– Application of liquid and gas expansion turbines can recover mechanical work (e.g., let-down of the CO_2-laden solvent, liquid ammonia, purge and fuel gas).

Steam system and waste heat recovery were improved by the following measures: increased pressure and superheating temperature of high-pressure steam; providing a part of the process steam by natural gas feed saturation [651], [1033], [1040]–[1042]; inclusion of a steam superheater downstream of the secondary reformer [985], [1043].

Process Control and Process Optimization. Progress in instrumentation and computer technology has led to increased use of advanced control systems and computerized plant optimization. Advanced control systems [1044]–[1053] allow operating parameters to be kept constant in spite of variations in external factors such as feedstock composition or ambient or cooling water temperatures. These systems may be operated in open loop fashion (set values changed manually by the operator) or in closed fashion (set points automatically adjusted to optimum values by using a computer model with input of operational and economic data). Also plant simulation [1054]–[1058] is possible by using extensive computer models of complete plants. These models can simulate in real time the dynamic response to changes in operating parameters, plant upsets, etc. Such systems are used for off-line optimization studies and for operator training [1058], [1059].

The above list, by no means complete, is also a survey of options for plant revamps (Chapter 6).

Many of these elements are strongly interrelated with each other and may affect different sections of the plant concept. It is thus a demanding engineering task to arrive at an optimum plant concept, which can only defined by the conditions set by the feedstock price, the site influences, and the economic premises of the customer. An evaluation of the individual merits of the described measures in terms of investment and operational cost in a generalized form is not possible and can be done only from case to case in real project studies.

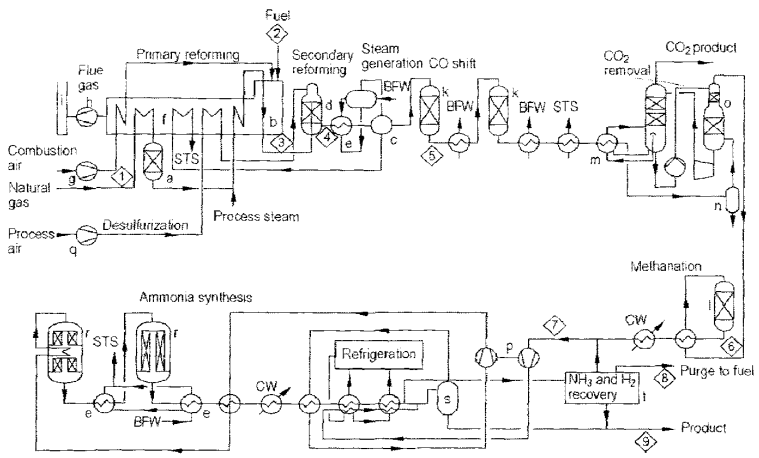
To illustrate the forgoing discussion of the concept of the single-train steam reforming plant, Figure 105 presents a modern low-energy ammonia plant with flow sheet and process streams (UHDE process).

Figure 106 shows a simplified diagram of the steam system. Even in such an advanced plant the quantity of steam generated from waste heat is as much as 3.4 times the weight of ammonia produced.

5.1.3. Minimum Energy Requirement for Steam Reforming Process

The energy saving measures described in Section 5.1.2 have considerably reduced the demand side (e.g., CO_2 removal, higher reforming pressure, lower steam to carbon ratio, etc.). On the supply side, the available energy has been increased by greater heat

Topsoe, Inc. – EX1003
Page 324 of 1210



	1	2	3	4	5	6	7	8	9
CH_4, mol%	91.24	91.24	14.13	0.60	0.53	0.65	1.16	24.34	0.12
C_nH_m, mol%	5.80	5.80							
CO_2, mol%	1.94	1.94	10.11	7.38	18.14	0.01			
CO, mol%			9.91	13.53	0.33	0.40			
Ar, mol%				0.28	0.25	0.30	0.37	7.21	0.01
H_2, mol%			65.52	54.57	59.85	73.08	73.54	21.72	0.03
N_2, mol%	1.02	1.02	0.33	23.64	20.90	25.56	24.93	46.55	0.02
NH_3, mol%								0.18	99.82
Dry gas, kmol/h	1713.7	534.43	5296.4	8414.2	9520.7	7764.0	8041.4	319.9	3676.6
H_2O, kmol/h			3520.6	4086.1	2979.6	22.8	13.3	0.2	0.9
Total, kg/h	30213	9422	121183	199555	199555	70084	71004	6496	62626
p, MPa	5.00	0.25	3.95	3.90	3.61	3.43	3.23	0.25	2.50
T, °C	25	25	808	976	229	50	35	38	20

Figure 105. Modern integrated single-train ammonia plant based on steam reforming of natural gas (Uhde process)
a) Sulfur removal; b) Primary reformer; c) Steam superheater; d) Secondary reformer; e) Waste heat boiler; f) Convection section; g) Forced draft fan; h) Induced draft fan; i) Stack; k) HT and LT shift converters; l) Methanator; m) CO_2 removal solvent boiler; n) Process condensate separator; o) CO_2 absorber; p) Synthesis gas compressor; q) Process air compressor; r) Ammonia converter; s) High-pressure ammonia separator; t) Ammonia and hydrogen recovery from purge and flash gas

recovery. The combined effects on both sides have pushed the energy balance into surplus. Because there is no longer an auxiliary boiler which can be turned down to bring the energy situation into perfect balance, the overall savings usually could not be translated into further actual reduction of the gross energy input to the plant (mainly natural gas). In some cases this situation can be used advantageously. If the possibility exists to export a substantial amount of steam, it can be economically favorable (depending on feedstock price and value assigned to the steam) to deliberately increase the steam export by using additional fuel, because the net energy consumption of the plant is simultaneously reduced (Table 37).

Topsoe, Inc. – EX1003
Page 325 of 1210

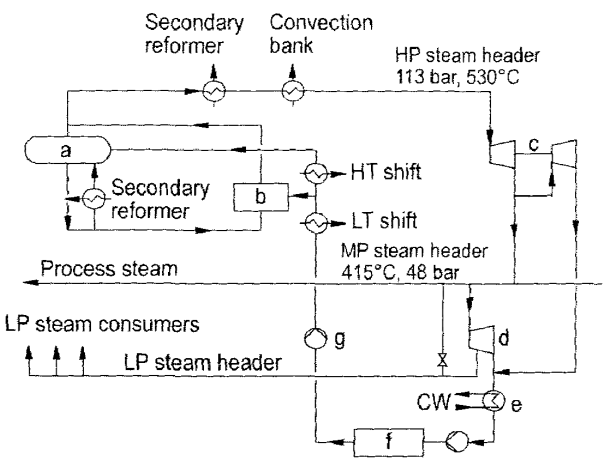


Figure 106. Steam system of a modern steam reforming
a) Steam drum, 125 bar; b) NH_3 loop; c) Turbine for syngas compressor; d) Turbine for process air compressor and alternator; e) Surface condenser; f) Condensate treatment; g) BFW pump

Table 37. Increase of plant efficiency by steam export (GJ/t NH_3)

	Plant		Difference
	A	B	
Natural gas	27.1	32.6	+ 5.5
Electric power	1.1	1.1	
Steam export		− 6.4	− 6.4
Total energy	28.2	27.3	− 0.9

A reduction in gross energy demand, that is, a lower natural gas input to the plant, can only be achieved by reducing fuel consumption, because the actual feedstock requirement is determined by the stoichiometry. So the only way is to decrease the firing in the primary reformer, which means the extent of reaction there is reduced. This can be done by shifting some of the reforming duty to the secondary reformer with surplus air or oxygen-enriched air, although this makes an additional step for the removal of surplus nitrogen necessary. A more radical step in this direction is total elimination of the fired primary reformer by using exchanger reformers like the ICI GHR and the Kellogg KRES.

Based on pure methane, it is possible to formulate a stoichiometric equation (95) for ammonia production by steam reforming:

$$CH_4 + \underbrace{0.3035\ O_2 + 1.131\ N_2}_{1.4345\ \text{air}} + 1.393\ H_2O \longrightarrow CO_2 + 2.262\ NH_3 \qquad (95)$$

$\Delta H = -86$ kJ/mol and $\Delta F = -101$ kJ/mol at 25 °C

From a mere thermodynamic point of view, in an ideal engine or fuel cell, heat and power should be obtainable from this reaction. Since real processes show a high degree of irreversibility, a considerable amount of energy is necessary to produce ammonia from methane, air and water. The stoichometric quantity of methane derived from the

Topsoe, Inc. – EX1003
Page 326 of 1210

Table 38. Specific energy requirement for ammonia production compared to the theoretical minimum

	GJ/t NH_3 (LHV)	% theory
Classical Haber–Bosch (coke)	80–90	(338–431)
Reforming, 0.5–10 bar (1953–55)	47–53	225–254
Reforming, 30–35 bar (1965–75)	33–45	139–215
Low energy concepts (1975–84)	29–33	139–158
Modern concepts (since 1991)	$\leq$ 28	134
Stoichiometric CH_4 demand	20.9	= 100

above reaction is 583 m^3 per tonne of ammonia, corresponding to 20.9 GJ/t NH_3 (LHV), which with some justification could be taken as minimum value. If full recovery of the reaction heat is assumed, then the minimum would be the lower heating value of ammonia, which is 18.6 GJ/t NH_3. Table 38 compares the specific energy requirement for ammonia production by steam reforming with the theoretical minimum.

Comparison of energy consumption figures without precise knowledge of design and evaluation criteria can be misleading. First of all the state of the ammonia product should be noted. Relative to the delivery of liquid ammonia to battery limits at ambient temperature, the production of 3 bar ammonia vapor at the same temperature would save 0.6 GJ/t NH_3, while delivery as liquid at – 33 °C would need an extra 0.3 GJ/t NH_3. The temperature of the available cooling medium has a considerable influence. Increasing the cooling water temperature from 20 to 30 °C increases energy consumption by 0.7 GJ/t NH_3. A detailed energy balance, listing all imports and exports, together with the caloric conversion factors used for steam and power is needed for a fair comparison of plants. The beneficial effect of energy export to the net energy consumption is discussed above. Gas composition is also of some importance. Nitrogen content is marginally beneficial: 10 mol% nitrogen leads to a saving of about 0.1 GJ/t NH_3, whereas a content of 10 mol% carbon dioxide would add 0.2 GJ/t NH_3 to the total consumption value [1060].

Energy requirements and energy saving possibilities are also discussed in [1016], [1018], [1025]–[1031].

The energy consumption figures discussed so far represent a thermodynamic analysis based on the first law of thermodynamics. The combination of the first and second laws of thermodynamics leads to the concept of ideal work, also called exergy. This concept can also be used to evaluate the efficiency of ammonia plants. Excellent studies using this approach are presented in [1061], [1062]. Table 39 [1061] compares the two methods. The analysis in Table 39 was based on pure methane, cooling water at 30 °C (both with required pressure at battery limits), steam/carbon ratio 2.5, synthesis at 140 bar in an indirectly cooled radial converter.

Almost 70% of the exergy loss in the process occurs in the reforming section and in steam generation. From conventional first law analysis it can be seen that almost all of the losses are transferred to the cooling water. As the analysis assumes water in liquid

Topsoe, Inc. – EX1003
Page 327 of 1210

Table 39. Energy analysis of a low energy ammonia plant (GJ/t NH_3)

	HHV	LHV	Exergy
Input			
Natural gas consumption			
Reformer feed	24.66	22.27	23.28
Reformer fuel	7.49	6.78	7.08
Auxiliary boiler fuel	0.34	0.29	0.33
Total consumption	32.49	29.34	30.69
Losses			
Reforming	0.38	0.38	1.94
Steam generation	0.33	0.33	2.39
Shift, CO_2 removal, methanation	1.30	1.30	0.67
Synthesis	1.70	1.70	1.55
Turbines and compressors	6.50	6.50	0.54
Others (including stack	1.30	0.68	0.46
Total losses	11.51	10.89	10.55
NH_3 product	20.98	17.12	20.14
Efficiency, %	64,60	58,40	65,60

state, the LHV analyses in Table 39 is not completely balanced. For a perfect balance the heat of evaporation of water (as a fictive heating value) would have to be included.

5.1.4. Commercial Steam Reforming Ammonia Plants

Especially with ammonia processes based on steam reforming technology it has become a habit to differentiate between processes from various licensors and engineering contractors. This is not so much the case for partial oxidation plants (see Section 5.2). Strong competition together with increased plant sizes and the associated financial commitment has reduced the number of licensors and engineering contractors to a few companies capable of offering world-scale plants, often on a lump-sum turnkey basis. In some cases these companies sub-license their processes and special engineering know-how to competent engineering companies possessing no knowledge of their own in the ammonia field. There are also several smaller companies with specific and sometimes proprietary know-how which specialize in revamps of existing plants or small plant concepts.

In the following, each of the commercially most important processes is discussed in some detail and a shorter description of economically less important processes is given. The process configuration offered and finally constructed by a given contractor may vary considerably from case to case, depending on economic and site conditions and the clients' wishes. Thus plants from the same contractor and vintage often differ considerably. It is possible to categorize steam reforming plants according to their configuration in the reforming section:

Topsoe, Inc. – EX1003
Page 328 of 1210

1) Advanced conventional processes with high duty primary reforming and stoichiometric process air in the secondary reformer
2) Processes with reduced primary reformer firing and surplus process air
3) Processes without a fired primary reformer (exchanger reformer)
4) Processes without a secondary reformer using nitrogen from an air separation plant

In principle the amount of flue gas emitted should be related to the extent of fired primary reforming, but generalizations are questionable, because sometimes the plant layout, as dictated by site requirements, may considerably change the picture for the specific flue gas value.

5.1.4.1. Advanced Conventional Processes

Kellogg Low-Energy Ammonia Process [1031], [1063]–[1070]. The Kellogg process is along traditional lines, operating with steam/carbon ratio of about 3.3 and stoichiometric amount of process air and low methane slip from the secondary reformer. The synthesis pressure depends on plant size and is between 140 and 180 bar. Temperatures of the mixed feed entering the primary reformer and of the process air entering the secondary reformer are raised to the maximum extent possible with today's metallurgy. This allows reformer firing to be reduced and, conversely, the reforming pressure to be increased to some extent to save compression costs. An important contribution comes from Kellogg's proprietary cross-flow horizontal converter, which operates with catalyst of small particle size, low inlet ammonia concentration, and high conversion. Low-energy carbon removal systems (Benfield LoHeat, aMDEA, Selexol) contribute to the energy optimization.

When possibilities to export steam or power are limited, part of the secondary reformer waste heat is used, in addition to steam generation, for steam superheating, a feature in common with other modern concepts. Proprietary items in addition to the horizontal converter are the traditional Kellogg reformer, transfer line and secondary reformer arrangement, waste-heat boiler, and unitized chiller in the refrigeration section.

According to Kellogg 27.9 GJ/t NH_3 can be achieved in a natural gas based plant with minimum energy export, but with export of larger quantities of steam this value could probably be brought down to about 27 GJ/t NH_3. Figure 107 shows a simplified flowsheet of the process [1069] with Selexol CO_2 removal unit.

Haldor Topsøe Process. In addition to technology supply, Haldor Topsøe also produces the full catalyst range needed in ammonia plants. The energy consumption of a basically classic plant configuration has been reduced considerably by applying systematic analysis and process engineering. Descriptions and operational experience are given in [464], [623], [1028], [1071]–[1082].

Topsøe offers two process versions. The first operates at steam/carbon ratio of 3.3 and with rather high residual methane content from the secondary reformer. Shift

Topsoe, Inc. – EX1003
Page 329 of 1210

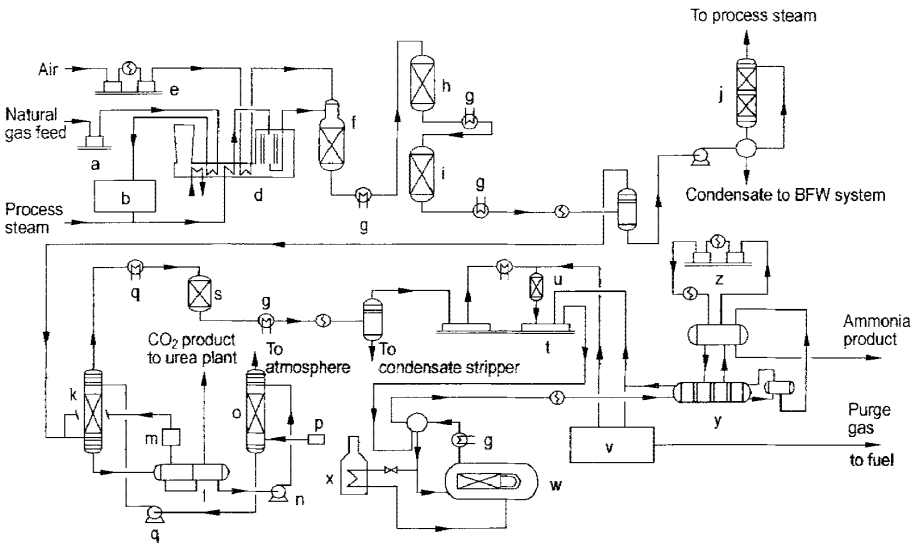


Figure 107. M. W. Kellogg's low energy process
a) Feed gas compressor; b) Desulfurization; d) Primary reformer; e) Air compressor; f) Secondary reformer; g) Heat recovery; h) High temperature shift converter; i) Low temperature shift converter; j) Condensate stripper; k) CO_2 absorber; l) CO_2 flash drum; m) Recycle compressor; n) Semi-lean Pump; o) Stripper (other options are, e.g., Benfield or BASF aMDEA); p) Stripper air blower; q) CO_2 lean pump; r) Methanator feed preheater; s) Methanator; t) Synthesis gas compressor; u) Dryer; v) Purge gas H_2 recovery; w) Ammonia converter; x) Start-up heater; y) Refrigeration exchanger; z) Refrigeration compressor

conversion is conventional, the Benfield or Vetrokoke process is used for carbon dioxide removal, and the synthesis pressure depends on plant size ranging between 140 and 220 bar when the proprietary Topsøe two-bed radial converter S 200 is used. A simplified flowsheet is presented in Figure 108.

