^3$ catalyst · s) as a function of temperature and ammonia concentration at 20 MPa pressure and 11 vol % inerts in the inlet synthesis gas
a) locus of temperatures resulting in maximum reaction rate at a given ammonia concentration

3.6.1.4). Following this initial adiabatic temperature rise, it is possible to minimize the required catalyst volume by cooling the reacting synthesis gas such that, as ammonia formation progresses, the temperature follows curve (a). In the days when converters were designed to operate at very high pressures and temperatures and before the advent of improved construction materials, the converter design represented a real limitation on plant capacity. To maximize converter output and plant capacity to achieve the most favorable overall manufacturing cost, it was necessary to optimize catalyst utilization. A converter temperature–concentration profile was often compared to the "ideal" for optimum usage of high-pressure vessel and catalyst volumes [841], [842].

4.5.3. Commercial Ammonia Converters

4.5.3.1. Principal Converter Configurations

Commercial converters can be classified into two main groups:

1) Internally cooled with cooling tubes running through the catalyst bed or with catalyst inside the tubes and the cooling medium on the shell side. The cooling

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medium is mostly the reactor feed gas, which can flow counter- or cocurrently to the gas flow in the synthesis catalyst volume (*tube-cooled converters*).

2) The catalyst volume is divided into several beds in which the reaction proceeds adiabatically. Between the individual catalyst beds heat is removed by injection of colder synthesis gas (*quench converters*) or by indirect cooling with synthesis gas or via boiler feed water heating or raising steam (*indirectly cooled multibed converters*).

The gas flow can have an axial, cross-flow or radial flow pattern. The different cooling methods can be combined in the same converter.

The severe conditions of high pressure, high temperature, and high hydrogen partial pressures place strict requirements on the construction materials and design for both groups. For example, almost all converters consist of an outer pressure vessel containing a separate inner vessel housing the catalyst and other internals, such as gas distributors and heat exchangers. Relatively cool converter feed gas flows through the annular space between the outer pressure shell and the internal "basket". This shields the outer shell from the high-temperature "basket", permitting use of comparatively low-alloy chromium–molybdenum steels for its construction. Often, part of the converter feed–effluent heat-exchange system surface is placed within the converter pressure shell. By this means, the nozzle penetration through the pressure shell for the converter effluent gas is also maintained at relatively low temperature. Today, this latter feature is not always necessary; the state of the art in converter construction materials now allows design of exit nozzles for the maximum anticipated temperatures, i.e., up to about 530 °C. References [843] and [844] review some literature on ammonia converters.

4.5.3.2. Tube-Cooled Converters

To remove the heat evolved in the synthesis reaction, the converters have cooling tubes in the catalyst beds. With these tubes, the heat is transferred to the converter feed gas to heat it to the reaction ignition temperature or to an external cooling medium. The known designs for such converters are suited only for small production capacities and therefore currently of limited interest. When designed to utilize the heat of reaction for heating the converter feed gas, such converters have the further disadvantage that temperature control is sluggish and temperature oscillations dampen out very slowly, if at all, a phenomenon called "hunting".

Countercurrent Design. Typical of such converters is the countercurrent design of the *Tennessee Valley Authority (TVA)* [812], [838], [842], [845]–[850]. Part of the feed gas to this unit enters the converter at the top and flows down through the annular space between the pressure shell and the basket. The main gas flow enters the converter at the bottom and joins the shell cooling gas. The mixture is heated to about 200 °C in an internal exchanger located beneath the catalyst bed. The gas then enters the cooling tubes that run through the catalyst bed (Fig. 83 A). There it absorbs the heat released in the reaction and reaches the required reaction ignition temperature of

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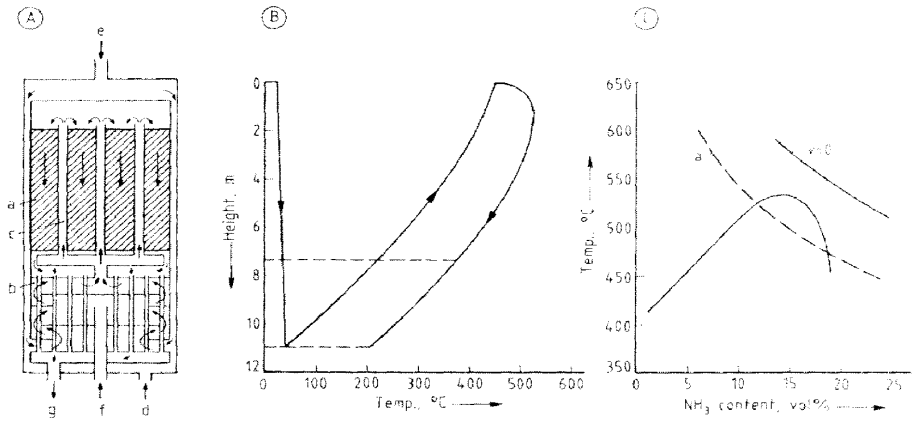


Figure 83. Countercurrent tube-cooled converter (TVA converter) [842]
A) Converter layout; a) Catalyst; b) Heat exchanger; c) Cooling tubes; d) Main gas inlet; e) Vessel wall cooling gas inlet; f) Temperature control gas (cold-shot) inlet; g) Gas exit
B) Gas temperature profile through the converter; C) Ammonia concentration versus temperature (cf. Fig. 82)

about 400 °C. The reaction begins almost adiabatically in the catalyst bed. As the reacting gas temperature rises, the temperature difference between the reacting gas and the cooling tubes increases, resulting in increasing heat removal (Fig. 83 B). As the reacting gas reaches the bottom of the catalyst bed, the rate of reaction begins to decrease sufficiently, because of high ammonia concentration, that cooling predominates and the temperature of the reacting gas begins to fall. Figure 83 C shows the converter temperature–concentration profile. The reaction temperature at first somewhat exceeds that for maximum reaction rate but eventually falls below curve (a). Cold converter feed gas can be admitted at a point within the internal heat exchanger to control both the total system and reaction temperature profiles through bypassing. *Casale* has employed a similar converter design concept [851].

Other tube-cooled converters with countercurrent flow are the *Mont Cenis reactor* [848], [852], [856], the original *Haber–Bosch reactors* [854], the *Claude converter* [856], [857], and the older Fauser design [852]. These converters were all used in relatively small plants and are now obsolete.

An interesting rebirth of the countercurrent principle is the new *ICI tube-cooled converter* used in the LCA process.

Recently a rather unique concept was developed by a *Fast Engineering Ltd.* in Russia [859]. The catalyst bed of the radial flow reactor is subdivided by cooling elements into several sections in a spiral-like configuration, as shown in Figure 84. In a revamp operation the existing converter of a 600 t/d ammonia plant in the Cherkassy production complex was equipped with a new basket having the innovative design filled with

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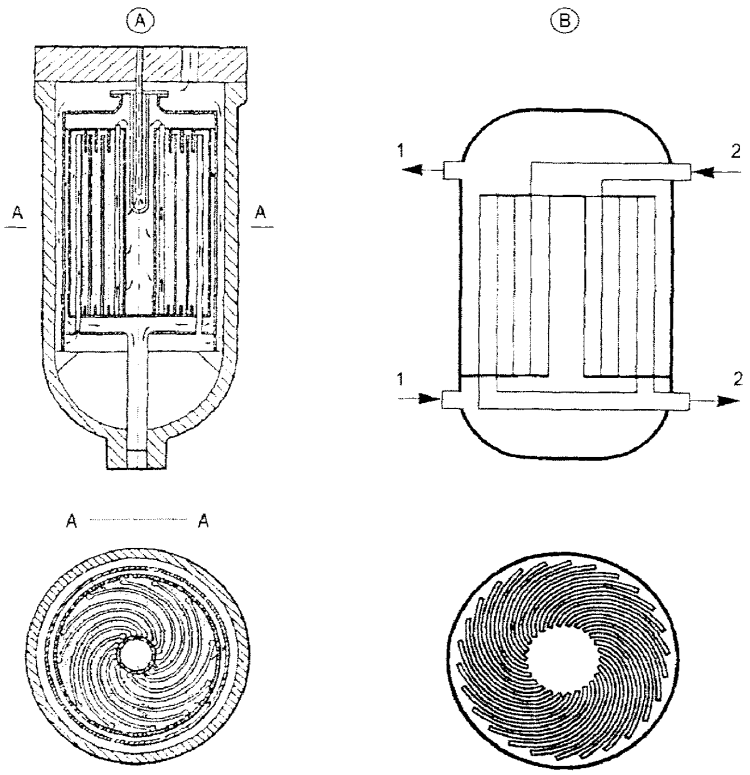


Figure 84. Tube cooled ammonia converter (Fast Engineering)

3 mm catalysts particles. The performance was in full agreement with the calculated characteristics of process kinetics, hydrodynamics, and heat transfer.

Cocurrent Design. The *Nitrogen Engineering Corporation (NEC) converter* applies cocurrent flow by means of bayonet tubes [842], [845], [847]–[849], [860]–[864]. This design places maximum heat-exchange temperature difference and thus thus maximum cooling performance at the catalyst bed inlet, the point of maximum reaction rate, and therefore maximum heat evolution. The intent is to obtain closer approach to curve (a) (cf. Fig. 85 C). Figure 85 A shows the general arrangement of the converter, catalyst bed, and heat exchanger; Figure 85 B, the temperature profile of the system. Chemico, a derivative of NEC, continued to apply such converters with only slight changes [852].

The converter of the Japanese Consulting Institute [867], [1495] combines a catalyst bed with co-current cooling tubes and adiabatic beds (Section 4.5.3.3). An older Uhde design uses U-tubes for cooling a single bed, having co-current and counter-current flow [853].

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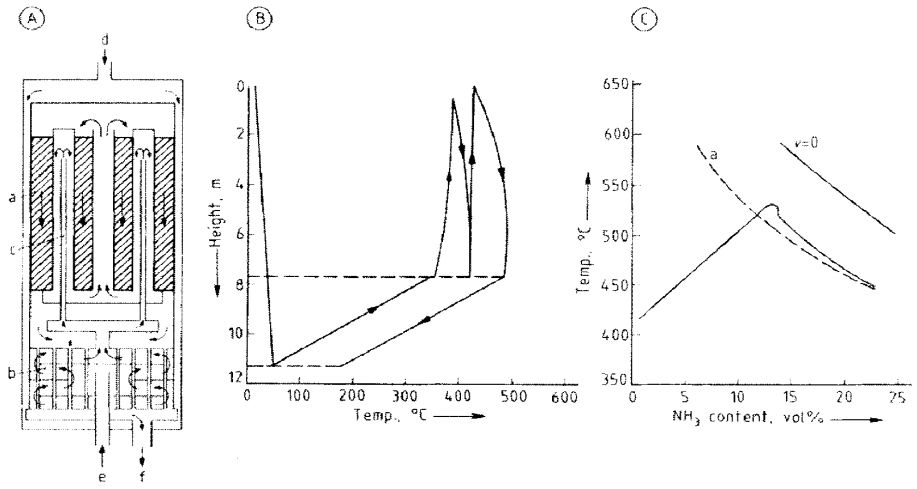


Figure 85. Cocurrent-flow tube-cooled converter [842]
A) Converter; a) Catalyst; b) Heat exchanger; c) Cooling tubes; d) Gas inlet; e) Temperature control gas (cold-shot) inlet; f) Gas exit
B) Gas temperature profile through the converter;
C) Ammonia concentration versus temperature (cf. Fig. 82)

4.5.3.3. Multibed Converters

Multibed Converters with Direct Cooling (Quench Converters). In quench converters cooling is effected by injection of cooler, unconverted synthesis gas (cold shot) between the catalyst beds. The catalyst beds may be separated by grids designed as mixing devices for main gas flow and cold shot, or be just defined by the location of cold gas injection tubes as for example in the ICI lozenge converter.

In this type of converter only a fraction of the recycle gas enters the first catalyst layer at about 400 °C. The catalyst volume of the bed is chosen so that the gas leaves it at ca. 500 °C (catalyst suppliers specify a maximum catalyst temperature of 530 °C). Before it enters the next catalyst bed, the gas is "quenched" by injection of cooler (125 – 200 °C) recycle gas. The same is done in subsequent beds. In this way the reaction profile describes a zig-zag path around the maximum reaction rate line. A schematic drawing of a quench converter together with its temperature/location and temperature/ammonia concentration profiles is presented in Figure 86.

A disadvantage is that not all of the recycle gas passes over the entire catalyst volume so that considerable ammonia formation occurs at higher ammonia concentration and therefore at lower reaction rate. Therefore a higher catalyst volume is needed compared to an indirectly cooled multibed converter. However, no extra space is required for interbed heat exchangers, so that the total volume of the high-pressure vessel will remain about the same as that for the indirectly cooled variant [865].

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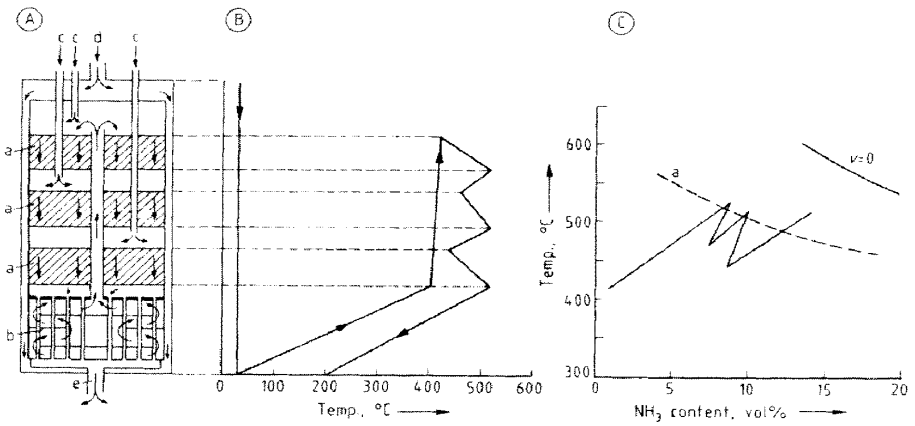


Figure 86. Multibed converter with quench cooling [864]
A) Converter; a) Catalyst; b) Heat exchanger; c) Quench gas inlets; d) Gas inlet; e) Gas exit
B) Gas temperature profile through the converter;
C) Ammonia concentration versus temperature (cf. Fig. 82)

As the quench concept was well suited to large capacity converters it had a triumphant success in the early generation of large single-train ammonia plants constructed in the 1960s and 1970s. Mechanical simplicity and very good temperature control contributed to the widespread acceptance. For example, M. W. Kellogg alone has installed more than 100 of its quench converters. Though being increasingly replaced by the indirect-cooling concept by revamp or substitution they are still extensively used. Descriptions of earlier designs of *Kellogg, BASF, and Uhde* can be found in [843]–[845], [866], [867].

The most important example is the *M. W. Kellogg three- or four-bed converter* [844], [868]–[870] (Figure 87). In this design, the catalyst "basket" is not easily removable from the pressure vessel. The catalyst can be changed by draining it at the bottom of the converter through "downcomers" that connect all catalyst beds with one another. The converter feed–effluent exchanger, attached to the top head, is designed for disassembly.

Other designs were used by *BASF* [844], *Casale* [844], *Chemico, Grand Paroisse* [843], *ICI* [867], *Uhde* [844], and others.

An interesting variant in this group is the *ICI lozenge converter* [280], [851], [868]. This design (Fig. 88) has a single catalyst bed that is divided into several zones (usually four) by quench gas distributors, through which colder recycle gas is injected evenly across the whole cross section of the catalyst bed. For this reason it is justifiable to classify this converter as a multibed type. The distributors consist of banks of transverse sparge pipes which deliver gas at regular intervals along their length. The spargers are in a void space within horizontal mesh-covered structures, whose cross section is lozenge shaped so that the catalyst particles can flow freely past them during loading and unloading. A special version of this reactor concept is the opposed flow

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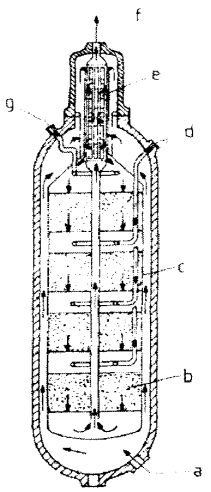


Figure 87. Kellogg four-bed vertical quench converter
a) Gas inlet; b) Catalyst bed; c) Basket; d) Quench; e) Interchanger; f) Gas outlet; g) Bypass

design [871], [872], suggested for very large capacities. In this configuration the converted gas is collected and withdrawn from the middle of the catalyst bed, with down-flow in the upper half and up-flow in the lower half of the catalyst bed. The uninterrupted catalyst bed is maintained in the opposed-flow converter. A design similar to that of ICI with direct injection of the quench gas into the single catalyst bed has been proposed by *Chemico* [873].

Converters with axial flow face a general problem: with increasing capacity the depth of the catalyst beds must be increased because for technical and economic reasons it is not possible to increase the bed diameter, and thus the pressure vessel diameter, above a certain limit. To compensate for the increasing pressure drop conventional axial flow converters have to use relatively large catalyst particles, which have the disadvantage of lower activity compared to smaller particles mainly on account of diffusion restriction. *Radial gas flow* in the converter avoids this dilemma, and with this concept it is possible to design converters for very large capacities without excessive diameters and with low pressure drop, even with small catalyst particle size. The advantages of radial flow are discussed in [874]–[877]. Radial flow has been also applied in tube-cooled converters [878]. The first radial flow converter introduced commercially and then widely used was the *Topsøe S 100 converter* [844], [852], [868], [879]–[884], which has two catalyst layers with a catalyst particle size of 1.5–3 mm. Figure 89 shows a schematic of the converter [402].

The major part of the gas enters the vessel at the top and flows down as shell cooling gas. It then passes through the feed–effluent heat exchanger and flows upwards through a central pipe to the first catalyst bed, which is traversed from the inside to the outside. After the effluent from the first bed has been quenched with cooler recycle gas, it enters the second bed and passes through it in the inward direction. The cold gas enters through the bottom of the vessel and is mixed with the inlet gas to the first bed for temperature control.

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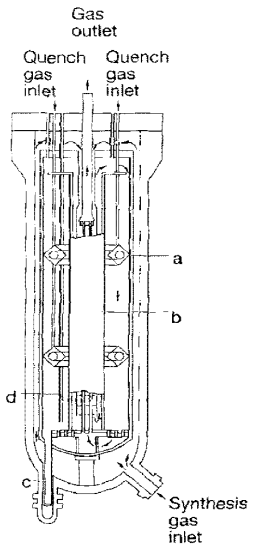


Figure 88. ICI lozenge converter
a) Quench gas distributors; b) Heat exchanger; c) Catalyst discharge nozzle; d) Tube for thermocouples

Radial flow quench converters have also been used by *Chemoproject* [885], *Österreichische Stickstoffwerke* [886], and *Lummus* [887].

Axial–radial flow pattern was introduced by Ammonia Casale. Converters with strictly radial gas flow require mechanical sealing of the top of each catalyst bed and dead catalyst volume with little or no flow to avoid bypassing of the catalyst. In the Casale concept there is no need for a dead catalyst zone as the annular catalyst bed is left open at the top to permit a portion of the gas to flow axially through the catalyst. The remainder of the gas flows radially through the bulk of the catalyst bed. As shown in Figure 90 this is achieved by leaving the upper part of the catalyst cartridge at outlet side unperforated so that gas entering from the top is forced to undergo partially axial flow.

Crossflow was chosen as a different approach by M. W. Kellogg in their horizontal quench converter to obtain low pressure drop even with small catalyst particles [843], [880], [881], [888]–[890]. The catalyst beds are arranged side by side in a removable cartridge which can be removed for catalyst loading and unloading through a full-bore closure of the horizontal pressure shell. As the cartridge is equipped with wheels it can be moved in and out on tracks, thus needing no crane. The gas flows vertically from the top to the bottom. The temperature difference between the top and the bottom requires special design measures to prevent uneven circumferential warming of the pressure shell and to avoid bending.