An actual plant has reported a consumption of 29.2 GI/tNH [1080].

The second version has a S/C ratio of 2.5 and shift conversion with medium- and low-temperature catalysts, both copper-based. For CO_2 removal Selexol or aMDEA is chosen. The synthesis is performed at 140 bar with a Topsøe two-bed S 200 radial converter, followed by a single-bed radial S 50 converter (S 250 configuration). After the converters, high-pressure steam is generated. An additional proprietary item is the side-fired reformer.

For this most energy-efficient concept, so far not been demonstrated in an industrial installation, a figure of 27.9 GI/tNH_3 is claimed for a stand-alone plant [1079].

Krupp–Uhde Process. Uhde (now Krupp–Uhde), in the ammonia business since 1928, markets a low-energy ammonia plant with classic process sequence and catalysts [1083]–[1090]. High plant reliability at competitive overall costs was a major objective.

Topsoe, Inc. – EX1003
Page 330 of 1210

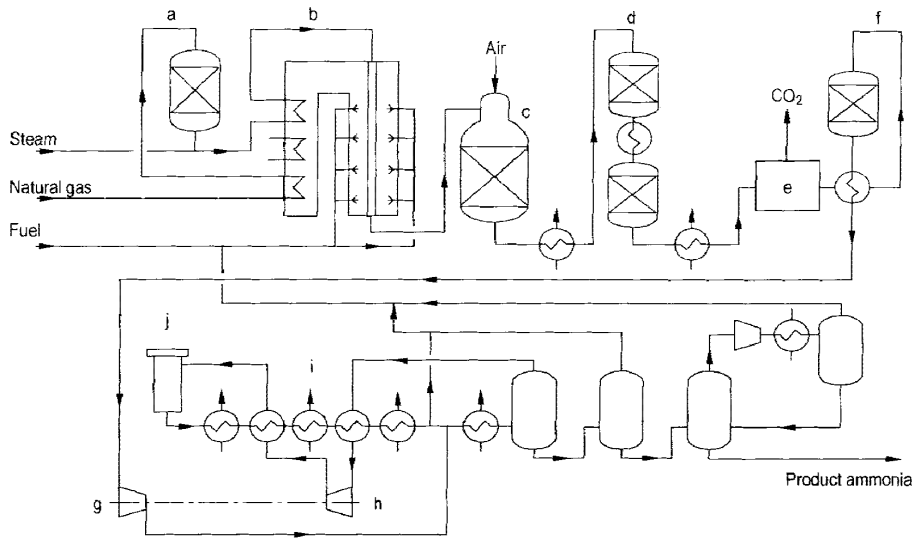


Figure 108. Haldor Topsøe's low energy process
a) Desulfurization; b) Primary reformer; c) Secondary reformer; d) Shift conversion; e) CO_2 removal; f) Methanation; g) Main compressor; h) Recycle compressor; i) Heat recovery; j) Converter

A process flow diagram together with the main process streams is presented in Figure 105.

Key features are the high reforming pressure (up to 41 bar) to save compression energy, use of Uhde's proprietary reformer design [1084] with rigid connection of the reformer tubes to the outlet header, also well proven in many installations for hydrogen and methanol service. Steam to carbon ratio is around 3 and methane slip from the secondary reformer is about 0.6 mol % (dry basis). The temperature of the mixed feed was raised to 580 °C and that of the process air to 600 °C. Shift conversion and methanation have a standard configuration, and for CO_2 removal BASF's aMDEA process is preferred, with the possibility of other process options, too. Synthesis is performed at about 180 bar in Uhde's proprietary converter concept with two catalyst beds in the first pressure vessel and the third catalyst bed in the second vessel.

After each converter vessel high pressure steam (125 – 130 bar, up to 1.5 t/t NH_3) is generated (Uhde also offers its own boiler design in cooperation with an experienced boiler maker). Heat exchange between inlet and outlet of the first bed is performed in the first vessel, and gas flow in all beds is radial. When only a minimum of energy export (steam or power) is possible, the process heat from the secondary reformer outlet is partly used to raise high-pressure steam, and partly for superheating high-pressure steam. Refrigeration uses screw compressors with high operational flexibility and efficiency.

Topsoe, Inc. – EX1003
Page 331 of 1210

Achieved net energy consumption is about 28 GJ/t NH_3 and UHDE's engineers expect values of below 27 GJ/t NH_3 when a gas turbine and large steam export is included [1088].

LEAD Process (Humphreys & Glasgow, now Jacobs) [940], [1091]. The LEAD process is a highly optimized conventional approach with synthesis at 125 bar and two converter vessels, the first of which contains two catalyst beds with axial-flow quenching, while the second has a third bed with small particle size catalyst and radial flow. A consumption of 29.3 GJ/t NH_3 is claimed.

Exxon Chemical Process. The Exxon Chemical process [1092], [1093] was specifically designed for the company's own site in Canada and so far not built for third parties. It uses a proprietary bottom-fired primary reformer furnace and a proprietary hot potash carbon dioxide removal system with a sterically hindered amine activator. Synthesis loop and converter are licensed by Haldor Topsøe A/S. Synthesis is carried out at 140 bar in a Topsøe S-200 converter and total energy consumption is reported to be 29 GJ/t NH_3.

Fluor Process. The Fluor process [280], [934], [940], [1094] uses the proprietary propylene carbonate based CO_2 removal system with adsorption refrigeration using low level heat downstream of the low-temperature shift. Methanation and CO_2 removal are placed between the compression stages and thus operate at higher pressure. With a value of 32 GJ/t NH_3 [934] this is not really a low-energy concept.

Lummus Process. For the Lummus process schemes [280], [940], [1095] – [1097] a consumption of 29.6 [941] to 33.5 GJ/t NH_3 [1099] is quoted. In the synthesis section either an axial flow quench converter or a radial flow converter with indirect cooling is used. CO_2 removal is performed with a physical solvent, and there are no special features compared to other conventional process configurations.

Integrating the ammonia and urea process into a single train was proposed by **Snamprogetti** to reduce investment and operating costs [1099] (see also Chapter 7).

5.1.4.2. Processes with Reduced Primary Reformer Firing

Braun Purifier Process [753], [940], [1100] – [1110]. Characteristic of the low-energy Braun purifier process (originally C. F. Braun, later Brown & Root, now M. W. Kellogg) is the reduced primary reformer duty, which is achieved by shifting a proportion of the reforming reaction to the secondary reformer by using about 150 % of the stoichiometric air flow. The excess nitrogen introduced in this way is removed after the methanation step in a cryogenic unit known as a purifier [1105], which also removes the methane and part of the argon. The result is a purer synthesis gas

Topsoe, Inc. – EX1003
Page 332 of 1210

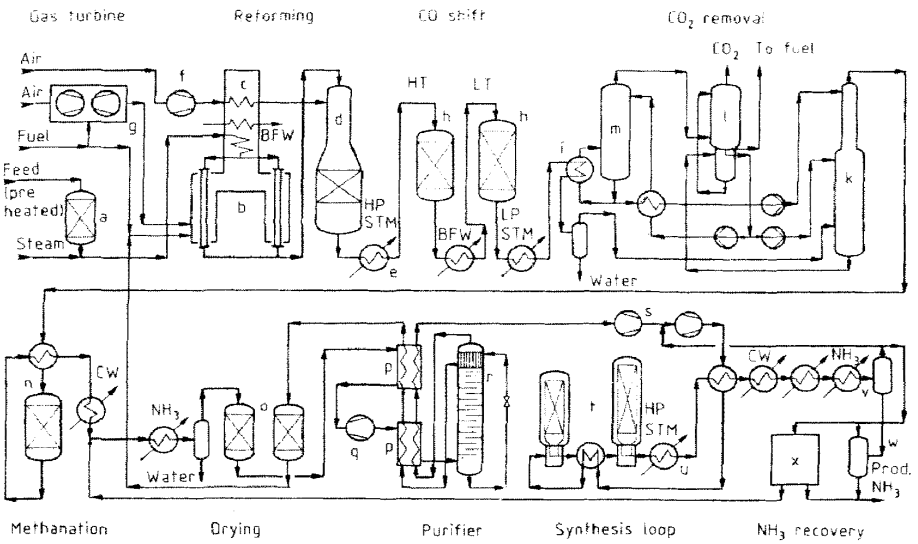


Figure 109. The Braun purifier ammonia process
a) Sulfur removal; b) Primary reformer; c) Convection section; d) Secondary reformer; e) Waste heat boiler; f) Process air compressor; g) Gas turbine; h) High- and low-temperature shift converters; i) CO_2 removal solvent reboiler; k) CO_2 absorber; l) CO_2 desorber; m) CO_2 stripper; n) Methanator; o) Driers; p) Purifier heat exchanger; q) Expansion turbine; r) Purifier column; s) Synthesis gas compressor; t) Synthesis converters; u) Waste heat boiler; v) High-pressure ammonia separator; w) Ammonia letdown vessel; x) Ammonia recovery from purge gas

compared to conventional processes, and only minimal purge from the loop is required. A typical flow diagram of this process is shown in Figure 109.

Synthesis is carried out in the proprietary Braun adiabatic hot-wall converter vessels (Figure 94). Each catalyst bed (of which three are now used in newer plants [1104]) is accommodated in a separate vessel with an inlet–outlet heat exchanger after the first and high-pressure steam boilers after the following. The smaller furnace produces less flue gas and consequently less waste heat, which makes it easier to design a balanced plant with no energy export. The lower reforming temperature allows a reduction of the steam/carbon ratio to about 2.75 without adverse effects on the HT shift, because of the less reductive character of the raw gas on account of its higher CO_2 content. In energy balanced plants, the use of waste heat in the secondary reformer effluent is split between steam raising and steam superheating.

The concept shows great flexibility [1106] for design options. It is possible, for example, to aim for minimal natural gas consumption, even at the cost of importing some electric power. On the other hand, it is possible to improve the overall efficiency further by exporting a greater amount of energy. In this latter case it is advantageous to incorporate a gas turbine to drive the process air compressor. The hot exhaust (about 500 °C) of the turbine contains 16–17 mol % of oxygen and can serve as preheated combustion air of the primary reformer. In addition it is possible to include an electric generator to cover the plant demand and export the surplus. The Braun & Root process

Topsoe, Inc. – EX1003
Page 333 of 1210

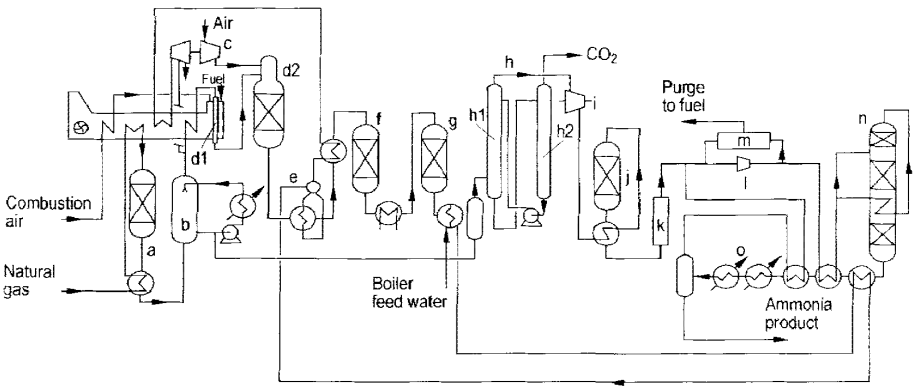


Figure 110. ICI AMV process
a) Desulfurization; b) Natural gas saturation; c) Process air compression; d1) Primary reformer; d2) Secondary Reformer; e) Boiler; f) High temperature shift; g) Low temperature shift; h) Selexol CO_2 removal; h1) CO_2 absorber; h2) Regenerator; i) Single stage compression; j) Methanation; k) Cooling and drying; l) Circulator; m) Hydrogen recovery; n) Ammonia converter; o) Refrigeration system

can attain 28 GJ/t NH_3 in a balanced plant, but with steam export and realization of the available improvement possibilities a value of 27 GJ/t NH_3 seems feasible.

ICI AMV Process. The ICI AMV process [1034], [1083], [1111]–[1122], also operates with reduced primary reforming (steam/carbon ratio 2.8) and a surplus of process air in the secondary reformer, which has a methane leakage of around 1 %. The nitrogen surplus is allowed to enter the synthesis loop, which operates at the very low pressure of 90 bar with an unusually large catalyst volume, the catalyst being a cobalt-enhanced version of the classical iron catalyst. The prototype was commissioned 1985 at Nitrogen Products (formerly CIL) in Canada, followed by additional plants in China. A flow sheet is shown in Figure 110.

In the Canadian plant, only the air compressor is driven by a steam turbine, which receives the total steam generated in the plant and has an electric generator on the same shaft. All other consumers, including synthesis gas compressor, are driven by electric motors. Separate machines are used for makeup gas and recycle compression. The makeup gas compressor is located upstream of the methanator to make use of the compression heat to warm up the cold gas coming from the Selexol carbon dioxide scrubber.

A further key feature is that about half of the process steam is supplied by feed gas saturation. The synthesis converter is a three-bed design with quench between the first two beds and an exchanger after the second bed to raise the gas temperature of the feed to the first bed. Excess nitrogen and inerts (methane and argon) are removed by taking a purge gas stream from the circulator delivery and treating it in a cryogenic unit operating at loop pressure. The recovered hydrogen is returned to the circulator suction. Demonstrated efficiency is 28.5 GJ/t NH_3.

Topsoe, Inc. – EX1003
Page 334 of 1210

Foster Wheeler AM2 Process. The Foster Wheeler AM2 process [1035], [1123], also belongs to the group of processes that shift load from the primary to the secondary reformer, but differs from the preceding concepts in that only 20 – 50 % of the total feedstock is treated in the tubular primary reformer. The remaining feed is directly sent to the secondary (autothermal) reformer which operates with a high surplus of process air (up to 200 %) and a rather high methane slip of 2.75 % (dry basis). After conventional shift, further purification is performed by Selexol CO_2 removal, methanation, and molecular sieve drying. A cryogenic unit operating at synthesis pressure rejects the nitrogen surplus from the loop. An energy consumption of 29.3 GJ/t NH_3 is claimed.

Humphreys & Glasgow BYAS Process. The Humphreys & Glasgow (now Jacobs) BYAS process [1113], [1124], [1125] resembles the above-described processes in its principal process features: a considerable proportion of the feed is sent directly to the secondary reformer, bypassing the fired primary reformer; use of excess air in the secondary reformer; installation of a cryogenic unit as last step of make-up gas production to remove excess nitrogen, residual methane, and the majority of the argon. As a consequence the inert level in the loop can be kept rather low, with only a small withdrawal of purge gas. An energy consumption as low as 28.7 GJ/t NH_3 is claimed [1126]. The process is especially suited for revamps, where it allows plant capacity to be increased.

Jacobs Plus Ammonia Technology [1127] is especially tailored for small capacities in the 300 to 450 t/d range, with a load shift from primary to secondary reformer and use of excess process air. To produce a stoichiometric synthesis gas the surplus nitrogen has to be rejected in the final purification. This is done in a PSA unit, which receives the purge gas and part of the synthesis gas taken ahead of the methanation step. All nitrogen, methane, residual carbon oxides, and argon are adsorbed to give a stream of pure hydrogen. Hydrogen and the remainder of the synthesis gas downstream of methanation are mixed to achieve a 3:1 H_2:N_2 gas composition, with a lower inerts content than the synthesis gas after methanation. The consumption figure reported for a totally energy-balanced plant is 28.8 GJ/t NH_3, and with substantial steam export a value of 26.8 GJ/t NH_3 is claimed.