Multibed Converters with Indirect Cooling. In converters of this type cooling between the individual beds is effected by indirect heat exchange with a cooling medium, which may be cooler synthesis gas and/or boiler feed water heating and steam raising. The heat exchanger may be installed together with the catalyst beds

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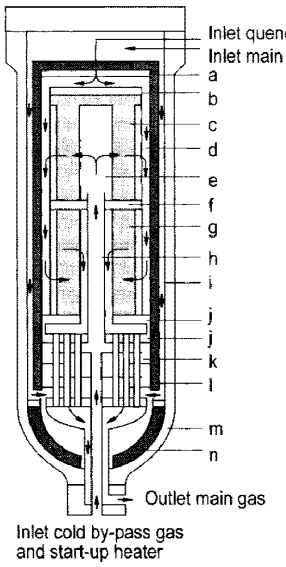


Figure 89: Haldor Topsøe S100 converter
a) Outer internal lid; b) Inner internal lid; c) First catalyst chamber; d) Inner annular space; e) Perforated center tube; f) Catalyst support plate 1; g) Second catalyst chamber; h) Transfer tube; i) Outer annular space; j) Catalyst support plate 2; k) Heat exchanger; l) Refractory fiber; m) Pressure shell; n) Refractory cement

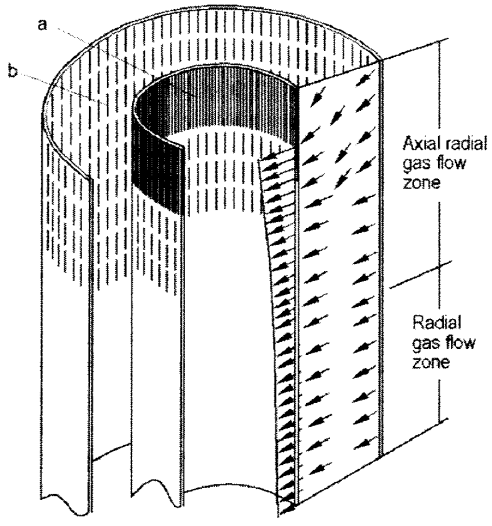


Figure 90. Ammonia Casale axial–radial flow pattern
a) Unperforated wall; b) Perforated wall

inside one pressure shell, but an attractive alternative, especially for large capacities, is to accommodate the individual catalyst beds in separate vessels and use separate heat exchangers. This approach is especially suitable when using the reaction heat for raising high-pressure steam. The indirect cooling principle is applied today in most large new ammonia plants, and also in revamps an increasing number of quench converters are modified to the indirect cooling mode. Figure 91 shows a schematic of

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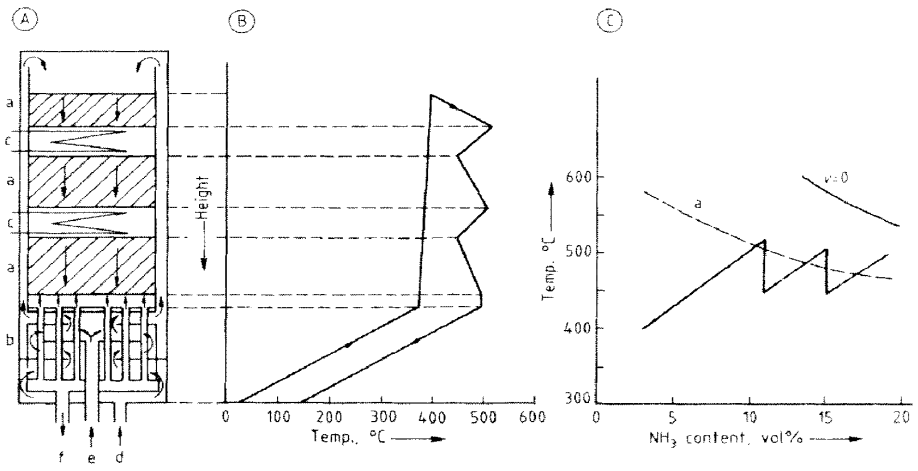


Figure 91. Multibed converter with indirect cooling
A) Converter; a) Catalyst; b) Heat exchanger; c) Cooling section; d) Gas inlet; e) Temperature control gas (cold-shot) inlet; f) Gas exit
B) Gas temperature profile through the converter;
C) Ammonia concentration versus temperature (cf. Fig. 82)

the principle together with temperature/location and temperature/ammonia concentration profile.

Converters with indirect cooling have been known since the early days of ammonia production, for example, the *Fauser–Montecatini reactor* [843], [844], [848], [867], [891]–[893]. In this converter, tube coils between catalyst beds transfer the reaction heat to a closed hot water cycle under pressure, operating by natural draft. The hot water releases the absorbed heat in an external steam boiler generating about 0.8 t of steam per tonne of ammonia at about 45 bar (ca. 250 °C).

In the well-known *Uhde–Chemie Linz converter* with three catalyst beds – described in various versions [841], [843], [844], [868], [894]–[897] – the indirect cooling is provided by converter feed gas. Feed gas enters at the top, passes down the annulus between basket and shell to cool the pressure wall, flows through the shell side of the lower feed–effluent heat exchanger, and then via the center pipe and interbed exchangers to the top of the first catalyst bed. The gas passes downwards through the catalyst beds and the tube side of the interbed exchangers and the lower heat exchanger to leave the reactor vessel. For trimming purposes a quench is foreseen.

Further development of the radial flow concept used in the quench converter Topsøe Series 100 has led to the successful launch of the *Topsøe Series 200* converter [623], [874], [898]–[904] designed for indirect cooling. Two versions are shown in Figure 92, with and without a lower internal heat exchanger. A "cold shot" ahead of the first catalyst bed is installed for temperature adjustment. In the converter without a lower

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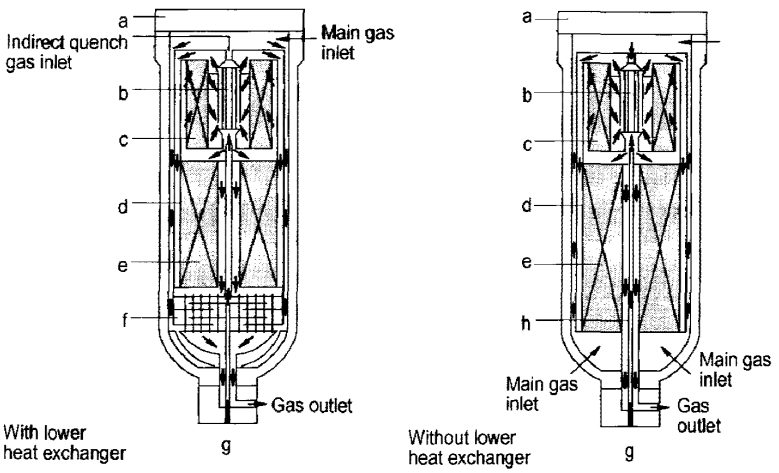


Figure 92. Topsøe Series 200 converter
a) Pressure shell; b) Interbed heat exchanger; c) 1st Catalyst bed; d) Annulus around catalyst bed; e) 2nd Catalyst bed; f) Lower heat exchanger; g) Cold bypass; h) Cold bypass pipe

exchanger the feed gas enters at the bottom and flows as pressure wall cooling gas to the top of the converter. After passing the centrally installed interbed exchanger on the tube side, the gas is mixed with cold gas for temperature adjustment and passes through the first catalyst bed radially from the outside to the inside. The exit gas flows through the shell side of the interbed exchanger before it enters the second bed, which is crossed in the same direction as the first one. Recently the *Topsøe Series 300 Converter*, which contains three catalyst beds and two central interbed exchangers in a single pressure shell has been commercialized.

Casale [905]–[910] has also successfully commercialized converters based on the axial–radial flow concept with indirect cooling.

Kellogg has re-engineered its *horizontal cross-flow* quench converter for *indirect cooling* [843], [888], [911]–[913] (Fig. 93). As in the quench version the pressure shell has a full-bore closure to remove the catalyst cartridge for loading and unloading. The reactor contains two catalyst beds, with the second one split into two parallel sections. Reactor feed gas passing between cartridge and shell is used to keep the pressure wall cool, and an inlet –outlet heat exchanger is located between first and second bed. A cold shot is installed for adjusting the inlet temperature of the first catalyst bed. A horizontal design with indirect cooling is also proposed in [914].

In the *C. F. Braun (today Brown & Root)* ammonia synthesis concept [915]–[920], separate vessels were used for the two catalyst beds of the original version. The feed–effluent heat exchanger was located between the first and second reactor vessel, and the second catalyst vessel was followed by a waste-heat boiler for high pressure steam. This basic concept was already introduced in the heyday of the quench converters and prior to the first energy crisis. Today Brown and Root uses three catalyst

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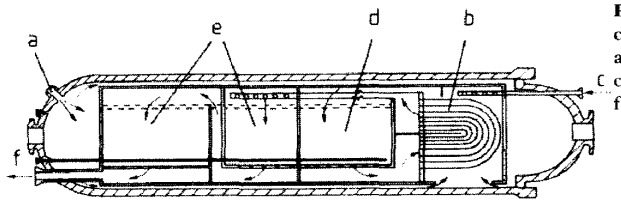


Figure 93. Kellogg horizontal intercooled ammonia converter
a) Inlet; b) Interbed heat exchanger; c) Bypass; d) Bed 1; e) Bed 2; f) Outlet

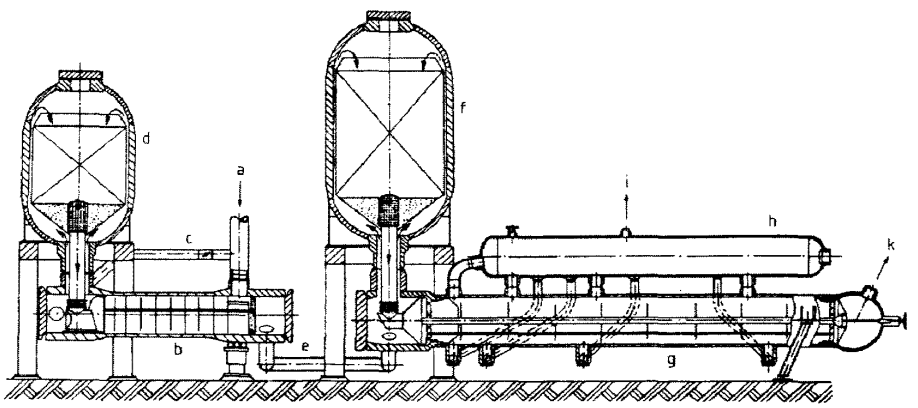


Figure 94: C. F. Braun converters with interbed heat exchanger and waste heat boiler
a) Gas inlet; b) Feed – first bed effluent exchanger; c) Bypass for temperature control; d) First bed; e) Line to second bed; f) Second bed; g) Waste heat boiler (Borsig); h) Steam drum; i) Steam outlet; k) Gas outlet

vessels [921] – [924] with boilers after the second and the third. The gas flow is axial and the mechanical design rather simple. Contrary to most converter designs, in which the pressure shell is kept below 250 °C by means of insulation or by flushing with cooler gas, the pressure vessel wall of the C. F. Braun reactors is at 400 °C, which is possible with modern steels in compliance with the Nelson diagram (see Chapter 8). Figure 94 shows the two-bed version of the C. F. Braun converter system.

To withstand the high outlet temperature level (450 – 500 °C) needed for the high-pressure boilers, a special design is employed to keep the outlet nozzle cool. Brown & Root has devised a good solution by direct coupling the boilers and the exchanger to the converter.

Uhde has used three catalyst beds for capacities up to 1800 t/d (Figure 99). The first two are accommodated in a single pressure vessel together with an inlet – outlet exchanger. Then a waste heat boiler generating high-pressure steam cools the gas before it enters the second vessel containing the third bed, which discharges through a second external high-pressure boiler. The gas flow is in radial mode in all three catalyst beds.

Topsøe has now introduced a hot-wall converter with only one catalyst bed and no internal heat-exchange equipment, similar to Brown & Root, but with radial flow. Three of these converters can be combined with an external heat exchanger and two

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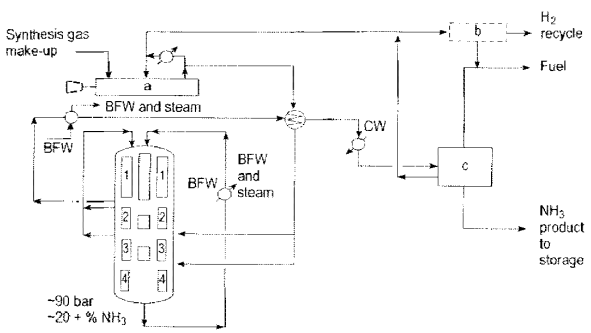


Figure 95. Kellogg advanced ammonia process (KAAP)
a) Compressor; b) PGRU; c) Refrigeration

high-pressure boilers to give an arrangement as described for Brown & Root. This *Topsøe Series 50 converter*, can also be combined with the Series 200 reactor and two external high-pressure boilers to attain the configuration as described for Uhde (Topsøe Series 250).

Kellogg has developed for its ruthenium catalyst based *KAAP ammonia process* [404], [478] a special converter design. Four radial flow beds are accommodated in a single pressure shell with intermediate heat exchangers after the first, second and third bed. The first bed is loaded with conventional iron catalyst, the following ones with the new ruthenium catalyst. Figure 95 is a simplified sketch of the converter and the synthesis loop of the KAAP for a new plant. For revamps Kellogg has also proposed a two-bed version completely loaded with ruthenium catalyst to be placed downstream of a conventional converter [398].

Optimizing the Temperatur Profile and Bed Dimensions in Multibed Converters is an important design aspect. With closer approach to equilibrium, the volume of catalyst required in the individual beds increases, requiring greater total catalyst volume and appropriate changes in the catalyst bed dimensions. The literature has frequently treated the problem of optimizing both the distribution of catalyst volume between a given number of beds and the bed inlet temperatures [815], [817], [842], [925] – [928]. Reference [929] examines optimizing the temperature profile in a given four-bed quench converter. For additional literature, refer to Section 4.5.2.

4.5.4. Waste-Heat Utilization and Cooling

The reaction heat of ammonia synthesis is 46.22 kJ/mol at STP, which corresponds to 2.72 GJ/t NH_3. Utilization of this heat at the highest possible temperature for generating high-pressure steam is a major contribution to the high total energy efficiency of modern ammonia plants [930]. Early converters, operating at about 300 bar, equipped with a lower heat exchanger for raising the inlet temperature for the (first) catalyst bed to the ignition temperature (ca. 400 °C) , received the converter feed at about ambient temperature and therefore had outlet temperatures of ca. 250 °C (ca. 15.5 °C per mol% of ammonia formed).

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Initially there was practically no heat recovery, and nearly the total heat content of the gas down to ambient temperature and thus the reaction heat was transferred to cooling water. Subsequently plants were modified to use this heat to some extent, but the low temperature level allowed only boiler feed water heating and generation of low-pressure steam (ca. 20 bar). In some instances, water circulation was installed to use this heat in other plants or production steps. As for any type of converter the outlet temperature rises with increasing inlet temperature (ΔT is determined by the degree of conversion), in further developments an additional heat exchanger for converter feed versus the converted gas was installed, downstream of the above-mentioned heat recovery. In this way the temperature level at which heat could be recovered was increased, ultimately to the point where the inlet temperature to waste-heat recovery is equal to the outlet temperature of the last catalyst bed. In practice this corresponds to moving the lower heat exchanger (which in multibed converters exchanges feed to the first catalyst bed against effluent from the last bed) partially or completely to a position outside of the converter and downstream of the waste-heat recovery installation. In this way the waste heat downstream of the synthesis converter in modern plants is available in the temperature range around 480 to 290 °C. The steam pressure, formerly 100 bar, has now been raised to 125 bar, which means that the gas can be cooled in the boiler to ca. 350 °C; the remaining recoverable heat is used for boiler feed water heating.

The trend followed in newer plants is to increase conversion per pass with the result of higher ammonia outlet concentrations and lower outlet temperatures from the last bed. However, as optimum energy efficiency of the whole ammonia plant requires maximum high-pressure steam generation, part of the heat must be recovered before the reaction is completed in the reactor system. This can be accomplished [900], [901], [930], [931] by using three catalyst beds in separate pressure vessels with boilers after the second and the third vessel and an inlet–outlet heat exchanger for the first catalyst bed.

Advanced ammonia concepts produce as much as 1.5 t of high-pressure steam per tonne of ammonia, which correspond roughly to 90% of the standard reaction enthalpy. Figure 96 is a temperature–enthalpy diagram for a converter system corresponding to the original C. F. Braun arrangement. High-pressure steam (113 bar, 320 °C) is generated in this example after the second catalyst bed.

Appropriate design of waste-heat boilers is described in Section 4.6.

4.5.5. Ammonia Recovery from the Synthesis Loop

In all commercial plants ammonia is recovered from the synthesis loop by cooling the synthesis gas to condense the ammonia under synthesis pressure. The liquid ammonia product is separated from the gas, which is recycled. Arrangement and location of the ammonia separator(s), recirculation compression, addition of makeup gas and extraction of purge gas are discussed in Section 4.5.1 (see also Figure 77).

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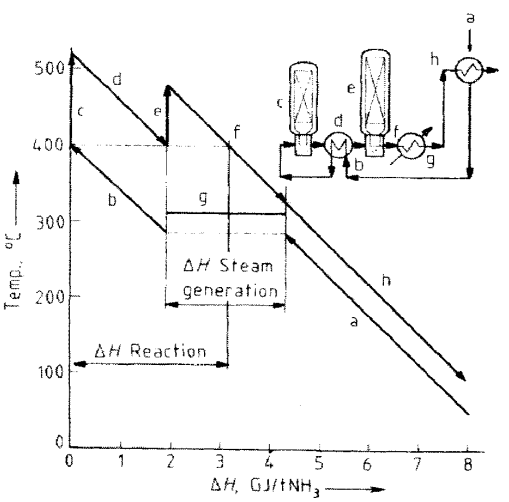


Figure 96. Temperature versus enthalpy diagram for a two-bed system with steam generation
a) Heating in main feed effluent exchanger; b) Further heating in feed – first bed effluent exchanger; c) Temperature rise in first bed; d) Cooling in feed – first bed effluent exchanger; e) Temperature rise in second bed; f) Cooling by steam generation; g) Temperature level of waste heat boiler; h) Cooling in main feed effluent exchanger

In high-pressure synthesis loops (> 450 bar) cooling by water and or air is sufficient to obtain the required low residual ammonia concentration in the gas. In more modern plants, which operate at moderate pressures, this cooling has to be supplemented by refrigeration, for which a mechanical ammonia refrigeration cycle, with one or more temperature levels is generally used. Refrigeration down to −25 °C is used, which with inclusion of the necessary temperature difference in the chiller requires ammonia evaporation at about atmospheric pressure. The amount of ammonia vaporized (and consequently reliquefied by compression and water or air cooling) can be substantial. At a loop pressure in the range 100 to 150 bar the quantity of reliquefied ammonia may be twice the ammonia product flow.

The liquid ammonia of the high-pressure separator is flashed to about 20 bar, whereby the majority of the dissolved gases are released in the let-down vessel. This gas is normally used as a fuel, preferably after removal of ammonia vapor to avoid NO_x formation in the combustion furnace.

The ammonia from the let-down vessel may be sent directly to downstream users or flashed further to atmospheric pressure for storage in a cold tank. All ammonia vapors removed from flash gases and from purge gas by water scrubbing can be recovered as pure liquid product by distillation if there is no direct use for the aqueous ammonia.

Absorption refrigeration with aqueous ammonia instead of a mechanical refrigeration system [932] – [937] did not find widespread application.

Although ammonia condensation was already used in HABER's lab-scale ammonia plant and in early pilot plants of BOSCH, the first commercial units of BASF used ammonia absorption in water to remove the product from the cool synthesis loop gas, because various technical problems were encountered with refrigeration at that time. It was only in 1926 that ammonia condensation was introduced in the Haber – Bosch

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plants. In the early 1920s LUIGI CASALE successfully used condensation for his first plant. Water cooling was sufficient on account of the very high synthesis pressure.

Recovery of ammonia by water scrubbing offers the advantage of achieving a very low residual ammonia content, but the drawback is that the whole recycle gas has to be dried afterwards and in addition distillation of aqueous ammonia is necessary to yield liquid ammonia. Nevertheless the scrubbing route was again proposed for a synthesis loop to be operated under extremely low pressure (around 40 bar) [938]. Snam Progetti [280], [939], [940] has proposed removing the ammonia from the loop gas at ambient temperature down to 0.5 mol% by absorption in dilute aqueous ammonia.

The extent to which the ammonia concentration in the gas can deviate from that expected for ideal behavior can be seen from Tables 4 and 5 (Section 3.1). For example, at 30 °C the ammonia vapor pressure according to Table 4 is 1.167 bar, corresponding to 5.84 mol% at the total pressure of 20 bar. In contrast, Table 5 gives the ammonia concentration in a 1/3 nitrogen/hydrogen mixture at 20 bar total pressure as 9.8 mol%.