Montedison Low-Pressure Process. The Montedison low-pressure process [940], [1036], [1128], [1129] involves a split flow to two primary reformers. About 65 % of the feed – steam mixture flows conventionally through the radiant tubes of a fired primary reformer followed by a secondary reformer. The balance of the feed – steam mixture passes through the tubes of a vertical exchanger reformer. This exchanger reformer has a tube sheet for the catalyst tubes at the mixed feed inlet. There is no tube sheet at the bottom of the tubes, where the reformed gas mixes directly with the secondary reformer effluent. The combined streams flow on the shell side to heat the reformer tubes in a manner similar to that described for the M. W. Kellogg KRES reformer, see Sections 4.1.1.8 and 5.1.4.3). The process air flow is stoichiometric. Synthesis is performed at 60 bar in a proprietary three-bed indirectly cooled converter with am-

Topsoe, Inc. – EX1003
Page 335 of 1210

monia separation by water, from which ammonia is then recovered by distillation using low-grade heat. Other process steps are conventional. As driver of the process air compressor the installation of a gas turbine is suggested with use of the hot exhaust as preheated combustion air for the fired primary reformer. For this process, which has been tested in a 50 bar pilot plant, an energy consumption of 28.1 GJ/t NH_3 is claimed [1036].

Kellogg's LEAP Process. In the late 1970s Kellogg [280], [938], [940], [1130] proposed a process which extends the basic idea of the concept described above even further. The flow of the preheated gas stream mixture is split into three streams, with 47% through catalyst tubes in the radiant section of the fired primary reformer, 12% through catalyst tubes in the convection section, and 41% through the tubes of an exchanger reformer heated by the effluent of a secondary reformer. It was intended to operate the ammonia synthesis at the pressure of the front end by using no synthesis gas compression or only a small booster. An enormous quantity of the classical ammonia synthesis catalyst would have been necessary, and for recovery of the ammonia from the loop a water wash with subsequent distillation was suggested, using low-level heat in an integrated absorption refrigerator. A consumption below 28 GJ/t NH_3 was calculated.

In the **GIAP concept** [1133] 46% of the feed is reformed in a traditional fired reformer and 54% in an exchanger reformer, heated by the effluent of the secondary reformer. The parallel operation avoids the need for air separation to provide oxygen-enriched air for the secondary reformer. In case of availability of oxygen at the site, the fired reformer may be eliminated and the whole reforming job is performed in the exchanger reformer/secondary reformer combination. A conventional HT and LT shift conversion is used, followed by an MDEA CO_2-removal unit. For final purification PSA is applied; there is no methanation step. The synthesis is performed at a pressure level of 72–80 bar using conventional ammonia catalyst in three identical blocks consisting of a reactor, a boiler, and an economizer. Ammonia is condensed at –10 and –27 °C. An overall consumption of 27.7 GJ/t NH_3 is claimed.

5.1.4.3. Processes without a Fired Reformer (Exchanger Reformer)

ICI LCA Process. The ICI LCA process [1131]–[1136] was a radical breakaway from the design philosophy of the highly integrated large plant used successfully for the previous 25 years. Figure 111 shows a diagram of the so-called core unit which includes only the sections essential for ammonia production (up to 450 t/d). A separate utility section, shown in Figure 112, supplies refrigeration, steam, electricity, includes cooling and water-demineralization system, and, if needed, recovers pure carbon dioxide. Both figures show the configuration of the first two plants built at Severnside (UK) with a capacity of 450 t/d each.

Topsoe, Inc. – EX1003
Page 336 of 1210

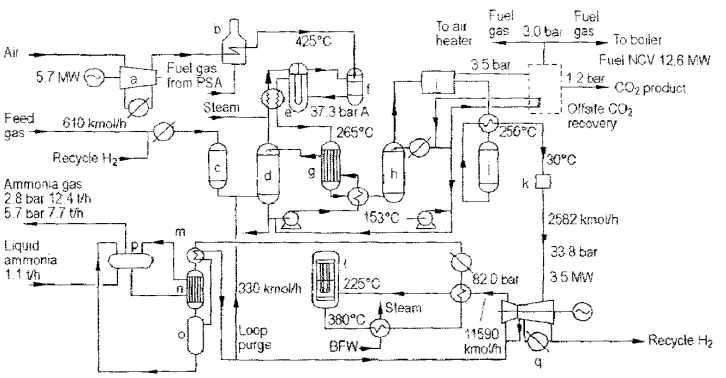


Figure 111. ICI LCA process (core unit)
a) Process air compressor; b) Start-up air heater; c) Hydrodesulfurization; d) Saturator; e) GHR; f) Secondary reformer; g) Shift converter; h) Desaturator; i) PSA system; j) Methanator; k) Gas dryer; l) Ammonia converter; m) Two-stage flash cooling (one stage shown); n) Chiller; o) Catchpot; p) Flash vessel q) Synthesis gas compressor.

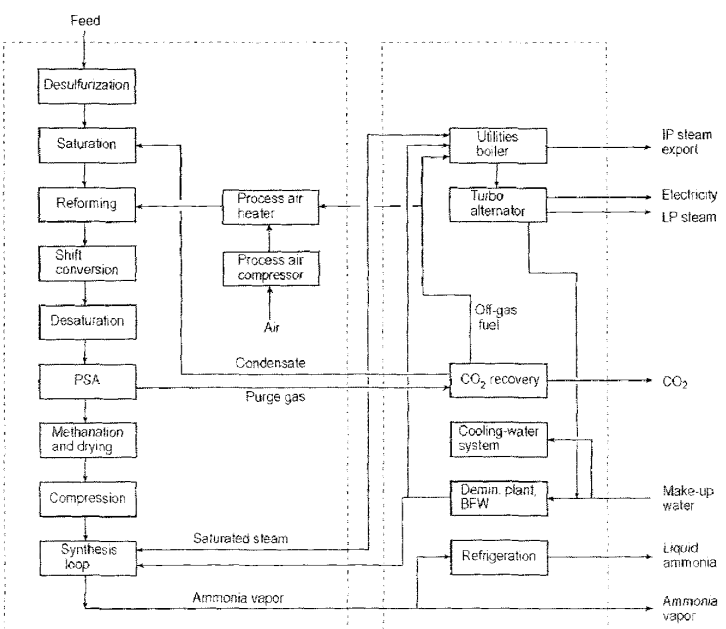


Figure 112. Arrangement of core units and utility section

Feed gas is purified in a hydrodesulfurization unit operating at lower than usual temperatures and passes through a saturator to supply a part of the process steam, while the balance is injected as steam. Heated in an inlet–outlet exchanger to 425 °C

Topsoe, Inc. – EX1003
Page 337 of 1210

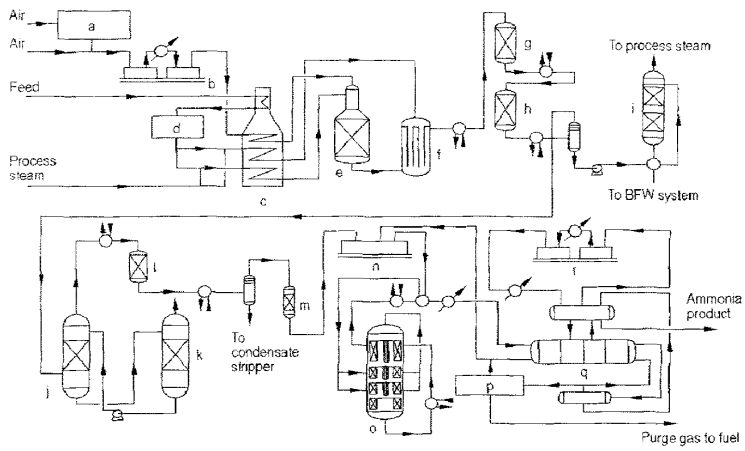


Figure 113. Kellogg's Ammonia 2000 process (integrated KRES/KAAP process)
a) Air separation unit; b) Air compressor; c) Process heater; d) Sulfur removal; e) Autothermal reformer; f) Reforming exchanger; g) HTS; h) LTS; i) Condensate stripper; j) CO_2 absorber; k) CO_2 stripper; l) Methanator; m) Dryer; n) Synthesis gas compressor; o) KAAP ammonia converter; p) Purge gas recovery unit; q) Refrigeration exchanger; r) Refrigeration compressor

the mixed feed enters the ICI gas heated reformer (GHR) [471]–[473] at 41 bar, passing to the secondary reformer at 715 °C. The shell side entrance temperature of the GHR (secondary reformer exit) is 970 °C, falling to 540 °C at the exit of the GHR. Methane levels at the GHR exit and the secondary reformer are 25% and 0.67% respectively (dry basis). Overall steam to carbon ratio is 2.5–2.7. The gas, cooled to 265 °C in the inlet/outlet exchanger, enters a single-stage shift conversion reactor with a special copper–zinc–alumina-based catalyst that operates in quasi-isothermal fashion and is equipped with cooling tubes in which hot water circulates, whereby the absorbed heat is used for feed gas saturation, as described above. CO_2 removal and further purification is effected by a PSA system, followed by methanation and drying.

Synthesis operates at 82 bar in a proprietary tubular converter loaded with a cobalt-enhanced formulation of the classical iron catalyst. Purge gas is recycled to the PSA unit, and pure CO_2 is recovered from the PSA waste gas by an aMDEA wash. Very little steam (60 bar) is generated in the synthesis loop and from waste gases and some natural gas in the utility boiler in the utility section, and all drivers are electric.

The original intention was to design an ammonia plant which can compete with modern large capacity plants in consumption and specific investment, and, by means of lower energy integration, to achieve greater flexibility for start-up and reduced-load operation, needing minimum staffing. The basic plant features (GHR, isothermal shift, and synthesis) can in principle be applied to larger capacities. The flow sheet energy consumption is 29.3 GJ/t NH_3.

Topsoe, Inc. – EX1003
Page 338 of 1210

Kellogg Ammonia 2000 Process [398], [476]–[478]. Kellogg has combined its KAAP synthesis loop (see Sections 4.5.2 and 4.5.3) with its KRES exchanger reformer/autothermal reformer combination (see Section 4.1.1.8) in Ammonia 2000, an optimized integrated concept for green-field plants, intended for use in world-scale single-train plants in the 1800 t/d range. Figure 113 presents a simplified flow diagram.

Desulfurized gas is mixed with steam and then split into two streams in approximate ratio 2:1. These are separately heated in a fired heater. The smaller of the two enters the exchanger reformer at 550–550 °C, while the remainder is passed directly to the autothermal reformer at 600–640 °C. The exchanger reformer and the autothermal reformer use conventional nickel-based primary and secondary reforming catalysts, respectively. To satisfy both the stoichiometry and the heat balance, the autothermal reformer is fed with enriched air (30 % O_2). The required heat for the endothermic reaction in the tubes of the exchanger reformer comes from the gases on the shell side, comprising a mixture of the effluent from the autothermal reformer and the gas emerging from the tubes. The shell side gas leaves the vessel at 40 bar.

Synthesis proceeds at about 90 bar in a four-bed radial-flow converter (hot-wall design) with interbed exchangers. The first bed is charged with conventional iron-based catalyst for bulk conversion and the others with Kellogg's high activity ruthenium-based catalyst, allowing an exit ammonia concentration in excess of 20 % to be obtained. The other process steps are more along traditional lines. The overall energy consumption claimed for this process can be as low as 27.2 GJ/t NH_3.

The LCA and Ammonia 2000 processes are environmentally favorable because atmospheric emissions of both nitrogen oxides and carbon dioxide are dramatically reduced as there is no reforming furnace.

Chiyoda Process [1137]. In this process the traditional fired primary reformer is also replaced by an exchanger reformer and the heat balance requires excess air in the secondary reformer with the consequence of a cryogenic unit as final step in the make-up gas preparation to remove the surplus of nitrogen. Additionally, gas turbines are proposed as drivers for the process air compressor and synthesis gas compressor with the hot exhaust being used for steam generation and feed gas preheating.

5.1.4.4. Processes without a Secondary Reformer (Nitrogen from Air Separation)

KTI PARC Process. The KTI PARC ammonia process [651], [1138]–[1144] uses the following process elements: air separation unit, classical primary reformer at 29 bar, standard HT shift, power generation in a Rankine cycle with CFC to generate electric power (optional), carbon dioxide removal (optional, only when pure CO_2 product is required), PSA, nitrogen addition, synthesis loop. In this concept four sections of the classical process sequence (secondary reforming, LT shift, CO_2 removal, methanation) can be replaced by the fully automatic high-efficiency PSA system, which has a proprietary configuration (UOP) in which nitrogen flushing enhances hydrogen recovery. The overall efficiency ranges from 29.3 to 31.8 GJ/t NH_3.

Topsoe, Inc. – EX1003
Page 339 of 1210

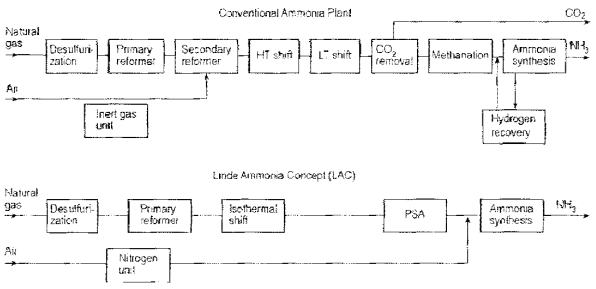


Figure 114. Comparison of Linde LAC process with a conventional process

Linde LAC Process. The recently announced Linde LAC process [1145]–[1149] consists essentially of a hydrogen plant with only a PSA unit to purify the synthesis gas, a standard cryogenic nitrogen unit, and an ammonia synthesis loop. In principle it is similar to the PARC process, but designed for world-scale capacities. A 1350 t/d plant is presently under construction. Figure 114 compares the LAC process to a conventional one. If pure CO_2 is needed, it can be recovered by scrubbing the off-gas from the PSA unit at low pressure or, probably with better energy efficiency, by installing the CO_2 removal unit directly in the synthesis gas train ahead of the PSA system. The synthesis converter and loop are based on ICI and Casale know-how. According to Linde the process should consume about 28.5 GJ/t NH_3 or, with inclusion of pure CO_2 recovery, 29.3 GJ/t NH_3.

Humphreys & Glasgow MDF Process (now Jacobs) [280], [1097], [1098], [1151]–[1153]. This concept has a configuration similar to the Linde LAC process. Energy consumption with inclusion of pure CO_2 recovery (which is optional) is 32.8 GJ/t NH_3.

5.2. Ammonia Plants based on Partial Oxidation

5.2.1. Ammonia Plants based on Heavy Hydrocarbons

Although partial oxidation processes can gasify any hydrocarbon feedstock, on account of its higher energy consumption and investment costs, commercial use of this technology is restricted to the processing of higher hydrocarbons, which can contain as much as 7% sulfur. Where natural gas is unavailable or the heavy feedstock can be obtained at a competitive price, this gasification technology can be an economic choice.

Topsoe, Inc. – EX1003
Page 340 of 1210

There are two commercially proven partial oxidation routes for heavy feedstocks: the Shell process and the Texaco process. Recently Lurgi has come out with an own partial oxidation variant, named LurgiSVZ MPG Process (Section 4.1.2.2). In contrast to the steam reforming, for which most contractors have their own proprietary technology for the individual process steps, the engineering firms which offer ammonia plants based on heavy hydrocarbons have often to rely for the individual process stages on different licensors. Lurgi, for example, has built very large capacity ammonia plants that use Shell's gasification process, its own proprietary version of the Rectisol process, Linde's air separation and liquid nitrogen wash, and Topsøe's technology for synthesis converter and loop.

Independent, experienced engineering companies, not directly active in ammonia plant design may be used as general contractors to coordinate a number of subcontractors supplying the different technologies required. This is in line with the fact that the degree of energy integration is usually lower than in steam reforming technology, because in absence of a large fired furnace, there is no large amount of flue gas and consequently less waste heat is available. Therefore, a separate auxiliary boiler is normally included to provide steam for mechanical energy and power generation. Nevertheless, some optimization has successfully reduced the overall energy consumption, for which in older installations values of around 38 GJ/t NH_3 were reported. In recent commercial bids, values as low as 33.5 GJ/t NH_3 have been quoted.

The arguments presented above suggest describing the two principal routes, Shell and Texaco, which differ in the gasification process, rather than listing all individual contractor design approaches. Figure 115 shows the classical sequence of process steps for both cases.

Processes Using Shell Gasification (e.g., Lurgi) [521]–[531]. A cryogenic air separation plant provides oxygen for the gasification and the nitrogen for the liquid nitrogen wash and for supplying the stoichiometric amount for the synthesis of ammonia. Oil enters the alumina-lined gasification vessel through a central jet in the burner nozzle. A substantial pressure drop is needed to ensure atomization of the oil and proper mixing with oxygen, fed through the annulus between the jet and the outer case of the burner nozzle. The temperature in the gasification vessel (generator) is between 1200 and 1400 °C, and the pressure between 35 and 65 bar.

The hot gas contains soot, formed because of insufficient mixing of the reactants, and fly ash. A waste-heat boiler, a proprietary item of the Shell process, raises 100 bar steam and cools the gas to 340 °C. Soot is removed from the raw gas in a two-stage water wash. Older installation used an elaborate technique to remove the soot from the water by extraction with naphtha and light oil to form soot pellets which could be burnt or recycled to the feed oil. In newer installations the carbon–water slurry is filtered off in automatic filters, and the moist filter cake is subjected to a controlled oxidation in a multiple-hearth furnace.

A selective Rectisol unit with methanol of about – 30 °C as solvent is used to remove H_2S and COS (together with some CO_2) to less than 0.1 %. The removed sulfur-rich

Topsoe, Inc. – EX1003
Page 341 of 1210

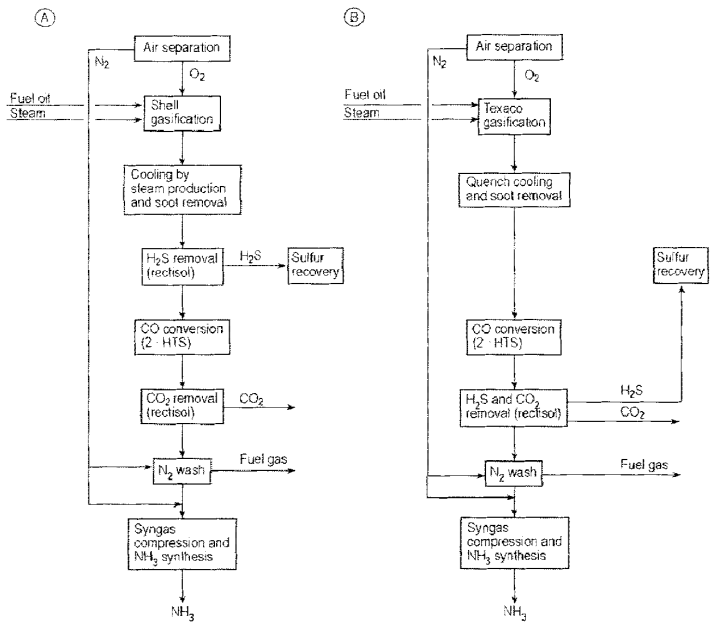


Figure 115. Flow diagrams of ammonia production from fuel oil or heavy residues by the Shell (A) and the Texaco (B) process (standard configuration)

fraction is sent to a Claus plant for recovery of elemental sulfur or converted to sulfuric acid. The gas is heated subsequently by heat exchange, supplied with steam in a saturator, and then fed to shift conversion, which proceeds stepwise with intermediate heat removal. The gas is cooled by a direct water cooler, and the hot water is recycled to the saturator.

A second Rectisol wash stage follows to remove CO_2 by absorption at – 65 °C in methanol, which is regenerated by flashing and stripping. Molecular sieve adsorption then removes residual traces of methanol and CO_2. To remove residual CO a liquid nitrogen wash is applied for final purification with the advantage of also lowering the argon content in the makeup gas, which is adjusted by nitrogen addition to the stoichiometric ratio $N_2:H_2 = 1:3$. Converter and synthesis loop configuration depend on the licensor chosen. Plant descriptions are given in [1154]–[1157].

Processes Using Texaco Gasification (e.g., Foster Wheeler, Linde, Uhde). Temperatures in the generator are similar to those in the Shell process; units with operating pressures up to 90 bar are in operation [513], [532], [533], [537], [540]–[542]. Some modern installations (e.g., Linde) use pumps for liquid oxygen instead of oxygen compressors. In contrast to the Shell arrangement, oxygen enters the gasifier through the central nozzle of the burner, and oil is fed through the annular space between central nozzle and outer burner tube. Instead of a waste-heat boiler a direct water

Topsoe, Inc. – EX1003
Page 342 of 1210

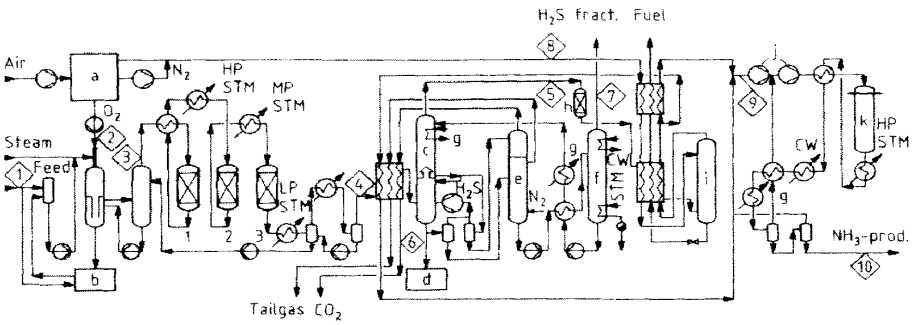
quench is applied for cooling the raw synthesis gas, which is subsequently scrubbed first in a Venturi scrubber and then in a packed tower to remove the soot. Texaco also offers a version operating with a waste-heat boiler instead of a water quench. Although this is preferable when producing CO-rich synthesis gases (e.g., methanol or oxogas), quench is thought to be more economical when hydrogen-rich gases are manufactured. Soot recovery from the water is performed by extraction with naphtha. The soot–naphtha suspension is mixed with feed oil, and the naphtha is distilled off and recycled to the extraction stage. The shift reaction uses a cobalt–molybdenum–alumina catalyst [630], [640]–[643] which is not only sulfur-tolerant but also requires a minimum sulfur content in the gas for proper performance. The conversion is subdivided into stages with intermediate cooling by raising steam. The following Rectisol process has a somewhat more elaborate configuration than the version used in the Shell route. The large amount of carbon dioxide formed in shift conversion lowers the H_2S concentration in the sour gas, and for this reason a special concentration step is required for methanol regeneration to obtain pure CO_2 and a fraction sufficiently rich in H_2S for a Claus plant or a sulfuric acid plant. The remaining process steps are identical with the Shell route. Figure 116 gives an example of a Linde flow diagram. Descriptions of plants using the Texaco process can be found in [630], [1158].

Topsøe Process. A concept using enriched air instead of pure oxygen and methanation instead of a liquid nitrogen wash was proposed by Topsøe [1159], [1160]. A Shell gasifier with a waste-heat boiler or a Texaco generator with a quench are equally well suited to this process. After soot removal, shift conversion is performed on a sulfur-tolerant catalyst in several beds with intermediate cooling, leaving a residual CO content of 0.6 mol %. An appropriate process (Rectisol or amine based) removes the sour gases H_2S, COS, and CO_2, and this is followed by methanation. Makeup gas drying, compression, and synthesis loop have no special features. The anticipated energy consumption is 34.8 GJ/t NH_3. A basically similar synthesis gas preparation, but based on gasification with pure oxygen, is already used in large commercial plant in Japan [1161].

Foster Wheeler Air Partial Oxidation process [1035], [1162] is a proposed modification of the Texaco gasification process. It is intended to operate at 70 bar with highly preheated air (815 °C) instead of pure oxygen. The synthesis gas purification train comprises soot scrubbing followed by shift conversion, acid gas removal (for example Selexol), and methanation. The gas is dried and finally fed to a cryogenic unit, which removes the surplus nitrogen by condensation together with methane, argon, and residual carbon monoxide. The rejected nitrogen is heated and expanded in a turbine, which helps to drive the air compressor.

A major aspect in the design concept is the separation of nitrogen and oxygen. A conventional air separation plant is based on the fractional distillation of oxygen and nitrogen, which differ in boiling point by only 13 °C. In the cryogenic unit for the Foster Wheeler process a lesser quantity of nitrogen is separated from hydrogen with a

Topsoe, Inc. – EX1003
Page 343 of 1210



①	②	⑩
Feed: heavy fuel oil	Oxygen	Ammonia
m = 44 t/h	m = 49.6 t/h	m = 56.25 t/h
p = 0.4 MPa	p = 9.0 MPa	p = 2.5 MPa
t = 90 °C	t = 150 °C	t = 11 °C
Composition, wt%	Purity	
C 84.6	O_2 = 98.5 vol%	
H 10.0	balance: Ar and N_2	
O 0.4		
N 0.4		
S 4.5		
Ash 0.1		

		③	④	⑤	⑥	⑦	⑧	⑨
H_2	vol%	43.0	60.8	96.3	0.9	0.1	–	75.00
CO	vol%	47.7	1.5	2.3	0.1	–	–	–
CO_2	vol%	6.9	35.8	–	98.8	67.4	–	–
N_2	vol%	0.1	0.1	0.2	0.1	2.5	100.00	25.00
CH_4	vol%	0.8	0.5	0.8	0.1	–	–	–
Ar	vol%	0.4	0.3	0.4	0.0	–	–	–
H_2S + COS	vol%	1.1	0.8	–	–	30.0	–	–
H_2O	vol%		0.2	–	–	–	–	–
kmol/h		5680	8250	5200	1800	200	1750	6650
p	MPa	8.37	7.65	7.30	0.15	0.25	7.4	7.1
t	°C	255	45	−63	−15	15	15	10

Figure 116. Ammonia production based on heavy fuel oil (Linde flow scheme with Texaco gasification)
a) Air separation unit; b) Soot extraction; c) CO_2 absorption; d) Methanol/H_2O distillation; e) Stripper; f) Hot regenerator; g) Refrigerant; h) Dryer; i) Liquid N_2 scrubber; j) Syngas compressor; k) NH_3 reactor
Material Balance

much higher boiling point difference (57 °C). According to Foster Wheeler this leads to considerable saving in capital investment and energy consumption compared to the traditional approach using pure oxygen from an air separation plant and a liquid nitrogen wash for gas purification. A figure of 35.6 – 37.6 GJ/t NH_3 is claimed for heavy oil feedstock and 31.4 – 32.7 for natural gas as feedstock. A similar variant also using air instead of pure oxygen is offered by *Humphreys & Glasgow* (now Jacobs) [1163].

Topsoe, Inc. – EX1003
Page 344 of 1210

5.2.2. Ammonia Plants Using Coal as Feedstock

In the early days the entire ammonia industry was based on coal feedstock. Today coal or coke (including coke oven gas) is no longer of major economic importance. In 1990, for example, only 13.5 % of the world ammonia capacity was based on this raw material [410]. Apart from a few plants operating in India and South Africa, the majority of coal-based ammonia plants is found in China. Commercially proven coal gasification processes are Lurgi (dry gasifier), British Gas/Lurgi (slagging gasifier), Winkler/HTW, Koppers–Totzek, Shell, Texaco, and Dow [544]–[546]. So far the Koppers–Totzek, Texaco, and Lurgi processes have commercial importance for ammonia production [548]–[554]. Pressureless Winkler gasification, which was used on large scale in the 1930s and 1950s, later found limited application in some countries. The Shell process, demonstrated commercially in another application with a capacity equivalent to a world-scale ammonia plant, is a potential candidate for ammonia production processes.

In recent years little development work has been done on complete ammonia plant concepts based on coal. The traditional leading ammonia contractors have to rely on proprietary processes licensed from different companies, which similarly tend not to have specific ammonia technology of their own. Again, compared to a steam reforming plant, the degree of integration is considerably lower; power generation facilities are usually separate. Thus it is difficult to identify specific ammonia processes for the individual contractors and the following descriptions serve as examples, without striving for completeness.

The Koppers–Totzek Process gasifies coal dust with oxygen in the temperature range 1500–1600 °C at about atmospheric pressure. For a more detailed description of the gasification, refer to Section 4.1.2.3 and [546], [555]–[561]. The cooled gas, free of coal dust and fly ash, contains about 60 % of CO. The next step is compression to about 30 bar, followed by sulfur removal at –38 °C with chilled methanol (Rectisol process). Steam is added for the shift conversion, carried out stepwise with intermediate heat removal and with a standard HTS catalyst. A second Rectisol stage, operating at –58 °C and 50 bar, removes the CO_2, and the final purification step is a liquid nitrogen wash. Any of the well known converter and synthesis loop concepts may be used, with no purge or minimal purge, due to the practically inert-free makeup gas. Several plants are operating in South Africa [1164], [1165] and India [1166].

The atmospheric-pressure gasification is a considerable disadvantage of this process route, which substantially increases equipment dimensions and costs, as well as the power required for synthesis gas compression. An energy input of 51.5 GJ/t NH_3 (LHV) has been reported. According to [563], the atmospheric ACGP gasifier (Section 4.1.2.3) could lower the consumption to 44 GJ/t NH_3 (HHV).

Lurgi Process. Lurgi [544], [545], [578]–[582], [1167] offers a concept using its proprietary Lurgi dry bottom gasifier, described in Section 4.1.2.3. The moving-bed

Topsoe, Inc. – EX1003
Page 345 of 1210

generator, which can handle any sort of coal (ash content may exceed 30 %), operates at 30 bar, and the product gas contains up to 15 % CH_4, higher hydrocarbons, troublesome phenolic material, and tars. After washing with process condensates to remove ash and dust, the gas is cooled further with recovery of waste heat. Several process steps treat the separated gas liquor to recover tar, phenols, and some ammonia. Shift conversion, Rectisol process, and liquid nitrogen wash are the further operations in the production of makeup gas. The liquid nitrogen wash produces a methane-rich fraction, which is separately processed in a steam reformer, and the reformed gas rejoins the main stream at the Rectisol unit for purification. The gasification has a power consumption of 32 – 34 GJ/t NH_3, and steam generation consumes 18 – 22 GJ/t NH_3, resulting in a total energy consumption of 50 – 56 GJ/t NH_3.

The Texaco Coal Gasification Process [545], [564] – [571], [1168] – [1172] (see Section 4.1.2.3) originates from Texaco's partial oxidation process for heavy oil fractions and processes a coal – water slurry containing 60 – 70 % coal. A lock hopper system removes ash and glassy slag as a suspension from the quench compartment of the generator. The process can handle bituminous and sub-bituminous coal but not lignite. The further gas purification steps used to arrive at pure makeup gas correspond to those described for an ammonia plant using the Texaco partial oxidation of heavy oil fractions.

Ube Industries commissioned a 1000 t/d ammonia plant in 1984 using Texaco's coal gasification process [1161], [1173]. An energy consumption of 44.3 GJ/t NH_3 is stated, which is lower than the 48.5 GJ/t NH_3 quoted for another Texaco coal gasification-based ammonia plant [544].

The other coal gasification technologies were discussed in Section 4.1.2.3, but so far no newer ammonia concepts are bases on them.

Topsoe, Inc. – EX1003
Page 346 of 1210

Copyright © WILEY-VCH Verlag GmbH, 1999

6. Modernization of Older Plants (Revamping)

6.1. Revamping Objectives

With rising feedstock prices and hard competition in the market, many producers have looked for possibilities to "revamp" or modernize their older, less efficient plants so that they can stay competitive. Most revamp projects have been combined with a moderate capacity increase because some of the original equipment was oversized and only specific bottlenecks had to be eliminated, not entailing excessive cost. As the market possibilities for a company do not increase in steps of 1000 or 1500 t/d but slowly and continuously, such a moderate capacity addition will involve less risk and will often be more economical than building a new plant.

For a revamp project first an updated base-line flow sheet of the existing plant should be prepared from which the proposed improvement can be measured [1174]–[1176]. Depending on the objective (energy saving and/or capacity increase) the following guidelines should be kept in mind: maximum use of capacity reserves in existing equipment; shifting duties from overtaxed units to oversized ones; if possible, simple modifications of existing equipment are preferable to replacement; the amount of additional equipment should be kept to a minimum [1175].

6.2. Revamping Options

To give an exhaustive list or description of the individual modification options is beyond the scope of this article, but reviews on this subject and useful information are given in [1027], [1177]–[1192]. Section 5.1.2 describes modifications that lower the energy consumption in newer plant generations compared to the first generation of single-train ammonia plants, and this also represents an overview of the revamp options for existing steam reforming plants.

Just a few of the frequently used revamp possibilities should be mentioned here. In steam reforming plants it is often possible to lower the steam/carbon ratio by using improved reforming catalysts and copper-promoted HT shift catalysts. More active LT shift catalysts lower the residual CO content, which will reduce H_2 loss (methanation) and inert content in the makeup gas. Drying of the makeup gas, addition of hydrogen recovery from purge gas, and installing a more effective CO_2 removal are other options. With the *aMDEA* system, for example, which can be flexibly tailored to fit into existing process configurations, it is, for example, possible to simply replace the MEA solvent with the promoted aMDEA solution, with zero or only minor equipment modification.

Other measures, involving more additional hardware and engineering work, are introduction of combustion air preheating and reducing the primary reformer load.

Topsoe, Inc. – EX1003
Page 347 of 1210

This latter option is used when the revamp objective is capacity increase and the primary reformer is identified as a bottleneck. One possibility is to increase the duty of the secondary reformer and use air in excess of the stoichiometric demand. Elegant variants of this principle are the *Jacobs BYAS process* [1113], [1124], [1125] and the *Foster Wheeler AM2 process* [1035], [1123], [1193]. Another method is to perform a part of the primary reforming in a pre-reformer [462] – [469] that uses low-level heat. Alternative methods to enlarge the reforming capacity make use of the process heat of the secondary reformer in an exchanger reformer such as *ICI's GHR* [1194] or *Kellogg's KRES* [478]. If oxygen is available, installation of a parallel autothermal reformer or a parallel *Uhde CAR unit* [483], [485] – [488] (see also Section 4.1.1.8) could be considered. Description of executed revamp projects are given in [1126], [1196] – [1201].