Ammonia recovery by adsorption on solids has been also proposed [1498], [1499].

4.5.6. Inert-Gas and Purge-Gas Management

Apart from nitrogen and hydrogen, the fresh make-up gas supplied to the synthesis loop usually contains small quantities of inert gases. These include methane (from gas generation), argon (from the process air), and helium (from the natural gas). Because they are inert , they tend to concentrate in the synthesis loop and must be removed to maintain the loop material balance. A portion of the inert gases dissolves in the liquid produced in the ammonia separator. Solubility data are found in Section 3.1. Table 6 gives the solubilities for 3/1 hydrogen/nitrogen mixtures and can be used as a rough approximation. Figure 4 gives vapor–liquid equilibrium ratios for use in making precise calculations of the dissolved quantities of inerts. If the synthesis gas pressure is high, for example, 300 bar), and the inert gas concentration in the synthesis loop make-up gas low enough, for example, under 0.2 vol% [941], then dissolution in the product ammonia suffices to remove the inerts from the synthesis loop.

With a higher inert gas content in the make-up gas this method is not applicable, because the required partial pressure of the inert gas at equilibrium in the loop gas would become so high that a synthesis under moderate pressure would be virtually impossible. So, in addition to removal as dissolved gases (flash gas), inerts have also to be removed from the gas phase by withdrawing a small purge-gas stream from the loop. At the same time expensive synthesis gas is also lost from the loop, unfortunately associated with the loss of valuable hydrogen and nitrogen, which lowers the ammonia yield. Therefore, determining the appropriate inert gas concentration requires a precise economic calculation.

A high inert gas level has various drawbacks. It decreases the specific converter performance by reducing the hydrogen and nitrogen partial pressures. The gas recycle

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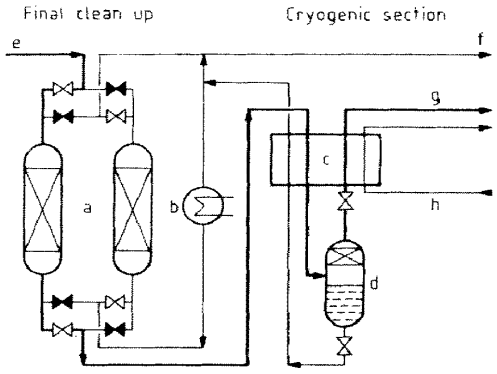


Figure 97. Simplified flow diagram of cryogenic hydrogen recovery unit
a) Molecular sieve adsorbers; b) Heater; c) Plate-fin exchanger; d) Separator; e) Ammonia-free purge gas; f) Fuel gas to reformer burners; g) Hydrogen product to syngas compressor; h) NH_3 refrigerant

flow is increased by the amount of inert gas. Piping and equipment must correspondingly be increased in size, and the associated power consumption for recycle gas increases. Moreover, there is an unfavorable effect on condensation of the ammonia product. Because of the dilution, less ammonia can be condensed from the recycle synthesis gas by less expensive air or water cooling or higher temperature level refrigeration.

There are several possibilities for reducing the losses associated with the purge gas. The most capital-intensive method consists of feeding the purge gas to a second synthesis loop operating at a slightly lower pressure [942], [943]. As this loop can operate at a very high inert level (40 % or more), only a very small final purge stream is necessary and no recompression is needed. Up to 75 % of the hydrogen from the first-loop purge stream can be recovered. This system has the advantage that nitrogen is also recovered, but it is too expensive for use in modern plants and revamps. For this reason other methods have been developed.

4.5.6.1. Hydrogen Recovery by Cyrogenic Units [944]

Ammonia is first removed from the purge gas by cooling or in a water wash operating at 7.5 MPa (75 bar). Molecular sieve adsorbers then eliminate moisture and traces of ammonia (Fig. 97). The dry, ammonia-free purge gas from the adsorbers next enters the cold box. Heat exchange with cold product hydrogen fraction and with gas rejected to fuel cools the purge gas to a temperature of about −188 °C. Partial condensation liquefies methane and argon as well as some of the nitrogen and helium. These are removed in a separator, leaving a hydrogen-rich gas.

The liquid flows through a control valve, reducing its pressure, and into a brazed aluminum (plate-fin or core-type) heat exchanger. The hydrogen-rich gas also flows into the same exchanger (in separate passages) where the vaporizing liquid and the hydrogen are warmed by cooling the entering purge gas. Liquid ammonia from the ammonia plant may be used to provide additional refrigeration, especially at plant startup.

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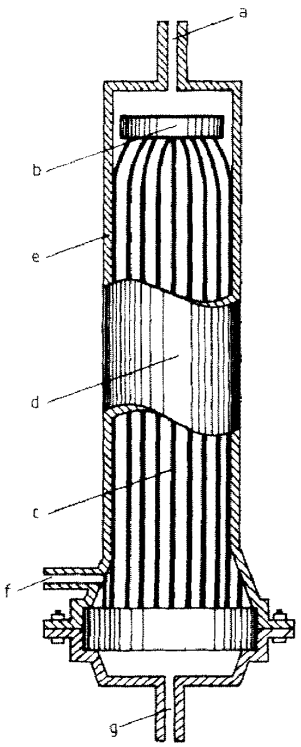


Figure 98. Gas separator module
a) Nonpermeate gas outlet; b) Fiber bundle plug; c) Hollow fiber; d) Separator (length, diameter, and number of separators determined by ammonia process); e) Coated carbon steel shell; f) Feed stream of mixed gases; g) Permeate gas outlet

The warm hydrogen-rich gas flows back to the suction side of the second stage of the synthesis gas compressor (6.5–7 MPa). About 90–95 % of the hydrogen and 30 % of the nitrogen in the purge gas can be recovered.

The remaining gas, with a high concentration of inerts, serves as fuel for the primary reformer. After heating in a preheater, a portion serves to regenerate the molecular sieves and then likewise flows to reformer fuel.

Cryogenic hydrogen recovery units are supplied by firms such as *Costain Engineering (formerly Petrocarbon Development)* [945]–[955], *Linde* [956], and *L'Air Liquide*, among others. Reference [957] reports on the changes in operating conditions of an ammonia plant resulting from the operation of a cryogenic hydrogen recovery unit.

4.5.6.2. Hydrogen Recovery by Membrane Separation

Monsanto has developed a new separator system known as Prism. The process uses selective gas permeation through membranes to separate gases. This principle has been applied to separating hydrogen from other gases [958]–[961]. The membranes are hollow fibers with diameters of about 0.5 mm. The fiber is a composite membrane consisting of an asymmetric polymer substrate and a polymer coating. The design of a

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single separator module (length, 3 – 6 m; diameter, 0.1 – 0.2 m) resembles a shell and tube heat exchanger. A bundle with many thousands of hollow fibers is sealed at one end and embedded in a tube sheet at the other. The entire bundle is encased in a vertical shell (Fig. 98).

The purge gas is water scrubbed at 135 – 145 bar, reducing the ammonia concentration to less than 200 ppm. The scrubbed purge gas is heated to 35 °C and sent directly to the Prism separators. Trace concentrations of ammonia and water vapor in the gas stream pose no problem to the membrane. Therefore, a dryer system is not required.

The gas stream enters the separator on the shell side, i.e., the outside of the hollow fibers. Hydrogen permeates through the wall of the fibers. Hydrogen-rich permeate gas flows down the bore of the fiber and through the tube sheet and is delivered at the bottom of the separator. The remaining (nonpermeating) gases, nitrogen, methane, and argon, are concentrated on the shell side, recovered through the top and pass to the next separator module. Several separators operate in series. The rate of permeation decreases across a bank of separators as the hydrogen partial pressure differential across the membrane approaches zero. Therefore, a second bank of separators with lower pressure on the tube side is used to increase the hydrogen recovery. Of the recovered hydrogen, 40 – 70% leaves the first bank of separators at 70 bar and is returned to the second-stage suction of the synthesis gas compressor. In the second bank, permeate hydrogen is recovered at 25 – 28 bar and returned to the first-stage suction of the syngas compressor. Overall hydrogen recovery is 90 – 95%. The remaining nonpermeate gas stream normally flows to primary reformer fuel.

The main advantages of the Prism separator system are simplicity, ease of operation, and low maintenance. Reference [962] compares membrane and cryogenic separation units for a large ammonia plant.

For further literature on gas separation by membranes, see [963] – [969].

Membrane technology is also offered by other licensors; an example is the *Polysep Membrane System of UOP* [970]. In addition to the systems based on hollow fibers, membrane modules have been developed in which the membrane is in the form of a sheet wrapped around a perforated center tube using spacers to separate the layers. The raw gas flows in axial direction in the high pressure spacer and the permeate is withdrawn in the low pressure spacer. Such a module, for example, is marketed under the name *Separex* [971], [972].

4.5.6.3. Hydrogen Recovery by Pressure Swing Adsorption

Pressure swing adsorption (PSA) on zeolite molecular sieves (see Section 4.3.2.6) may be also used for hydrogen recovery from purge gas [761]. The process, originally developed by Union Carbide under the name HYSIV, is now marketed as *Polybed PSA by UOP* [970], [973], [974]. PSA technology is also offered by *Linde* and other companies. If required, the process also offers the possibility to supply pure hydrogen from

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the purge gas for other uses. PSA units usually operate at adsorption pressures of 20–30 bar and achieve recovery rates higher than 82% for hydrogen and 20% for nitrogen. Carbon-based *adsorbents* for pressure swing adsorption have also been investigated [973], [974] and a process developed by *Bergbau-Forschung* [975] is offered by Costain.

4.5.6.4. Hydrogen Recovery with Mixed Metal Hydrides

A proprietary hydrogen separation process utilizing the reversible and selective adsorption capability of mixed metal hydrides has been proposed. The hydride, forming compounds, such as $LaNi_5$, FeTi, or Mg_2Cu, are in the form of ballasted pellets. The ballast material serves as a heat sink to store the heat of adsorption. Subsequently, this is used to supply the heat of desorption. The ballast also is the binder for the pellets, preventing attrition. Each type of metal hydride is susceptible to certain contaminants. Therefore, selection of the metal hydride must be based on the analysis of the gas to be treated. No ammonia removal step is required upstream of the unit. The system yields 99 mol% hydrogen product at a recovery efficiency of 90–93% [972], [976], [977]. No large commercial installations are known to be in operation at this time.