Similarly, numerous modernization possibilities exist for partial oxidation plants, and they may even outnumber those for steam reforming plants. Common to both plant types is the potential for improvement of the synthesis loop and converter. Application of indirect cooling and smaller catalyst particles are frequently chosen to reduce energy consumption through lower pressure drop, reduced synthesis pressure, higher conversion, or a combination thereof. Apart from replacing existing converters, in situ modification of the internals of installed converters is a very economic approach. *Topsøe* [1182], [1202] mostly uses its Series 200 configuration; and *Ammonia Casale* [905] – [908], [1203] – [1207] its proprietary ACAR technology, with which more than 90 plants have been revamped so far. With a "split-flow" configuration Kellogg proposed an in situ revamp option to change its four-bed quench converter into a two-stage intercooled converter (with two parallel beds for the second stage) using smaller catalyst particles of 1.5 – 3.5 mm and 3 – 6 mm [1208], [1209]. A promising loop modernization option for the future will be the *Kellogg KAAP process* [398], [1210].

The fact that more than 40 % of world ammonia plants are older than 20 years suggests that there is a major potential for revamp projects, even in plants which have already made modifications.

Topsoe, Inc. – EX1003
Page 348 of 1210

Copyright © WILEY-VCH Verlag GmbH, 1999

7. Integration of Other Processes into an Ammonia Plant

There are — at least theoretically — many possibilities to integrate other processes into an ammonia plant. To a limited extent this is possible with an existing ammonia plant, but in this case the production rate of the side product should be small compared to ammonia production. A very simple case with practically no interference with the operation of ammonia production (only a small loss of production if it is not compensated by an adequate increase of synthesis gas generation) is the production of pure hydrogen from the synthesis purge gas by PSA, for example. Carbon monoxide may be produced from a sidestream upstream of the HT shift. With the use of the COSORB process it should be posible to produce in typical 1000 t/d ammonia plant 2000 m^3/h CO with only 2% more feed and 3% additional fuel according to calculations of KTI [650]. Hydrogen production from a sidestream by using PSA is of course possible, too. Designing a grass-root steam reforming plant for a sizeable co-production of, e.g., methanol seems to be economically not very promising, especially if a flexible production rate for the two products is required. Because of the high degree of energy integration in a steam reforming plant an investment penalty is most likely. But in the less integrated partial oxidation plant this seems to be an attractive option, and there are several large installations producing ammonia, methanol, and hydrogen [1214], [1215]. A few years ago, when ammonia prices were low and the methanol prices were sky-rocketing, some producers considered total conversion of an ammonia plant to methanol, but looking at the longer term the prices usualy develop in parallel.

Under favorable conditions, when the front end of an existing ammonia plant has capacity reserves, and the bottleneck is, for example, compression and synthesis, and probably also CO_2 removal, a revamp to incorporate parallel methanol production might be economically attractive. Options for a partial retrofit are described in [1216]; [1496]; an example for a co-production in a side stream with a separate methanol loop is given in Figure 117 [1217].

Integrating ammonia and urea production [1218] has been discussed frequently in the past, in most cases with respect to energy and CO_2 supply. For total conversion of the ammonia, the CO_2 produced in partial oxidation plants suffices but is at deficit in plants based on steam reforming of natural gas.

An integration of ammonia und urea on the process side has been suggested for example by **Toyo Koatsu** [1219], [1220], **M. W. Kellogg** [1221] and **Snamprogetti** [1222] – [1224]. In these ideas the main point of integration is the carbon dioxide removal stage, which is performed by washing with an ammonium carbamate/ammonia solution. The Snamprogetti concept uses a falling film adsorber. A falling film absorber could also be applied for ammonia recovery from the synthesis loop with the aquaeous ammonia being sent directly to the urea reactor. The introduction of the raw CO_2-containing synthesis gas into the urea reactor was even proposed in one publication.

Topsoe, Inc. – EX1003
Page 349 of 1210

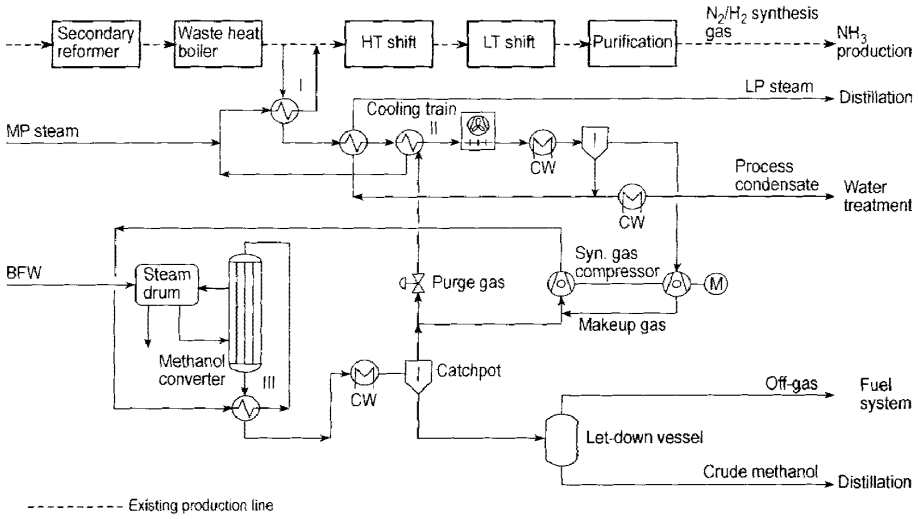


Figure 117. Methanol co-production (sidestream loop)

Topsoe, Inc. – EX1003
Page 350 of 1210

Copyright © WILEY-VCH Verlag GmbH, 1999

8. Material Considerations for Equipment Fabrication

8.1. Hydrogen Attack

In several steps of the ammonia production process, especially in the synthesis section, the pressure shells of reaction vessels as well as the connecting pipes are in contact with hydrogen at elevated pressure and temperature with a potential risk of material deterioration [1211]–[1213], [1484].

Chemical Hydrogen Attack. Under certain conditions chemical hydrogen attack [1225], [1226], [1228] can occur. Hydrogen diffuses into the steel and reacts with the carbon that is responsible for the strength of the material to form methane, which on account of its higher molecular volume cannot escape. The resulting pressure causes cavity growth along the grain boundaries, transforming the steel from a ductile to a brittle state. This may finally reach a point where the affected vessel or pipe ruptures, in most cases without any significant prior deformation. This phenomenon was already recognized and principally understood by BOSCH et al. [1] when they developed the first ammonia process. The resistance of steel against this sort of attack can be enhanced by alloy components which react with the carbon to form stable carbides (e.g., molybdenum, chromium, tungsten, and others). The rate of deterioration of the material depends on the pressure of the trapped methane, the creep rate of the material, and its grain structure. Areas highly susceptible to attack are those which have the greatest probability of containing unstable carbides, such as welding seams [1227]. The type of carbides and their activity are strongly influenced by the quality of post-weld heat treatment (PWHT). The risk of attack may exist at quite moderate temperatures (ca. 200 °C) and a hydrogen partial pressure as low as 7 bar.

Numerous studies, experiments and careful investigations of failures have made it possible to largely prevent hydrogen attack in modern ammonia plants by proper selection of hydrogen-tolerant alloys with the appropriate content of metals that form stable alloys. Of great importance in this field was the work of NELSON [1226], [1228], [1229], who summarized available experimental and operational experience in graphical form. These Nelson diagrams give the stability limits for various steels as a function of temperature and hydrogen partial pressure. In [1230], [1231], CLASS gives an extensive survey, still valid today, on this subject. Newer experience gained in industrial applications required several revisions of the original Nelson diagram. For example, 0.25 and 0.5 Mo steels are now regarded as ordinary nonalloyed steels with respect to their hydrogen resistance [1228].

Physical Hydrogen Attack. A related phenomenon is physical hydrogen attack, which may happen simultaneously with chemical attack. It occurs when adsorbed

Topsoe, Inc. – EX1003
Page 351 of 1210

molecular hydrogen dissociates at higher temperatures into atomic hydrogen, which can diffuse through the material structure. Wherever hydrogen atoms recombine to molecules in the material structure (at second-phase particles or material defects such as dislocations) internal stress becomes established within the material. The result is a progressive deterioration of the material that lowers its toughness until the affected piece of equipment cracks and ultimately ruptures.

The phenomenon is also referred to as hydrogen embrittlement. It is most likely to occur in welds that not received proper PWHT. Holding a weld and the heat-affected zone for a prolonged period at elevated temperature (an operation known as soaking) allows the majority of included hydrogen to diffuse out of the material. But this may not be sufficient if moisture was present during the original welding operation (for example if wet electrodes or hygroscopic fluxes were used), because traces of atomic hydrogen are formed by thermal decomposition of water under the intense heat of the welding procedure. Highly critical in this respect are dissimilar welds, such as those between ferritic and austenitic steels [1232], where the formation of martensite, which is sensitive to hydrogen attack, may increase the risk of brittle fracture.

At higher temperature and partial pressure, hydrogen is always soluble to a minor extent in construction steels. For this reason it is advisable not to cool vessels too rapidly when taking them out of service, and to hold them at atmospheric pressure for some hours at 300 °C so that the hydrogen can largely diffuse out (soaking). In contrast to the hydrogen attack described above this phenomenon is reversible.

It has been reported [1233], [1234] that hot-wall converters in which the pressure shell is in contact with ammonia-containing synthesis gas at 400 °C have developed cracks in circumferential welding seams to a depth nearly approaching the wall thickness in places. This was surprising because the operating conditions for the material (2 1/4Cr-1Mo) were well below the Nelson curve. One investigation [1235] concluded that hydrogen attack had occurred by a special mechanism at temperatures lower than predicted by the Nelson diagram. Nitriding proceeding along microcracks could transform carbides normally stable against hydrogen into nitrides and carbonitrides to give free active carbon, which is hydrogenated to methane. High residual welding stress and internal pressure are considered to be essential for the propagation of the cracks. A rival theory [1234], [1236] attributes the damage to physical hydrogen attack resulting from the use of agglomerated hygroscopic flux in combination with insufficient soaking. However, no problems were experienced for the same converter design in other cases where non-hygroscopic flux was used for welding and a more conservative vessel code was adopted, leading to less stress on account of thicker walls. Recent unpublished observations seem to support the nitriding mechanism.

Topsoe, Inc. – EX1003
Page 352 of 1210

8.2. Nitriding

Nitriding is a problem specific to the ammonia converter. It occurs in the presence of ammonia on the surface of steel at temperatures above 300 °C [1237] – [1240]. With unalloyed and low-alloy steels, the nitride layer grows with time to a thickness of several millimeters. Austenitic steel, used for the converter basket, develops very thin but hard and brittle nitride layers, which tend to flake off. In the nitrided areas, the risk of formation of brittle surface cracks exists.

8.3. Temper Embrittlement

For heat-resistant steels long-term service at temperatures above 400 °C (e.g., high-pressure steam pipes) can lead to a decline in impact strength. Normally, transition temperatures (precipitous decline of notched bar impact values) of below 0 °C are encountered, but this can increase to 60 °C and more (temper embrittlement).

The susceptibility to temper embrittlement can be reduced by controlling the level of trace elements (Si, Mn, P, Sn) in steels [1241], [1242]. Vessels for which temper embrittlement is anticipated should not be pressurized below a certain temperature.

8.4. Metal Dusting

Metal dusting [1243] – [1249] is a corrosion phenomenon which has come into focus again in the last few years with the introduction of exchanger reformer technology and the operation of steam superheaters in the hot process gas downstream of the secondary reformer waste heat boiler. Conventional carburization is a familiar problem with high-temperature alloys in steam reforming furnaces caused by inward migration of carbon leading to formation of carbides in the metal matrix. It happens at high temperatures, typically above 800 °C, and the carbon originates from cracking of hydrocarbons. In contrast, metal dusting occurs at 500 – 800 °C on iron – nickel and iron – cobalt based alloys with gases containing carbon monoxide. The Boudouard reaction, strongly catalyzed by iron, nickel, and cobalt, is generally regarded as the source of the carbon in this case. It is assumed that thermodynamically favored sites exist for these elements at the surface and enhance the carbon deposition if the gas composition corresponds to a carbon activity > 1 [1247], [1248].

As the name implies, the affected material disintegrates into fine metal and metal oxide particles mixed with carbon. Depending on the defects in a protective oxide film on the metal surface and the ability of the material to sustain this film, an induction period may be observed until metal dusting manifests itself as pitting or general attack. A possible mechanism was proposed by GRABKE [1250] and HOCHMANN [1251].

Topsoe, Inc. – EX1003
Page 353 of 1210

At least from a theoretical point of view, alloys formulated to form chromium, aluminum, or silicon oxide films should exhibit an increased resistance. Efforts to find solutions for this problem are continuing, but at present the following situation must be accepted: virtually all high-temperature alloys are vulnerable to metal dusting; higher steam/carbon ratios reduces this sort of corrosion; improvements may be expected by additional surface coating (for example with aluminum). With materials such as Inconel 601, 601H, 625 and similar alloys it is at least possible to reduce the attack to a level which is tolerable in practical operation. The active sites at the metal surface which catalyze the Boudourd reaction can be poisoned by H_2S, thus inhibiting the initiation of metal dusting [1248].

8.5. Hydrogen Sulfide Corrosion

Corrosion by hydrogen sulfide in partial oxidation plants can be controlled by the use of austenitic steels, but special care to ensure proper stress relief of welds is advisable to avoid stress corrosion cracking in these plants caused by traces of chlorine sometimes present in the feed oil.

8.6. Stress Corrosion Cracking

Stress corrosion cracking (SCC) of many steels in liquid ammonia is a peculiar phenomenon. It occurs at ambient temperature under pressure as well as in atmospheric storage tanks at – 33 °C. Extensive studies [1252] – [1265] have defined the conditions under which SSC in liquid ammonia is likely to occur and how it may largely be prevented, but the mechanism is so far not fully understood. Preventive measures include maintaining a certain water content in the ammonia and excluding even traces of oxygen and carbon dioxide. Welds in pressurized vessels must be properly stress-relieved, and in atmospheric tanks it is important to select the appropriate welding electrodes, avoid excessive differences of the thickness of plates welded together and choose the correct geometry of welding seams (see also Section 9.1.1).

Topsoe, Inc. – EX1003
Page 354 of 1210

Copyright © WILEY-VCH Verlag GmbH, 1999

9. Storage and Shipping

Producing and processing ammonia requires storage facilities to smooth out fluctuations in production and usage or shipments. If manufacture and use occur in separate locations, then appropriate transport must be arranged [1266]. This may be by ocean-going ships, river barges, rail or tank cars, or by pipeline. Ammonia is usually handled in liquid form, but in some cases delivery of ammonia vapor to downstream consumers on site may have some advantage due to savings of refrigeration energy in the ammonia plant. If there is an opportunity for on-site usage or marketing of aqueous ammonia, obtained as a byproduct of purge-gas scrubbing or, less frequently, deliberately produced, storage and handling facilities for this product will also be needed, but compared to liquid ammonia the demand is negligible.

Liquid ammonia is a liquefied gas. Its storage and distribution technologies therefore have much in common with other liquefied gases. Reference [399, vol. IV] summarizes the literature on storage, handling, and transportation of ammonia.

9.1. Storage

Three methods exist for storing liquid ammonia [1267], [1268]:

1) Pressure storage at ambient temperature in spherical or cylindrical pressure vessels having capacities up to about 1500 t
2) Atmospheric storage at −33 °C in insulated cylindrical tanks for amounts to about 50 000 t per vessel
3) Reduced pressure storage at about 0 °C in insulated, usually spherical pressure vessels for quantities up to about 2500 t per sphere

The first two methods are preferred, and there is growing opinion that reduced-pressure storage is less attractive [399]. However, in many cases, the combination of atmospheric and pressure storage may be the most economic concept (Fig. 118). The determining factors for the type of storage – apart from the required size – are temperature and the quantity of ammonia flowing into and out of storage [1269].

Characteristic features of the three types of storage are summarized in Table 40 [402]. For pressurized storage, spheres with a capacity up to 1500 t have been constructed, in which case the ratio tonnes ammonia per tonne of steel will become about 6.5.

Topsoe, Inc. – EX1003
Page 355 of 1210

Table 40. Characteristic features of ammonia storage tanks

Type	Typical pressure, bar	Design temperature, °C	t ammonia per t steel	Capacity, t ammonia	Refrigeration compressor
Pressure storage	16–18	ambient	2.8	< 270*	none
Semi-refrigerated storage	3–5	ca. 0	10	450–2700	single stage
Low-temperature storage	1.1–1.2	−33	41–45	4500–45 000	two-stage

*) Refers to cylindrical tanks ("bullets"); spherical vessels see Section 9.1.1.

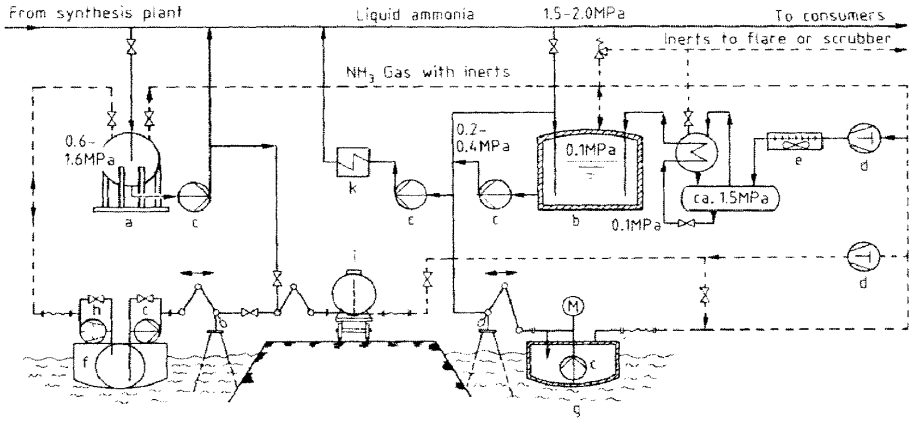


Figure 118. Ammonia terminal with loading and unloading facilities
a) Sphere at ambient temperature; b) Tank at ambient pressure (refrigerated); c) Pumps; d) Compressors; e) Air-cooled condenser; f) Barge with pressure tank; g) Barge for ammonia at ambient pressure; h) Booster; i) Rail car or truck; k) Heater

9.1.1. Pressure Storage

This system is especially suitable for:

- Storing small quantities of ammonia
- Balancing production variations with downstream units processing pressurized ammonia
- Loading and unloading trucks, tank cars, and marine vessels carrying pressurized ammonia
- Entrance to or exit from pipeline systems

Usually, cylindrical pressure vessels are designed for about 2.5 MPa. The larger spherical vessels are designed only for about 1.6 MPa to avoid wall thicknesses above 30 mm. A coat of reflecting paint or, frequently in hot climates, an outer covering of insulation may be used on the vessels to avoid solar radiation heating. Spraying the

Topsoe, Inc. – EX1003
Page 356 of 1210

vessel with water is very effective against intense solar radiation but does stain and damage the paint. As a rule, liquid ammonia fed to storage from a synthesis loop carries inert gases with it. Besides the prescribed safety relief valves, pressure control is provided for the storage drum by controlled bleeding of the inert gases through a pressure-reducing valve, for example, into a water wash system (Fig. 118).

Sometimes high-strength or fine-grained steels are used in making pressure vessels. These may be susceptible to stress corrosion cracking by ammonia. Safely avoiding this hazard requires careful thermal stress relief after completing all welding on the vessel.

The shape of the vessel depends above all on its capacity:

Cylindrical, usually horizontal for up to about 150 t
Spherical vessels resting on tangentially arranged support columns but also more recently, for static and safety reasons, in a suitably shaped shallow depression for about 250 – 1500 t.

Ancillary equipment, designed for at least 2.5 MPa (25 bar): meters and flow controls for pressurized ammonia feed and effluent streams; centrifugal pumps for discharging into liquid ammonia supply piping and for liquid ammonia loading; equipment for safe pressure relief for ammonia vapor and inerts (see Fig. 118 and [1268]). Design of pressure storage tanks and the related safety aspects are discussed in [1270].

Stress corrosion cracking (see also in Section 8.6 in pressurized ammonia vessels and tanks is a problem which has been discussed in many papers [1252] – [1265], [1271] – [1276]. The mechanism of this phenomenon, the influence of water, and the role of oxygen are not yet completely understood, in spite of extensive research. A review is given in [1277]. As it is generally accepted that addition of water may inhibit stress corrosion [1263], [1264] it has become a widely used practice to maintain a water content of 0.2 % in transport vessels [1264]. Protection may also be achieved by aluminum or zinc metal spray coating [1275], [1277]. More recent research [1273], [1277], however, has shown that water may not give complete protection.

The prevailing opinion was that stress corrosion should occur in atmospheric storage tanks [1278]. Therefore, it was somewhat surprising when cases of stress corrosion in atmospheric ammonia tanks were reported [1279] – [1281]. Descriptions of further incidents, inspection techniques, and repair procedures can be found in [1276], [1282] – [1289], [1290].

In 1995, the capital investment, including ancillary equipment, for a 1000-t pressurized ammonia storage facility amounted to about \$ 3.5×10^6 (6×10^6 DM).

9.1.2. Low-Temperature Storage

Modern single-train plants need to have large-volume storage facilities available to compensate for ammonia production or consumption outages. Storage equivalent to about 20 days is customary for this. Moreover, transporting large amounts of ammonia by ship or pipeline and stockpiling to balance fluctuations in the ammonia market have

Topsoe, Inc. – EX1003
Page 357 of 1210

great importance. Therefore, correspondingly large storage facilities are necessary at ship and pipeline loading and unloading points.

For comparable large storage volumes, the capital investment costs for atmospheric pressure storage are substantially lower than for pressure storage. In spite of higher energy costs for maintaining the pressure and for feed into and out of atmospheric storage, it is still more economical than pressure storage. This applies especially to storage of ammonia coming from the synthesis loop at low temperature and loading and unloading of refrigerated ships.

For atmospheric storage at −33 °C single tanks with a capacity up to 50 000 t of ammonia are available [1290]. Design pressure is usually 1.1 – 1.5 bar (plus the static pressure of the ammonia). The cylindrical tanks have a flat bottom and a domed roof and are completely insulated. Refrigeration is provided by recompression of the boil-off, usually with two-stage reciprocating compressors. Incoming ammonia of ambient temperature is flashed to − 33 °C before entering the tank, and the vapors from the flash vessel are also fed to the refrigeration unit. Refrigeration units have at least one stand-by unit, mostly powered by a diesel engine. Single-wall and double wall tanks are used in the industry.

Single-Wall Tanks. The single-wall tank has a single-shell designed for the full operating pressure. Mats or panels of rock wool or foamed organics (e.g., in-situ applied polyurethane foam) are used for insulation of single wall tanks. The outside insulation must be completely vapor tight to avoid icing and requires the highest standards of construction and maintenance to avoid hazardous deterioration by meteorological influences. A metal sheet covering is normally applied, and sometimes a bond wall of reinforced concrete or steel is added [1291], [1292].

Double-wall tanks are known in various designs. In the simplest version an inner tank designed for storage temperature and pressure is surrounded by a second tank. The annular space between the two walls is filled with insulation material, for example, Perlite. The main purpose of the outer shell is to contain and hold the insulation. Today's usual practice is to design the outer shell to the same standard as the inner shell. This so-called double-integrity tank concept provides an additional safety measure as the outer tank can hold the full content if the inner shell fails.

Further safety provisions include surrounding the tanks by dikes or placing them in concrete basins to contain the liquid ammonia in the event of a total failure. Discussions of such secondary containment are found in [1285], [1291] – [1293].

Two principle "double integrity" designs are used as shown in Figure 119. In Figure 119 A and B the inner tank has a solid steel roof and is pressure-tight, whereas the gap between inner and outer shell, which can withstand the full hydrostatic pressure at operating temperature, is only covered by the water-tight insulation. The insulation for the inner shell may fill the total annular space [e.g., lightweight concrete [1294] or Perlite (B)] or may consist of an organic foam attached to the outside of the inner shell (A).

Topsoe, Inc. – EX1003
Page 358 of 1210

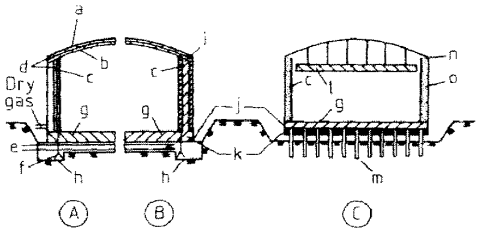


Figure 119. Arrangements of refrigerated ammonia tanks
a) Waterproof roofing; b) Steel roof; c) Inner steel shell; d) Foamed organic materials or rock wool; e) Heating coils; f) Stay bolts; g) Inner steel base; h) Concrete ring wall; i) Loose Perlite or lightweight concrete and rock wool; j) Outer steel shell and base; k) Cellular glass or lightweight concrete; l) Suspended deck with insulation; m) Pile foundation; n) Steel roof and shell or prestressed concrete lined for vapor containment; o) Loose Perlite or insulation on liner or in space

In the design according to Figure 119 C the outer tank is pressure-tight. The inner tank has a suspended roof and the insulation fills the annular gap, which contains an atmosphere of ammonia vapor.

Because of the static loading, cellular glass or lightweight concrete [1294] is used for the floor insulation in all cold tank systems. A foundation as shown in Figure 119 A and B requires underground heating to prevent formation of a continuous ice sheet under the tank, which could lift it. If, as in Figure 119 C, the tank bottom is on piles above ground level, heating is unnecessary.

The tanks are fabricated by welding on site, from steels which retain their notch ductility strength at low temperature. Corresponding to the decreasing static pressure, steel plate thickness in the cylindrical shell is reduced stepwise from bottom to top. Technical details and design questions are treated in [399 Vol IV], [1293], [1295] – [1297]. Influence of climatic conditions on design and operation is considered in [1298]. Specific cases and foundation problems are discussed in [1296], [1299] – [1301]. Retrofitting of existing storage tanks is described in [1302], [1307]. Maintenance and inspection procedures are covered in [1303] – [1309]. For stress corrosion occurred in atmospheric tanks see Section 9.1.1.

A rough budget figure of the capital investment in 1996 for double-integrity tank with a capacity of 20 000 t is around 15×10^6 DM. For large capacity storage (> 20 000 t) presently 600 – 800 DM/t NH_3 have to be invested [1476]. Inclusion of facilities to receive or deliver pressurized ammonia at ambient temperature would add a few millions more. Additional costs may result from high safety standards (e.g., dikes, emmission monitoring systems, ammonia sensors, and computerized control systems) and long transfer lines to shipping terminals.

Energy consumption would also increase considerably, to about 80 kWh/t ammonia throughput. In addition, substantial investment will be necessary for a complete terminal including, for example, a jetty and equipment for ship loading and facilities for loading rail and/or tank cars.

Topsoe, Inc. – EX1003
Page 359 of 1210

9.1.3. Underground Storage

For years, the liquefied petroleum gas (LPG) industry has used pressurized underground liquefied gas storage. This technique has been applied to ammonia also. DuPont has operated a rock cavern in the United States with a capacity of 20 000 t. Norsk Hydro has one in Norway at 50 000 t. Because of the contaminants occurring in liquid ammonia stored this way and the lack of suitable construction sites, no further storage facilities of this kind have been built for a long time. Underground fertilizer ammonia storage was planned in Russia [1310].

9.1.4. Storage of Aqueous Ammonia

To allow storage and transportation at temperatures up to 35 °C, the concentration of aqueous ammonia should not exceed 25 %, because of its vapor pressure. A small facility uses mostly cylindrical vessels. The capacity of the transporting equipment determines the storage volume, e.g., at least 40 m^3 storage volume for 30 m^3 tank cars. For larger capacities, tanks are used. If it is necessary to avoid contaminating the aqueous ammonia by iron hydroxide, austenitic (stainless) steels may be used instead of the usual carbon steels.

9.2. Transportation

9.2.1. Transportation in Small Containers

The most common containers are:

- Cylindrical steel bottles and pressurized flasks for about 20 – 200 kg anhydrous ammonia to meet the requirements of laboratories, small refrigeration systems, and the like
- Polyethylene canisters, metal casks, and the like for 25 % aqueous ammonia.

9.2.2. Transportation in Trucks and Rail Cars

The most widely used methods are:

With pressure vessels for anhydrous ammonia (maximum allowable operating pressure about 2.5 MPa)
With atmospheric pressure vessels for 25 % aqueous ammonia

Topsoe, Inc. – EX1003
Page 360 of 1210

With vessels designed for elevated pressure for high-concentration aqueous ammonia (maximum allowable operating pressure in accordance with the ammonia content up to 1.6 MPa).

A modern rail car loading station for anhydrous and aqueous ammonia is described in [1311], [1312].

The distribution in rail cars (capacities normally up to 100 m^3; Jumbo rail cars 150 m^3) and trucks primarily serves to supply smaller processing operations and wholesale merchants. However, rail transport of liquid ammonia may to some extent supplement large marine and pipeline shipments. Reference [1318] examines rail freight cost. Normally, shipping liquid ammonia by truck is used only where other means of transport are not available, e.g., in the agricultural practice of direct fertilization.

9.2.3. Shipping in Ocean-Going Vessels and River Barges

Regarding the transport volume, shipping of anhydrous ammonia is far more important than transport by rail. In 1991, for example, a total of 10×10^6 t of anhydrous ammonia was transported by ocean-going vessels (IFA statistics). Overseas shipping gained great momentum through exports from producers in countries with low natural gas prices or low-price policies [1314]. A comparison of shipping costs is given in [1315]; for more up-to-date information consult the journal *Nitrogen*, published by British Sulfur, which regularly reports shipping prices. Most river barges have loading capacities of 400 to 2500 t and mostly have refrigerated load, but a few are pressure vessels. Ocean-going vessels may transport as much as 50 000 t of fully refrigerated ammonia.

9.2.4. Transport by Pipelines

Transport of large volumes of ammonia by pipeline [1315], [1316] over great distances is far more economical than by river barge or rail. In the USA the MidAmerica Pipeline System (MAPCO) extends from northern Texas, across Oklahoma, Kansas, Nebraska and Iowa and ends in Minnesota, all intensive agricultural areas. The total length is 1754 km. The Gulf Central Pipeline is with 3057 km the longest system and connects the major producers along the Texas and Louisiana Gulf coast with terminals in Arkansas, Iowa, Illinois, Indiana, Nebraska, and Missouri [1317], [1324], [1325]. Another shorter system (132 km) is the Tampa Bay Pipeline (Florida). MidAmerica Pipeline, for example, has a peak delivery capacity of 8000 t/d for a number of destinations [1318], the hold up is about 20 000 t. Maintenance is described in [1319].

Topsoe, Inc. – EX1003
Page 361 of 1210

As ammonia is transported at a temperature of at least 2 °C (pressure between 22 and 100 bar) it has to be warmed up at the supplier terminal and cooled down again to −33 °C at the receiver terminal. Main branches have diameters of 200 and 250 mm (8 – 10 in). Exact knowledge of the $p-V-T$ properties is important [1320]. Automatic lock valves are installed at intervals of 10 miles, so that the volume which can be released between two valves is limited to 400 t.

The world's longest ammonia pipeline has been in operation since 1983 in Russia, connecting the large production facilities Togliatti/Gordlovka with the terminals Grigorowski/Odessa at the Black Sea over a distance of 2424 km [1315]. Apart from some short pipeline connections, most of them shorter than 50 km, there is no significant pipeline transport in Europe, where ammonia is predominantly further processed in downstream facilities on site and where no widespread direct application to agricultural crops exists.

Topsoe, Inc. – EX1003
Page 362 of 1210

Copyright © WILEY-VCH Verlag GmbH, 1999

10. Quality Specifications and Analysis

The quality of the ammonia product depends to some extent on the operating conditions of the production plant and storage. For example, water content from a synthesis loop receiving a dry make-up gas is about zero, whereas plants which receive the feedgas after a methanation without further drying may give a water content of 0.1 – 0.2 %. Oil may be introduced by the seal oil of the synthesis compressor, but on account of its low solubility in liquid ammonia it usually settles out on storage, so that only a minor concentration will remain in commercial deliveries. There are two commercial qualities of anhydrous ammonia: commercial (technical) grade (ammonia as received from production and storage) and refrigeration grade (technical product purified by distillation [1321] or molecular sieve adsorption). Table 41 lists the commercial specifications. The relevant standards are US Specification OA-445a, Supplement 5 (1963) and, in Germany, DIN 8960 (1972) for refrigeration-grade ammonia. To inhibit stress corrosion cracking a water content of at least 0.2 % for shipped and pipelined liquid ammonia is generally recommended and is mandatory in the USA.

Table 41. Minimum quality requirements for ammonia

Quality		Commercial grade		Refrigeration grade	
		USA	FRG	USA	FRG
Purity	wt%, min	99.5	99.5	99.98	99.98 *
Water	wt%, max	0.5	0.2	0.015	0.2
Inerts **	mL/g, max	not spec'd	not spec'd	0.1	0.08
Oil	ppm by wt	5.0	5.0	3.0	not spec'd
Free of H_2S, pyridine, and naphthene					

* Allowable boiling point change on vaporization of 5 – 97 % of the test sample, 0.9 °C

** The noncondensable gases dissolved in ammonia are H_2, N_2, CH_4, and Ar. Their amounts depend on the methods of synthesis and storage. The inerts amount to about 50 mL/kg for atmospheric storage.

Various concentrations and purities of *aqueous ammonia* are on the market. Mostly, the concentration is 25 – 30 % NH_3 and the iron content less than 10 ppm. Shipping in pressure vessels is necessary for ammonia contents above 25 % because of its elevated vapor pressure. For more stringent purity requirements for aqueous ammonia, the containers should be made of seawater-resistant aluminum (magnesium alloyed) or austenitic steels.

Analysis. Ammonia is readily detectable in air in the range of a few parts per million by its characteristic odor and alkaline reaction. Specific indicators, such as Nessler's reagent (HgJ in KOH), can detect ammonia in a concentration of 1 ppm. For the quantitative determination of ammonia in air, synthesis gas, and aqueous solutions, individual (manual) and continuous (recorded) analyses can be made (for a measure-

Topsoe, Inc. – EX1003
Page 363 of 1210

ment station for automatic determination of ammonium/ammonia, see [1322]). The methods used include, among others:

Acidimetry and volumetric analysis by absorption
Gas chromatography
Infrared absorption
Thermal conductivity measurement
Electrical conductivity measurement
Measurement of heat of neutralization
Density measurement (for aqueous ammonia)

Normally, the water content of liquid ammonia is determined volumetrically as the ammonia-containing residue on evaporation or gravimetrically by fully vaporizing the ammonia sample and absorbing the water on KOH.