4.5.6.5. Argon Recovery from Ammonia Purge Gas

The waste gas from hydrogen recovery plants is more highly enriched in argon than the purge gas. If potential markets for argon exist, then it may be possible to supplement the hydrogen recovery plant with one for recovering argon. Cryogenic argon recovery from ammonia purge gas is discussed in [978]–[980]. Typical argon recoveries are in excess of 90%, with a purity of 99.999%.

4.5.7. Influence of Pressure and Other Variables of the Synthesis Loop

The influences of individual parameters can be summarized as given in [981]:

- Pressure: increasing pressure will increase conversion due to higher reaction rate and more favorable ammonia equilibrium.
- Inlet temperature: there are two opposed effects as increasing temperature enhances reaction rate but decreases the adiabatic equilibrium concentration.
- Space velocity: increasing the space velocity normally lowers the outlet ammonia concentration, but increases total ammonia production.
- Inert level: increasing the inert level lowers the reaction rate for kinetic and thermodynamic reasons (Section 3.5).

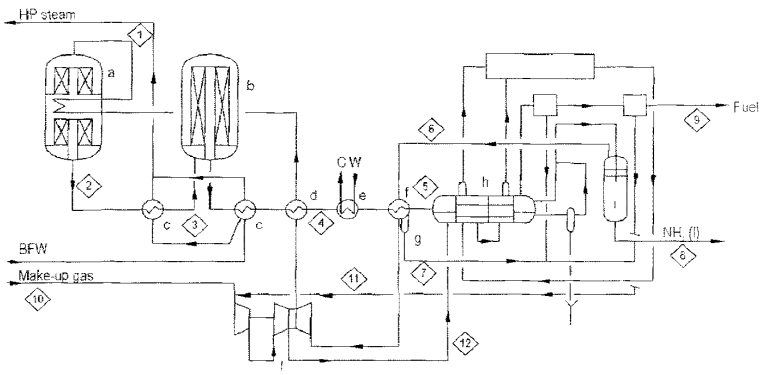
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- Hydrogen/nitrogen ratio: a true maximum reaction rate for a certain H/N ratio; at lower temperatures the maximum lies at lower H/N ratios (Section 3.5). Position of the maximum also depends on the space velocity values (Section 4.5.2).
- Recycle rate: at constant pressure and production rate, the consequence of higher recycle rate is a lower ammonia concentration. In this case the difference to the equilibrium concentration and thus the reaction rate increases with the result that less catalyst is required. However, the temperature level for waste heat recovery decreases and with lower temperature differences, larger heat exchanger surface areas become necessary and the cross sections of piping and equipment have to be enlarged on account of the higher gas flow.
- Separator temperature: together with pressure and location of make-up gas addition, the temperature of the ammonia separator determines the ammonia concentration at the converter inlet. A lower temperature means lower ammonia concentration, which translates into either a lower catalyst volume or a higher conversion.
- Catalyst particle size (Section 3.6.1.2): smaller catalyst particles give higher conversion because of lower diffusion restrictions (higher pore efficiency)

The question of the best synthesis pressure is rather difficult and extremely dependent on optimization parameters such as feedstock price, required return on investment, and site requirements. In principle it is possible to calculate the minimum amount of mechanical work needed in the synthesis loop. If plots of kilowatt hours versus synthesis pressure for makeup gas compression, recycle, and refrigeration are superimposed the result will be a minimum, for which a value of 155 bar is reported in [982], [983]. The result is strongly dependent on assumed boundary conditions, and other studies came to higher values in the range 180 – 220 bar. However, such diagrams should be interpreted with care. First, this type of plot is strongly influenced by the catalyst activity, and thus by any factors that affect it, such as grain size and minimum possible temperature for the first bed, and especially the equilibrium temperature of the last bed [984]. Second, this approach considers only the mechanical energy and ignores completely the recovered energy of reaction, its energy level, and its impact on the energy balance of the complete ammonia plant. Third, the temperature attainable at a given site by air or water cooling will affect the refrigeration duty. And fourth, the type of front end can profoundly alter the result. The front-end pressure determines the suction pressure of the synthesis gas machine. In a plant based on partial oxidation with an operating pressure of 80 bar, less than half as much energy is needed to compress the makeup gas to 180 bar, for example, as in a steam reforming plant with a suction pressure of only 25 bar.

Thus the problem of choosing the best synthesis pressure is complex because not only does the entire energy balance have to be examined, but also the mechanical design and the associated investment costs. For an actual project, the costs for energy (i.e., the feedstock) have to be weighed against investment. With the exception of some processes which used extremely high pressures (Casale, Claude) a pressure of around 300 bar was common for the old multi-stream plants operated with reciprocating

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No.	Flow rate,	T, °C	p, MPa	Gas composition, mol %					Production of NH_3
	kmol/h			N_2	H_2	CH_4	Ar	NH_3	liquid, t/h
1	28344	295	18.80	23.53	61.20	8.20	2.89	4.18	
2	25368	469	18.48	20.43	50.79	9.15	3.23	16.40	
3	25368	401	18.38	20.43	50.79	9.15	3.23	16.40	
4	24672	336	18.26	19.60	47.99	9.43	3.31	19.67	
5	21613	21	18.02	22.33	54.71	10.67	3.78	8.51	
6	28344	0	17.88	23.54	61.20	8.20	2.88	4.18	
7	3060	21	18.02	0.30	0.55	0.50	0.09	98.55	51.36
8	3678	20	2.50	0.02	0.03	0.12	0.01	99.82	62.51
9	320	38	0.25	46.55	21.72	24.34	7.21	0.18	0.01
10	7667	35	3.23	25.89	72.73	1.07	0.31	0.00	
11	374	38	3.25	5.22	90.20	2.86	1.72	0.00	
12	8041	35	18.20	24.93	73.54	1.16	0.37	0.00	

Figure 99. Example of a synthesis loop for 1500 t/d NH_3 (Krupp – Uhde)
a) Converter with two radial beds and internal heat exchange; b) Converter with one radial bed; c) Waste heat recovery; d) Heat exchanger; e) Water cooling; f) Heat exchanger; g) No. 1 separator; h) Refrigerated cooling; i) No. 2 separator; j) NH_3 recovery; k) H_2 recovery

compressors. The centrifugal compressor is one of the most important features of single-train ammonia plants. The first of these plants, with a capacity of 600 t/d, were built in the mid-1960s and the maximum attainable synthesis pressure was restricted to ca. 150 bar by technical limitations of the centrifugal compressor, which needed a minimum gas flow (see also Section 4.4). Of course, at current plant sizes of 1200 – 1800 t/d this constraint is no longer of importance. These plants usually operate in the pressure range of 170 – 190 bar and it is a confirmation of the argumentation presented above that the different pressures are not reflected in the overall energy consumption of the complete ammonia plant. Analysis of the effects of various parameters on the energy consumption of the synthesis loop are also reported in [900], [901]. At constant equilibrium temperature for the effluent from the last bed (constant ammonia concentration) energy consumption of the loop was found to be almost independent of pressure in the range of 80 – 220 bar [984].

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4.5.8. Example of an Industrial Synthesis Loop

Figure 99 is an example of modern ammonia synthesis loop (Krupp – Uhde) with a two-vessel converter system and three indirectly cooled catalyst beds producing 1500 t/d NH_3 at 188 bar.

The gas enters the converter (a) at 295 °C and is subsequently heated in the internal heat exchanger to 390 °C before it enters the first catalyst layer. The outlet gas from the first layer then passes through the aforementioned heat exchanger and enters the second bed, after which the gas leaves the converter with 469 °C and passes a waste heat boiler generating 125 bar steam. The inlet gas of the second vessel, which accommodates the third catalyst bed, has a temperature of 401 °C and the outlet enters a further waste heat boiler generating 125 bar steam.

4.6. Waste-Heat Boilers for High-Pressure Steam Generation

Though high pressure steam generation in waste heat boilers [404], [985] does not represent a separate process step comparable to those described in the preceding sections, a special section seems to be appropriate because of its great influence on efficiency and reliability of the plants. The operating conditions are more severe than those normally encountered in power plants; on account of the high pressure on both sides, the heat transfer rates and thus the thermal stresses induced are much higher.

After the secondary reformer of steam reforming plants the gas has to be brought down from around 1000 °C to about 350 °C for the HT shift. In earlier-generation plants two boilers were usually installed in series, with a bypass around the second to control the inlet temperature for the HTS. Common practice for a long time was to use a water-tube design. A famous example is the Kellogg bayonet-tube boiler, applied in more than 100 plants. Because of size limitations two parallel units were installed. For sufficient natural water circulation these boilers needed a steam drum at a rather high elevation and a considerable number of downcomers (feed water) and risers (steam/water mixture).

In contrast, fire-tube boilers are much better suited for natural circulation and the steam drum can sit in piggyback-fashion, right on top of the boiler. This makes it possible to provide each boiler with its own separate steam drum, which allows greater flexibility in the plot plan. But it took some time before this boiler type was accepted in ammonia plants as the stress pattern is more complex and less predictable than in water-tube boilers.

In a fire-tube boiler, the inlet tube sheet and the tube sheet welds are exposed to the extreme temperature of the reformed gas, which creates rather large temperature gradients and therefore high expansive stress. A positive feature of the fire-tube design, however, is that debris in feed water (mainly magnetite particles spalling from the water-side surface of the tubes) can collect at the bottom of the horizontally-mounted

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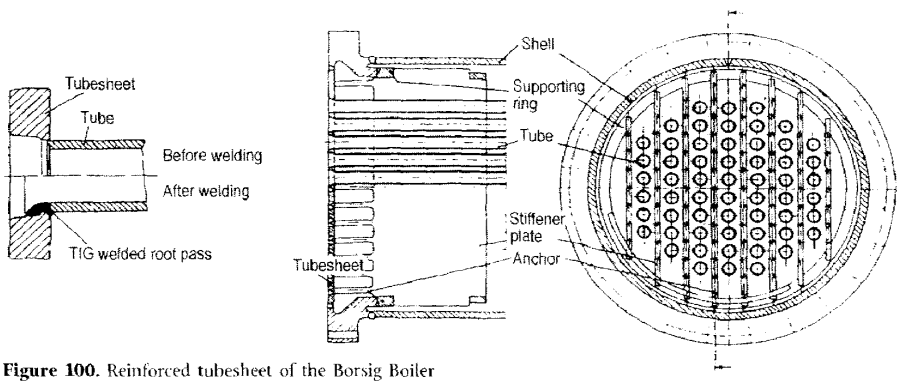


Figure 100. Reinforced tubesheet of the Borsig Boiler

vessel without creating difficulties and are removed easily by blow down. Water-tube boilers, especially bayonet-types, are very sensitive in this respect, since the deposits may collect in the lowest and most intensively heated part of the tube. In an extreme case of scaling, this may restrict the water flow to the point where boiling occurs irregularly (film boiling). The risk is overheating and tube failure.