The oil content of liquid ammonia can be tested gravimetrically by first evaporating the ammonia liquid and then concentrating the ether extract of the residue. Iron, aluminum, calcium (ammonia catalyst) and other impurities can then be determined in the ether-insoluble residue.

The inert gas content is analyzed volumetrically after the vaporized ammonia has been absorbed in water. Then the inert gas composition is analyzed chromatographically.

Topsoe, Inc. – EX1003
Page 364 of 1210

Copyright © WILEY-VCH Verlag GmbH, 1999

11. Environmental, Safety, and Health Aspects

11.1. Environmental Aspects of Ammonia Production and Handling

Measured by its overall environmental impact – air, water and soil pollution, materials and energy consumption – ammonia production is a rather clean technology, with low emissions, low energy consumption due to high-efficiency process design, and no severe cross-media dilemmas, in which improving one environmental effect worsens another. Typical emissions are given in EFMA's publication Production of Ammonia in the series "Best Available Techniques and Control in the European Fertilizer Industry" [1323].

Steam Reforming Ammonia Plants. Table 42 summarizes the achievable emission values for steam reforming ammonia plants [1323].

Table 42. Emissions from steam reforming ammonia plants

			Existing plants	New plants
Emission to air	NO_x (as NO_2)*	ppmv (mL/m^3)	150	75
		mg/Nm^3	300	150
		kg/t NH_3	0.9	0.45
Emission to water	NH_3/NH_4 (as N)	kg/t NH_3	0.1	0.1
Waste material**		kg/t NH_3	< 0.2	< 0.2

* At 3% O_2.** Spent catalysts.

The source of the NO_x emissions is the flue gas of the fired primary reformer, and in plants without a fired tubular reformer NO_x is emitted from fired heaters and auxiliary boilers, but in considerably smaller quantities. However, NO_x emissions from ammonia production, compared to the total amount from human activities, is in fact a marginal quantity. Only about 0.16 % of the anthropogenic NO_x emissions come from ammonia production. Emissions to water, generally originating from the condensate from the condensation of surplus process steam ahead of the carbon dioxide removal system, can largely be avoided. Minor concentrations of methanol and amines can be removed and recycled to the reformer feed by stripping with process steam, and the stripped condensate can be recycled to the boiler feed water after polishing with ion exchangers. Steam stripping without recycling to the reformer would produce a cross media effect, because in this case the pollutants would be transferred from water to air. Another possibility is use of the process condensate for feed gas saturation [1033].

Topsoe, Inc. – EX1003
Page 365 of 1210

Partial oxidation ammonia plants have the same emission sources except for the primary reformer flue gas. The plants have an auxiliary boiler to generate steam for power production and fired heaters, which on account of the sulfur content of the fuel oil release a flue gas containing SO_2 (< 1500 mg/m^3). Other possible emissions are H_2S (< 0.3 ppmv), CO (30 ppmv) and traces of dust. The NO_x content of the flue gas depends on the configuration of the auxiliary boiler and on the extent electric power generation on the site as opposed to outside supply. The total NO_x emission per tonne of product may be somewhat lower than for steam reforming plants.

Noise. An increasing awareness has developed for noise generation and emission from ammonia plants especially in the neighborhood of residential areas [1326]. Many investigations have dealt with noise generation and noise abatement in ammonia plants [1327]–[1331]. The following major sources can be identified: depressurizing of large gas quantities for control or venting, steam blowing, burner noise, resonance vibrations in the flue gas ducts, and noise from compressors, blowers, and pumps. Measures for noise reduction include installing low-noise let-down valves, use of silencers, sound-reducing enclosures for compressors or housing them in closed buildings.

Emission Limits and Guideline Values for Ammonia Production. There are two categories of regulations:

1) Legally binding emission values for certain pollutants associated with ammonia production
2) Guideline values not legally binding but providing the background for requirements laid down in individual operating permits

In Europe such legally binding emission levels relevant to ammonia production exist only in Germany. In the Netherlands and Germany limits for emissions from boilers also apply for ammonia plants, for example for the reformer furnace. The present limit in Germany is 200 mg NO_x/m^3 for furnaces up to 300 MW_{th}. Specific emission guideline values are laid down in the United Kingdom. In the other European countries no national emission limits or guidelines exist; individual operation permits are negotiated, usually orientated on other cases and countries. In the United States, for example, NO_x emission level values are categorized in the Clean Air Act, which defines a significance level for the source according to the total emission (10 to 100 t/a) on the one hand, and assigns a threshold limit to the geographical area (100 t/a to 10 t/a) on the other.

For ammonia in air the authorities in Germany require that the achievable minimum level should correspond to the state of the art; originally projected values in a draft of TA Luft [1332], were not subsequently adopted; some MIK values (maximum imission concentrations) are given in VDI Richtlinie 2310 (Sept. 1974). In Germany there is no maximum ammonia concentration laid down for wastewater, it is only referred to the general interdiction to introduce poisons or harmful substances into

Topsoe, Inc. – EX1003
Page 366 of 1210

rivers and lakes. A concentration of 1.25 mg NH_3 per liter, stated to be harmful to fish, could serve as a guideline. In the "Catalog of Water Endangering Substances" (Germany) anhydrous ammonia is not listed, but aqueous ammonia is classified in the Water Endangering Group 1 as a weakly endangering substance.

To harmonize European regulations concerning emission value permits for industrial production, the EU commission has proposed a Council Directive Concerning Integrated Pollution Prevention Control (IPPC Directive). A key element is the concept of Best Available Techniques (BAT). This directive requests an exchange between national environmental authorities, industry and nongovernmental organizations with the aim of preparing IPPC BAT Reference Documents (BREFs), which could provide a common accepted basis for emission limit value regulations of the individual EU member states. A BREF for ammonia is being prepared to serve as pilot project. A previous BAT document on ammonia was published in 1990 [1333]. For noise emissions usually local permits are negotiated, whereby in most instances the contribution to the sound level in the surrounding residential areas will be limited. For the limitation of sound levels at working places within the plant occupational safety regulations are valid which also require ear protection above a certain level. The European Fertilizer Manufacturer's Associacion (EFMA) has published a series: "Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry". Booklet No. 1 is "Production of Ammonia".

11.2. Safety Features

In ammonia production three potential hazard events can be identified: fire/explosion hazard from the hydrocarbon feed system; fire/explosion hazard due to leaks in the synthesis gas generation and purification, compression, or synthesis section (75 % hydrogen); and toxic hazard from release of liquid ammonia from the synthesis loop. In addition there is also a potential toxic hazard in handling and storing of liquid ammonia. The long history of ammonia production since 1913 has demonstrated that this production technology is a very safe operation. The severe impacts of rare events with explosions seem to be confined to a radius of around 60 m [1323]. The long industrial experience is summarized in a number of national codes and standards which have to be applied for design, material selection, fabrication, operation, and periodic technical inspections of the equipment used. This is especially important for equipment operating at high temperatures and/or pressures. Apart from proper design, skilled and well-trained operators and effective and timely maintenance are essential for safe plant operation. General practice today is to make so-called HAZOP-Studies (HAZOP = hazards and operability) with an experienced team consisting of operating personnel, process engineers (also from contractors), experts in process control, and safety experts (often independent consultants from outside the company) in which, following a very meticulous procedure, apparatus after apparatus

Topsoe, Inc. – EX1003
Page 367 of 1210

is checked for potential failure and risk possibilities together with a proposal for the appropriate remedies. HAZOP-Studies and risk analysis procedures introduced by ICI [1339] – [1342] for general application in chemical plants proved to be very helpful not only for existing plants but also in the planning phase of new ones. It is especially important to define and configure trip systems and trip strategies for safe plant shut downs in case of offset conditions.

An area which deserves special attention with respect to safety is the storage of liquid ammonia. In contrast to some other liquefied gases (e.g., LPG, LNG), ammonia is toxic and even a short exposure to concentrations of 2500 ppm may be fatal. The explosion hazard from air/ammonia mixtures is rather low, as the flammability limits [1334] – [1338], [1343] of 15 – 27 % are rather narrow. The ignition temperature is 651 °C. Ammonia vapor at the boiling point of – 33 °C has vapor density of ca. 70 % of that of ambient air. However, ammonia and air, under certain conditions, can form mixtures which are denser than air, because the mixture is at lower temperature due to evaporation of ammonia. On accidental release. the resulting cloud can contain a mist of liquid ammonia, and the density of the cloud may be greater than that of air [1334] – [1344]. This behavior has to be taken into account in dispersion models.

Regulations and Guidelines. For maintaining safety in ammonia storage, transfer, and handling many regulations and guidelines exist in the various countries. It is beyond the scope of this article to list them completely and to check for the most up-to-date status. As an illustration only, some relevant regulations in Germany are listed here (for a summary of regulations in the USA, refer to [1345]):

- Verordnung über Druckbehälter, Druckgasbehälter und Füllanlagen (Druckbeh. V vom 27. Febr. 1980)
- Unfallverhütungsvorschriften der Berufsgenossenschaft der chemischen Industrie: e.g. UVV 29 Gase, UVV 20 Kälteanlagen, UVV 39 Arbeiten an Gasleitungen
- Gesetz zum Schutz vor gefährlichen Stoffen (Chem. G. vom 16. September 1980)
- Verordnung über Anlagen zum Lagern, Abfüllung und Umschlag wassergefährdender Stoffe (VAwS von 1983)

The respective "Technische Regelwerke" (technical standards) supplement these regulations and ordnances [1346]:

TRG	Technische Regeln Druckgase
TRB	Technische Regeln Druckbehälter
TRgA	Technische Regeln Gefährliche Arbeitsstoffe
AD	Merkblätter für Druckbehälter (Unterlagen für Auslegung und Berechnung)
SEW	Stahl-Eisen-Werkstoffblätter

Relevant DIN regulations govern design of pressure vessels and other equipment. The German Institute for Standardization (Deutsches Institut für Normung) provides information covering German technical rules and international and foreign standards [1347].

Topsoe, Inc. – EX1003
Page 368 of 1210

The following regulations are relevant to transportation of ammonia:

GGVE	Gefahrgutverordnung Eisenbahn (FRG)
GGVS	Gefahrgutverordnung Straße (FRG)
RID	Règlement international concernant le transport des marchandises dangereuses par chemin de fer (Europe)
ADR	Accord européen relatif au transport international des marchandises dangereuses par route (Europe)
ADNR	Accord européen relatif au transport international des marchandises dangereuses par navigation sur le Rhin [1348] (Europe)
IMDG	International maritime dangerous goods code [1349]

Publication of GGVE and RID, GGVS and ADR in a synoptic edition is planned [1355].

In addition the Technical Committee of APEA together with a joint Technical Group of ISMA have collected recommendations for erecting and operating ammonia terminals, transfer installations, etc.:

- Safety Recommendations for Large Scale Storage of Ammonia
- Recommendations for the Loading and Unloading of Ammonia Tankers (Maritime Ports)
- Safety Recommendations for the Installation of State Ammonia Tanks on Customers Premises
- Note on the Inflammability of Ammonia
- Safety Recommendations for the Use of Ammonia in Agriculture
- Recommendations Concerning Rubber Hose for Ammonia
- Safety Recommendations for the Construction of Tank-Cars for the Transport of Ammonia by Road

These brochures appeared (1974) in English, French, and German, partly in new editions [1337].

Likewise, in the United Kingdom, a joint working party of renowned companies collected a number of codes of practice published by the CIA:

1) Safe Handling and Transport of Ammonia in Bulk by Road
2) Safe Handling and Transport of Ammonia in Bulk by Rail
3) Demountable Vessels and Containers
4) Transfer Connections
5) Ammonia Storage Installations at Industrial Consumers' Premises
6) Systems and Equipment for the Direct Application of Ammonia in Agriculture
7) Maintenance of Ammonia Systems

In the appendices of the brochures are statutory regulations, recommendations, and bibliographies for reference [1351].

In like manner, for the United States one may mention: safety manuals and standards for the storage, transport, and handling of anhydrous ammonia compiled

Topsoe, Inc. – EX1003
Page 369 of 1210

by the ANI [1352], and the Chemical Safety Data Sheets of the Manufacturing Chemists Association [1353].

All larger ammonia producers make available technical instructional brochures, in which they also prescribe necessary protective measures and first aid for dealing with ammonia.

Ammonia Spills. In an ammonia spill a portion of the liquid ammonia released flashes as ammonia vapor. This instantaneous flash is followed by a period of slow evaporation of the remaining liquid ammonia [1344], [1354]. In a release from a refrigerated tank operating slightly above atmospheric pressure, the amount of the initial flash is only a few percent of the total, whereas in a release from a pressure vessel at about 9 bar and 24 °C approximately 20 % of the spilled ammonia would flash. Figures for the proportion flashed as a function of pressure and temperature of the spilled ammonia are given in [1354]. This reference also provides quantitative information on temperature development and evaporation rate of small and large ammonia pools at certain wind velocities and also takes radiation influences (sunny or overcast sky, day or night) into account.

Spill experiments on land and on water in various dimensions have been carried out by various companies and organizations. Underwater releases were also studied. Models have been developed to mathematically describe ammonia dispersion in such events [1355] – [1360].

A number of real incidents with tank cars, rail cars, tanks, loading/unloading of ships and barges, and pipeline transport in which major spills occurred is described in [1361] – [1370] and in an excellent review on safety in ammonia storage [1371]. Training of operating personal for ammonia handling with special regard to ammonia spills is important [1369], [1372], [1373].

11.3. Health Aspects and Toxicity of Ammonia

In ammonia production, storage, and handling the main potential health hazard is the toxicity of the product itself. For this reason this section concentrates on ammonia only. Other toxic substances such as carbon monoxide or traces of nickel carbonyl (which may be formed during shut down in the methanation stage) may be only a risk in maintenance operations and need appropriate protection provisions as well as blanketing or flushing with nitrogen.

Human Exposure. The threshold of perception of ammonia varies from person to person and may also be influenced by atmospheric conditions, values as low as 0.4 – 2 mg/m^3 (0.5 – 3 ppm) are reported in [1374], but 50 ppm may easily detected by everybody [1375]. Surveys [1376] found concentrations from 9 – 45 ppm in various

Topsoe, Inc. – EX1003
Page 370 of 1210

plant areas. Though initially irritated, exposed persons may quickly become accustomed to these concentrations. Another report [1377] gives concentration limits for short time exposures as follows: 100 ppm (10 min); 75 ppm (30 min) 50 ppm (60 min). The time-weighted average Threshhold Limit Value (TLV) of the ACGIH is 25 ppm (or 18 mg/m^3) [1378], [1383]. This recommendation was supplemented by a value for short-time exposure: 35 ppm for 15 min. The MAK value is 50 ppm. A review of the present situation in the United States is given in [1384].

Exposure to higher ammonia concentration has the following effects: 50–72 ppm does not disturb respiration significantly [1379]; 100 ppm irritates the nose and throat and causes a burning sensation in the eyes and tachypnoe [1379]; 200 ppm will cause headache and nausea, in addition to the above symptoms [1380]; at 250–500 ppm tachypnoe and tachycardia [1380]; at 700 ppm, immediate onset of burning sensations in the eyes [1381]; 1000 ppm causes immediate coughing [1382]. The symptomatology of various exposure levels is also described in [1378], [1383]–[1385]. At 1700 ppm coughing with labored breathing, sometimes with momentary inability to breath (coughing of rescued persons may continue for hours). 2500 to 4500 ppm may be fatal after short exposure; 5000 ppm and higher causes death by respiratory arrest [1371].

The metabolism seems not to be significantly changed after exposure to 800 ppm [1382]. A discussion of metabolism and of acute and chronic health problems caused by ammonia can be found in [1386].

Toxicology. Ammonia is a strong local irritant. On mucous membranes alkaline ammonium hydroxide is formed, which dissolves cellular proteins and causes severe necrosis (corrosive effect).

The primary target organ is the pulmonary system, and the following symptoms can be observed: pharyngitis, laryngitis, tracheobronchitis, nausea, vomiting, increased salivation, reflectoric bradycardia, and life-threatening symptoms, such as edema of the glottis, laryngospasm, bronchospasm, and interstitial lung edema [1387].

Ammonia or ammonium hydroxide can penetrate the cornea rapidly, leading to keratitis, damage of the iris, cataract, and glaucoma [1388].

Oral ingestion of aqueous ammonia can corrode the mucous membranes of the oral cavity, pharynx, and esophagus and cause the shock syndrome, toxic hepatitis, and nephritis. Because of its corrosive action constrictions of the esophagus may result.

Ammonia is absorbed rapidly by the wet membranes of body surfaces as ammonium hydroxide, converted to urea, and excreted by the kidneys [1389]. The capacity of detoxification via urea is sufficient to eliminate the ammonium ion when ammonia is inhaled in nonirritating concentrations. The inhaled ammonia is partly neutralized by carbon dioxide present in the alveoli [1390]. Only a small fraction of the ammonia is exhaled unchanged by the lungs (12.3% at an inhalation concentration of 230 ppm) [1391]. Repeated inhalation can cause a higher tolerance because the mucous membranes become increasingly resistant [1392]. Additional information on the toxicology of ammonia can be found in [1393]–[1409].