The key factor which allowed the use of fire-tube boilers after the secondary reformer was the development of thin-tube-sheet designs. Thick tube sheets in this kind of service are too rigid and have too big a temperature gradient, and the resultant high stress on the tube-to-tubesheet welds can lead to cracks. The inherent flexibility of thin tube sheets assists in dispersing stresses and reduces the risk of fatigue failure of the tube-to-tubesheet welds and tubesheet-to-shell welds. In all that various designs using this concept, the tubesheet is only 25 – 30 mm thick. The hot inlet channel and the tubesheet are shielded by a refractory layer, and the tube inlets are protected by ferrules.

In the *Uhde* [986], [987] and *Steinmüller* [989] concept the tubesheet is anchored to and supported by the tubes to withstand the differential pressure, which imposes some restriction on the tube length. *Babcock-Borsig's* [988], [990], [991] tubesheet is reinforced by stiffening plates on the back side (Figure 100). Both solutions have full-penetration tube-to-tubesheet welds for the tubes to prevent crevice corrosion. *Struthers* [992] reduces stress by making the tubesheet-to-shell connection flexible.

The synthesis loop boiler on the exit of the converter is also a very important piece of equipment. In some modern plants not equipped with an auxiliary boiler it supplies nearly half of the total steam generation. It may generate as much as 1.5 t of steam per tonne of ammonia, equivalent to about 90% of the reaction heat. Fire-tube versions have been also used, including Babcock–Borsig's thin-tubesheet design. But compared to the secondary reformer service, where the gas pressure is lower than the steam pressure, the conditions and stress patterns are different. In the synthesis loop boiler the opposite is the case, with the result that the tubes are subjected to longitudinal compression instead of being under tension. Several failures in this application have been reported [993], and there was some discussion of whether this type of boiler is the best solution for the synthesis loop waste-heat duty.

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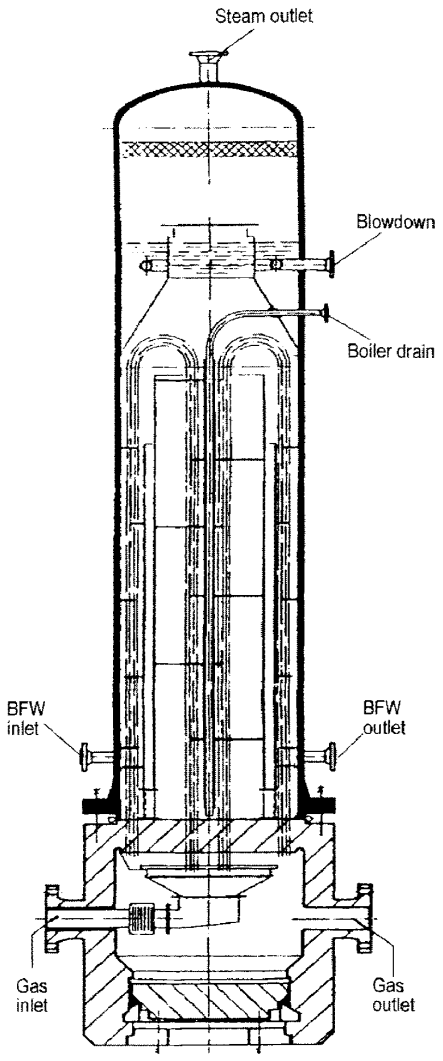


Figure 101. U-tube synthesis loop boiler

More generally accepted now are thick-tubesheet concepts in various configurations. Proven U-type designs are available from *Uhde* [931], *Balcke-Dürr* [994], [995], [997], *Kellogg* [996] and *Babcock-Borsig* [991]. A special advantage is that the tube bundle, being rigidly mounted at the end only, is essentially free of stress. The main tubesheet is protected in various ways against damage by the hot gas. The principle is shown in Figure 101. A variation offered by Uhde for use as first first boiler in the synthesis loop has cooling channels in the tube sheet fed by incoming boiler feed water.

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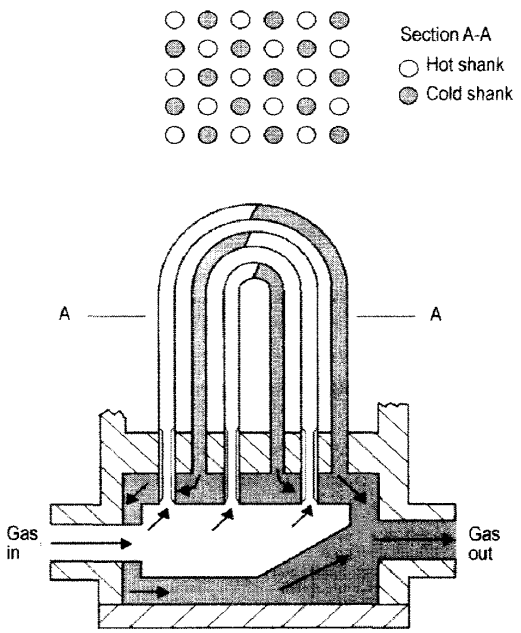


Figure 102: Babcock – Borsig's hot/cold synthesis loop boiler

An interesting approach is *Babcock – Borsig's Hot/Cold Tubesheet* [998]. The hot and cold ends of the tubes are arranged alternately, so that a hot shank is always next to a cold shank and vice versa (Figure 102). The advantage is that the tubesheet and the hot end tube wall temperature inside the tubesheet can be kept below 380 °C, which avoids nitriding and allows ferritic ferrules to be used. The entire tubesheet surface is shielded additionally by the cooled gas exiting from the cold ends of boiler tubes.

Another very successful design is the *horizontal synthesis loop waste*-heat boiler of *Balcke-Dürr AG* [999]. This boiler is a straight-tube design with thick tubesheets on both ends. A particular feature is the welding of the tubes to the 6 mm Inconel cladding of the tubesheet. This weld is mainly for sealing purposes; the mechanical tube-to-tubesheet joint which accomodates the stress is provided by hydraulic expansion of the tubes over the entire thickness of the tubesheet [1000], [1001]. The hydraulic expansion provides redundant gas-tightness.

Waste-heat boilers in partial oxidation plants, which cool the exit gas of the generator from 1400 °C to around 350 °C, face additional difficulties. The gas contains soot and probably some fly ash particles. Very high gas velocities and appropriate design are necessary to prevent any deposition on the heat exchange surfaces and to reduce the danger of attrition as well. A special design (L. u. C. Steinmüller GmbH) for use with Texaco gasifications is shown in Figure 103 [1002]. Good circulation rate on the water side helps to stand the high heat flux (700 $kJ\ m^{-2}\ s^{-1}$) in the entrance nozzles to the

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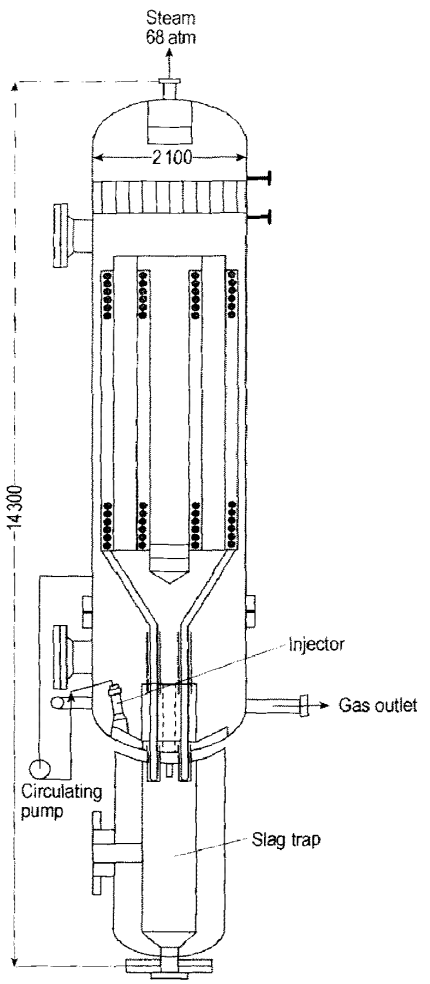


Figure 103. Waste-heat boiler for Texaco gasification

spiral-wound tubes. The Shell process uses also proprietary designs (Fasel-Lentjes) [1003].

Additional information on waste-heat boilers is found in [895], [929], [930], [1004].

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5. Complete Ammonia Production Plants

The previous sections mainly considered the individual process steps involved in the production of ammonia and the progress made in recent years. The way in which these process components are combined with respect to mass and energy flow has a major influence on efficiency and reliability. Apart from the feedstock, many of the differences between various commercial ammonia processes lie in the way in which the process elements are integrated. Formerly the term ammonia technology referred mostly to "ammonia synthesis technology" (catalyst, converters, and synthesis loop), whereas today it is interpreted as the complete series of industrial operations leading from the primary feedstock to the final product ammonia.

The major determinant for process configuration is the type of feedstock, which largely governs the mode of gas generation and purification. The other important factor is the plant capacity, which, together with consumption and costs of feedstock and energy, is decisive for the production economics. An important development was the concept of single-train plants, first introduced for steam reforming based production by M. W. Kellogg in 1963 with a capacity of 600 t/d. Before then maximum capacities had mostly been about 400 t/d, with several parallel trains in the synthesis gas preparation stage and the synthesis loop. Today world-scale plants have capacities of 1200 – 1500 t/d, and some have 1800 t/d. The lowest capital cost and energy consumption result when steam reforming of natural gas is used. In addition site requirements can influence the layout considerably. In contrast to a stand-alone plant, ammonia production at a developed industrial site may import and/or export steam and power, which affects the total energy consumption.

With the exception of the Koppers – Totzek coal gasification process, which operates at near atmospheric pressure, all modern gasification processes operate at elevated pressure. Steam reforming of light hydrocarbons at 30 – 40 bar and partial oxidation of heavy hydrocarbons at 40 – 90 bar are generally used.

5.1. Steam Reforming Ammonia Plants

5.1.1. The Basic Concept of Single-Train Plants

The innovative single-train concept was a technical and an economical breakthrough and triggered a tremendous increase in world ammonia capacity. No parallel lines, even for high capacity, and a highly efficient use of energy, with process steps in surplus supplying those in deficit, were the main features. Figure 104 shows a block flow diagram and the gas temperature profile for a steam reforming ammonia plant.

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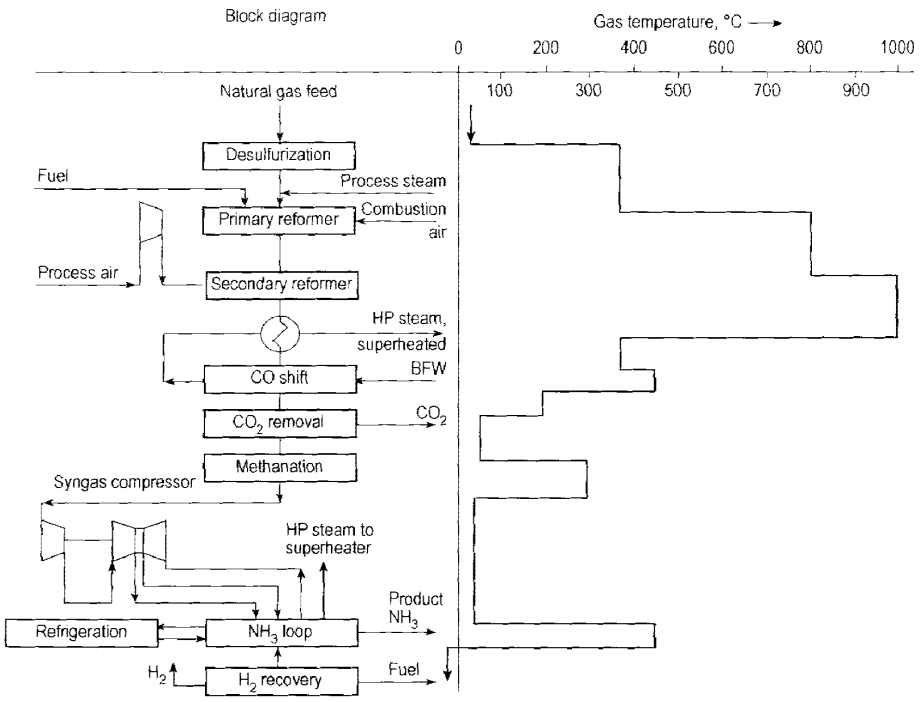


Figure 104. Block diagram and gas temperature profile for a steam reforming ammonia plant

High level surplus energy is available from the flue gas of the reformer and the process gas streams of various sections, while heat is needed, for example, for the process steam for the reforming reaction and in the solvent regenerator of the carbon dioxide removal system. Because considerable mechanical energy is needed to drive compressors, pumps, and blowers, it was most appropriate to use steam turbine drives, since sufficient steam could be generated from the waste heat. As the level was high enough to raise high-pressure steam (100 bar) it was possible to use the process steam first to generate mechanical energy in the synthesis gas compressor turbine before extracting it at the pressure level of the primary reformer. Table 35 lists all significant energy sources and sinks within the process.

The earlier plants operated at deficit, and needed an auxiliary boiler, which was integrated in the flue gas duct. Auxiliary burners in tunnels or flue gas duet were additionally used in some instances. This situation was partially caused by inadequate waste heat recovery and low efficiency in some energy consumers. Typically, the furnace flue gas was discharged in the stack at rather high temperature because there was no air preheating and too much of the reaction heat in the synthesis loop was rejected to the cooling media (water or air). In addition, efficiency of the mechanical drivers was low and the heat demand for regenerating the solvent from the CO_2 removal unit (at

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Table 35. Main energy sources and sinks in the steam reforming ammonia process

Process section	Origin	Contribution
Reforming	primary reforming duty	demand
	flue gas	surplus
	process gas	surplus
Shift conversion	heat of reaction	surplus
CO_2 removal	heat of solvent regeneration	demand
Methanation	heat of reaction	surplus
Synthesis	heat of reaction	surplus
Machinery	drivers	demand
Unavoidable loss	stack and general	demand
Balance	auxiliary boiler or import	deficit
	export	surplus

that time aqueous MEA) was high. Maximum use was made of direct steam turbine drive, not only for the major machines such as synthesis gas, process air, and refrigeration, but even for relatively small pumps and blowers. The outcome was a rather complex steam system. Even after substitution of the smaller turbines by electric motors in more recent installations, the steam system in the modern plant is still a complex system as shown in Figure 106. Ammonia plant steam systems and steam generation are described in [402], [404], [985], [1004] – [1006].

The first generation of the single-train steam reforming plants is discussed in [426], [1007] – [1012], and the required catalysts are reviewed in [633], [1013] – [1014]. A survey of the development of the steam reforming concept through 1972 can be found in [1015]. Other references which cover the development of the steam reforming before the introduction of the single-train concept (1940 to 1960) can be found in [402 p. 276].

The new plant concept had a triumphant success story. By 1969, 30 new Kellogg large single-train plants with capacities of 1000 t/d or more were in operation, and other contractors were offering similar concepts.

The decrease in energy consumption compared to the older technology was dramatic, and with the low gas prices at that time it is understandable that greater emphasis was placed on low investment cost, although there was a considerable potential for further reducing the energy consumption.

With the advent of the single-train steam reforming plants, it became standard for licensors and engineering contractors to express the total net energy consumption per tonne of ammonia in terms of the lower heating value of the feedstock used. The total net energy consumption is the difference between all energy imports (mainly feedstock) and all energy exports (mostly steam and/or electric power) expressed as lower heating values, whereby electric power is converted with an efficiency of 25 – 30 % and steam is accounted for with its caloric value.

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Table 36. Development of the net energy consumption of natural gas based steam reforming ammonia plants (real plant data) in GJ/t NH_3

Year	1966	1973	1977	1980	1991
Plant	A	B	C	D	E
Feed	23.90	23.32	23.48	23.36	22.65
Fuel, reformer	13.00	9.21	7.35	5.56	5.90
Fuel, auxiliary boiler	2.60	5.02	3.06	1.17	
Export					0.55
Total	39.50	37.55	33.89	30.18	28.00

5.1.2. Further Development

The significant changes in energy prices from 1973 onwards were a strong challenge to process licensors, engineering contractors and plant owners to obtain better energy efficiency. The overall energy consumption was reduced from around 45 GJ/t NH_3 for the first large single-train units to less than 29 GJ/t NH_3 (Table 36).

Energy saving modifications are described in [1016] – [1025], [1027], [1029] – [1031]. Some of the most important improvements compared to the first generation of plants are discussed below.

Feedstock Purification. In feedstock purification, mainly desulfurization, adsorption on active carbon was replaced by catalytic hydrogenation over cobalt – molybdenum or nickel – molybdenum catalyst, followed by absorption of the H_2S on ZnO pellets with formation of ZnS. By itself this measure has no direct influence on the energy consumption but is a prerequisite for other energy saving measures, especially in reforming and shift conversion.

Reforming Section. In the reforming section energy savings were achieved by several, often interrelated, measures, of which the most important are the following:

- Reduction of the flue gas stack temperature to reduce heat losses to the atmosphere [623]
- Avoiding excessive heat loss by better insulation of the reformer furnace
- Introduction of combustion air preheating [1028]
- Preheating the reformer fuel
- Increased preheat temperatures for feed, process steam and process air
- Increased operating pressure (made possible by using improved alloys for the reformer tubes and improved catalysts)
- Lowering of the steam to carbon ratio [1032]
- Shifting some reformer duty from primary to secondary reformer with the use of excess air [753], [1033] or oxygen-enriched air [1034] in the secondary reformer, including the possibility of partially bypassing the primary reformer [1035], [1124]

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- Installing a prereformer or rich-gas step is another possibility to reduce primary reformer duty and stack temperature of the flue gas [462]–[470], especially in LPG- and naphtha-based plants

A more recent development that breaks away from the usual plant configuration is to replace the traditional fired primary reformer with an exchanger reformer which uses the heat of the effluent of the secondary reformer [471]–[478], [1036], [1037]. Also other applications have been reported in which flue gas [1038] heat from the fired reformer is used to perform a part of the reforming.

Shift Conversion. Improved LT shift catalysts can operate at lower temperatures to achieve a very low residual CO content and low byproduct formation. A new generation of HT shift catalysts largely avoids hydrocarbon formation by Fischer–Tropsch reaction at low vapor partial pressure, thus allowing lower steam to carbon ratio in the reforming section (see Section 4.2.1.1.1).

Carbon Dioxide Removal Section. In the carbon dioxide removal section the first generation of single-train plants often used MEA with a rather high demand of low-grade heat for solvent regeneration. With additives such as UCAR Amine Guard [651], [655], solvent circulation could be reduced, saving heat and mechanical energy. Much greater reduction of energy consumption was achieved with new solvents and processes, for example BASF aMDEA or Benfield LoHeat. Other hot potash systems (Giammarco Vetrocoke, Catacarb) and physical solvents (Selexol) were introduced (Section 4.3.1).

Final makeup gas purification was improved by removing the water and carbon dioxide traces to a very low level by using molecular sieves. Some concepts included cryogenic processes with the benefit of additional removal of methane and argon.

Ammonia Synthesis Section. In the ammonia synthesis section conversion was increased by improved converter designs (see Section 4.5.3), larger catalyst volumes, and to some extent with improved catalysts. The main advances in converter design were the use of indirect cooling instead of quenching, which allowed the recovery of reaction heat as high pressure steam. Radial or crossflow pattern for the synthesis gas instead of axial flow was introduced. All modern plants include installations for hydrogen recovery (cryogenic, membrane, or PSA technology; see Section 4.5.6).

Machinery. Developments in compressor and turbine manufacturing have led to higher efficiencies.

- Gas turbine drive for a compressor and/or an electric generator combined with the use of the hot exhaust as combustion air for the primary reformer or raising steam (combined cycle) [804], [807]–[810], [1038].
- Employing electric motors instead of condensation turbines [1039].

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