Topsoe, Inc. – EX1003
Page 371 of 1210

Carcinogenicity. Ammonia failed to produce an increase in the incidence of tumors in Sprague Dawley rats even when the protein ratio in the diet was increased or when urea was added [1410].

Lifetime ingestion of ammonium hydroxide in drinking water by mice was without any carcinogenic effects [1411].

Mutagenicity. Ammonia is not mutagenic in the Ames *Salmonella* system and in *Saccharomyces cerevisiae* [1412].

Topsoe, Inc. – EX1003
Page 372 of 1210

Copyright © WILEY-VCH Verlag GmbH, 1999

12. Chemical Reactions and Uses of Ammonia

12.1. Reactions of Ammonia

By addition of a proton ammonia forms the ammonium ion which is similar to the alkali metal ions with respect to its alkaline and salt-forming properties.

The free radical NH_4 has been isolated only in the form of its amalgam (DAVY, 1811) which precipitates the more noble metals, such as copper, cadmium, and zinc, from their solutions. Solutions of ammonium in liquid ammonia are blue and usually exhibit properties similar to liquid ammonia solutions of sodium and potassium.

Aqueous solutions of ammonia react as weak bases because hydroxyl ions result from the addition of a proton or H_3O^+ from the water to the ammonia molecule. However, the equilibrium is very strongly shifted to the side of free ammonia, as may be seen from the equilibrium constant at 18 °C:

$$\frac{[NH_4^+]\,[OH^-]}{[NH_3]} = K\,[H_2O] = K'_{NH_3} = 1.75 \times 10^{-5} \qquad (96)$$

A 1 N solution of ammonium hydroxide has a pH of 11.77 at 18 °C.

Ammonium salts result from reaction with acids in aqueous solution or in the gas phase.

Ammonia is oxidized by oxygen or air, depending on the reaction conditions, to NO, NO_2, or N_2O or to nitrogen and water. On alkaline surfaces, such as quicklime or soda lime, ammonia–air mixtures are oxidized readily at 350 °C to nitrite and further to nitrate. The reaction rate can be increased by adding traces of nickel and cobalt oxides to the catalyst surfaces [1413]. Gaseous ammonia reacts very violently or even explosively with nitrogen oxides to form nitrogen, water, ammonium nitrate or nitrite. The reaction with N_2O requires ignition. The controlled catalytic oxidation of ammonia to produce nitric acid or pure NO for hydroxylamine production is described in [1419] – [1421].

At higher temperatures, especially in the presence of surface-active materials, ammonia forms *hydrogen cyanide* with carbon monoxide, methane, or charcoal. The catalytic oxidation of methane in the presence of ammonia is employed for the industrial production of hydrogen cyanide. With CO_2, SO_3, and P_2O_5, NH_3 forms amides of carbonic acid (e.g., Urea [1422]), sulfuric acid [1423], and phosphoric acid [1424].

Metals may replace one or all of the hydrogen atoms of ammonia. *Sodium amide* ($NaNH_2$), for example, is obtained with evolution of hydrogen by passing ammonia vapor over metallic sodium. Sodium amide reacts with N_2O to form the highly explosive sodium *azide*. An ammonium azide, NH_4N_3, may be prepared also. The *imide*, for example, lithium imide, Li_2NH, results from replacing a further hydrogen

Topsoe, Inc. – EX1003
Page 373 of 1210

atom by metals. Finally, there are the *nitrides*, such as lithium or magnesium nitride, Li_3N or Mg_3N_2. The nitrides of reactive metals, such as lithium, magnesium, calcium, aluminum, and titanium, are formed directly from the elements at elevated temperature. In many cases, it is better to obtain nitrides through the action of ammonia on the metals or metal compounds at higher temperature. A nitride also may result from thermal decomposition of an amide.

Sulfur, phosphorus, and halogens also can take the place of the hydrogen atoms in ammonia. At relatively low temperatures, halogens react with ammonia to form *nitrogen–halogen compounds* and *ammonium halides*. At higher temperatures the products are nitrogen and hydrogen halides. With sodium hypochlorite, ammonia forms *hydrazine hydrate* (Raschig synthesis) with chloramine, H_2NCl, as an intermediate.

Reactions in liquid ammonia [1414] sometimes proceed differently from those in water because of the solubility difference of many salts between water and ammonia. For example, the reaction

$$2\,AgNO_3 + BaCl_2 \xrightleftharpoons[NH_3]{H_2O} 2\,AgCl + Ba(NO_3)_2 \qquad (97)$$

leads in water to precipitation of silver chloride, and in ammonia, to precipitation of barium chloride. In liquid ammonia, ammonium salts have an "acid" character. For example, alkali and alkaline-earth metals, cerium, lanthanum, manganese, cobalt, nickel, and iron and its alloys are soluble in solutions of ammonium bromide, iodide, cyanide, and thiocyanide, with formation of the corresponding metal amine salt and evolution of hydrogen:

$$2\,NH_4^+ + Mg \longrightarrow Mg^{2+} + 2\,NH_3 + H_2 \qquad (98)$$

Correspondingly, metal amides in liquid ammonia have a "basic" character. The reaction of ammonium salt with metal amide in liquid ammonia is analogous to the neutralization of acid and base in water. The heats of neutralization in ammonia are even larger than in water. The process of hydrolysis corresponds to ammonolysis in ammonia. This results in ammonobasic compounds, for example, in the infusible precipitate $HgNH_2Cl$ from $HgCl_2$.

Liquid ammonia is a good solvent for white phosphorus. Rhombic sulfur is dissolved by liquid ammonia at −11.5 °C. Once dissolved, at lower temperature a blue solution results in which partial ammonolysis of sulfur to sulfur nitride and ammonium sulfides or polysulfides takes place.

Liquid ammonia's ability to dissolve alkali and alkaline-earth metals has been well known for a long time. In concentrated solutions, the metals largely remain in the metallic state. The magnetic properties and the electrical conductivity, which is comparable to that of mercury, confirm this. In the more dilute blue solutions, the metals are completely dissociated to positive metal ions and solvated electrons [1415]. The ammoniacal solutions allow preparation of many compounds otherwise unobtainable

Topsoe, Inc. – EX1003
Page 374 of 1210

or obtainable only with difficulty. Examples are the sodium selenides, Na_2Se through Na_2Se_6, tellurides up to Na_2Te_4, antimonides, arsenides, polystannides, and polyplumbides. Introducing oxygen into the solution of alkali metals forms peroxides, Na_2O_2, K_2O_2, as well as dioxides, KO_2, RbO_2, and CsO_2. White explosive salts of the hypothetical acetylenediols, such as KO–C≡C–OK, result with carbon monoxide [1416]; with acetylene, NaC≡CH; and with phosphine, KPH_2. Reactions of ammoniacal metal solutions with halogen-containing organic compounds can be used for the synthesis of higher hydrocarbons, amines, and free radicals. For example, reacting triphenylchloromethane with dissolved sodium produces the triphenylmethyl radical $Ph_3C\cdot$.

Generally liquid ammonia is a good solvent for many salts, such as nitrates, nitrites, iodides, cyanides, thiocyanides, and acetates. Ammonium salts are especially soluble. The hydroxides, fluorides, and salts with di- and trivalent anions, such as oxides and sulfides, in general are insoluble. Apart from alkali metals, some other metals and nonmetals are also soluble. A compilation of the solubilities of organic compounds in liquid ammonia shows notable solubility of saccharoses [1417].

Because of its dipole moment, the ammonia molecule interacts with these ions to form solvates in a manner analogous to the water molecule in aqueous solutions. Solutions in liquid ammonia show significant electrical conductance. Pure ammonia, like water, itself has a conductivity that, although limited, is based on dissociation according to:

$$2\,NH_3 \rightleftharpoons NH_4^+\,NH_2^- \qquad (99)$$

Liquid ammonia in combination with water as antisolvent and methylamine as prosolvnet is also an excellent extraction medium for all types of petroleum fractions [1418].

A survey of organic reactions in liquid ammonia appears in [1494].

12.2. Uses of Ammonia

In 1997 about 85 % of ammonia production was consumed for fertilizers. Ammonia is either converted into solid fertilizers (urea; ammonium nitrate, phosphate, sulfate) or directly applied to arable soil.

The industrial use of ammonia is around 15 %. Actually every nitrogen atom in industrially produced chemical compounds comes directly or indirectly from ammonia. An important use of the ammonia nitrogen, partly after conversion to nitric acid, is the production of plastics and fibers, such as polyamides, urea – formaldehyde – phenol resins, melamine-based resins, polyurethanes, and polyacrylonitrile.

Some examples of industrially important uses are the following reactions: With alkyl halides or alcohols *amines* or *imines* can be manufactured. For example, methanol forms mono- through trimethylamine; dichloromethane yields ethylene imine in the presence of calcium oxide. Amines can also be produced by reacting ammonia with alkyl halides in multistage processes [1425].

Topsoe, Inc. – EX1003
Page 375 of 1210

Acid Amides can be produced by acylating ammonia with esters, acid anhydrides, or the acids themselves (above 100 °C); an important product is formamide from methyl formate. Alternatively acid amides can be synthesized by reacting acid halides with ammonia. Catalytic hydrogenation converts the acid amides to *primary amines*. Ammonia and aldehydes or ketones are the basis for different stable products. With formaldehyde hexamethylenetetramine (urotropine) is obtained; with acetaldehyde, ammono acetaldehyde; with benzaldehyde, hydrobenzamide; with ethylene and propylene oxides, aqueous ammonia reacts to form ethanol- or propanolamine.

The catalytic gas-phase oxidation of olefins in the presence of ammonia on vanadium- or molybdenum-containing catalysts, so-called *ammonoxidation,* results in economic yields of the commercially important *acid nitriles,* for example, acrylonitrile from propylene [1426]. Ammonoxidation of *o*-xylene yields phthalodinitrile in a single reaction step.

Another application is the manufacture of explosives, hydrazine, amines, amides, nitriles and other organic nitrogen compounds, which serve as intermediates for dyes and pharmaceuticals.

Major inorganic products are *nitric acid, sodium nitrate, sodium cyanide, ammonium chloride,* and *ammonium bicarbonate. Urea production* consumed about 40 % of the ammonia produced in 1995.

In the environmental sector ammonia is used in various processes for removing SO_2 from flue gases of fossil-fuel power plants. The resulting ammonium sulfate is sold as fertilizer. In the *selective catalytic reduction process (SCR) the* NO_x in flue gases is reduced in a catalytic reaction of the nitrogen oxides with a stoichiometric amount of ammonia [1427] – [1430]. Also noncatalytic reduction is applied with ammonia or urea solutions.

Ammonia is also applied as a solvent in certain processes. Another application is the *nitriding of steel.* An old an still flourishing business is the use of *ammonia as refrigerant,* based on its low boiling point and its high heat of evaporation. For some time heavy competition came from chlorofluorocarbons (CFCs), but with increasing environmental concern regarding the application of CFCs ammonia's position is strenghening again. Ammonia is applied in a large number of industrial and commercial refrigeration units and air-conditioning installations [1431] – [1434]. In addition to the high specific refrigeration effect, the ammonia has the following advantages: it is noncorrosive; it tolerates moisture, dirt, and oil contaminants; it is cheap and there are many suppliers. A drawback is its toxicity.

The production of smaller volumes of hydrogen/nitrogen mixtures used as protective gases for chemical products [1435] and for metal-working processes [1436] by *decomposition of ammonia* over iron- or nickel-based catalysts at 800 – 900 °C may be an economic alternative where production or purchase of pure hydrogen is too expensive [1437], [1443]. Energy-related applications of ammonia are proposed in [1429].

Topsoe, Inc. – EX1003
Page 376 of 1210

Copyright © WILEY-VCH Verlag GmbH, 1999

13. Economic Aspects

13.1. Capacity and Production

About 1.6% of the world consumption of fossil energy (not including combustion of wood) goes into the production of ammonia. In developing countries, ammonia is generally one of the first products of industrialization. As 85% of world nitrogen consumption is for fertilizers it might be expected that ammonia production should develop approximately in proportion to the growth of world population. This was roughly the case in the mid-1980s as can be seen from Figure 120 [404]; since then the rate of increase in production has been markedly slower than that of world population. This has been mainly for economic reasons in developing countries and for ecological reasons in industrialized countries.

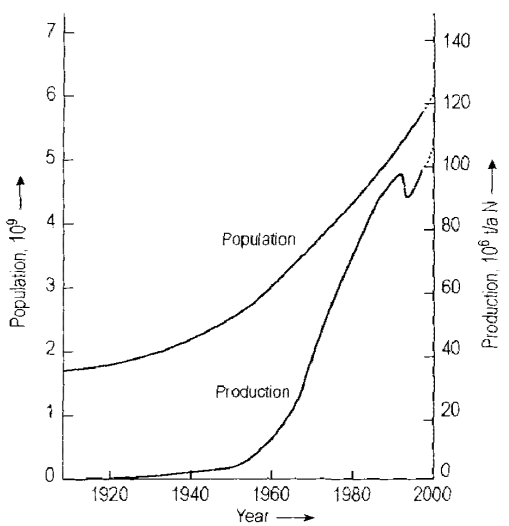


Figure 120. Development of ammonia production and world polulation

The political changes in the former Eastern Bloc caused a dramatic slump in 1991 – 1993. The present forecast figures signalize faster growth for the next few years and, as can be seen from Table 43, an average capacity utilization rate above 82% will be necessary at the end of the century, a value probably not achievable on a global scale. To cope with this situation in the shorter term, plant efficiency in Eastern Europe and some developing countries must be improved. Revamp projects and, in addition to those already under construction, new plants will be necessary to improve supply situation in the medium- to long-term perspective. In the last few years a number of new ammonia projects materialized, but it is difficult to assess what influence the present Asian crises will have. It generally can be expected that in these countries a

Topsoe, Inc. – EX1003
Page 377 of 1210

Table 43. World ammonia supply/demand balance (10^6 t/a N) [1438] – [1440], [1479]

	Year									
	1985	1990	1991	1992	1994	1995	1996	1998	2000	2001
Capacity	118.5	122.5	122.5	124.5	116.3	117.5	117.9	124.5	131.3	135.7
Demand	92.0	94.4	93.1	93.1	93.4	95.2	97.7	102.7	107.8	110.7
Capacity utilization, %	77.7	78.7	80.2	74.7	80.3	81.0	82.9	82.5	82.7	81.6

retreat from government subsidizing with a shift to more private and bank financing will occure. As this is associated with a more critical attitude towards profitability this development could have some retarding effect on future investments [1445], [1474]. To construct and commission a new ammonia plant takes about 3 years and for legal matters, project financing and authority approvals another 1 – 2 years will be necessary. This means that estimates of capacity development beyond a 4 – 5 years horizon are very uncertain.

Another uncertainty is introduced by the need to replace a great number of older plants for economic and environmental reasons, which might also retard the growth of capacity. This applies for a number of plants all over the world which cannot be revamped economically. Outstanding examples are plants in the People's Republic of China [1480], with a 21 % share in the world ammonia capacity. China's large production comes from around 900 individual plants [1475], which, on average, reach about 65 % of the nominal capacity. Only about 30 plants are modern world-scale plants, more than 50 plants have capacities between 80 000 and 150 000 t/a. The rest are very small plants with capacities often below 30 000 t/a. Most of these tiny village ammonia plants use coal as feedstock which is gasified with outdated watergas/generator gas technology (with some minor improvements), known from early days of ammonia production. The ammonia is recovered in these plants usually as aqua ammonia and converted either to ammonium bicarbonate or ammonium chloride, used as fertilizer for rice growing. Other sources [1482], [1483] state an even higher number for these small plants in China and give their capacities as 3000 – 10 000 t/a. About 65 % of China's total production is based on coal. Since China is deficient in natural gas and oil in the long term, it can be expected that further expansions of ammonia capacity will be coal-based as well, probably with modern technology in world-scale plants. Excluding China, as number and locations of the smaller plants are rather uncertain, the situation in the rest of the world in 1998 is as follows: Ammonia is produced at about 310 locations all over the world. About 470 plants were operated by nearly 250 different companies [1481]. The approximate average plant capacity which results from these figures is around 260 000 t/a NH_3. Situation in 1991 is found in [1447].

The geographical distribution of world ammonia capacity together with the apparent capacity utilization in 1994 is shown in Table 44. Europe and North America, which now together have a 25 % capacity share, lost their leading position (54 % in 1969) to Asia, which now accounts for 38 % (17 % in 1969), as may be seen from Figure 121. This

Topsoe, Inc. – EX1003
Page 378 of 1210

Table 44. Geographical distribution of ammonia capacity and capacity utilization rate (1994)

	Capacity share, %	Capacity utilization, %
Western Europe	10.3	83
Eastern Europe	7.6	60
Former Soviet Union	17.7	58
Middle East	4.0	85
Africa	3.2	70
North America	14.2	102
Central America	3.3	95
South America	1.8	79
South and East Asia, Oceania	17.4	84
Asia CPE*	20.5	88
World	100	81

* Centrally planned economies.

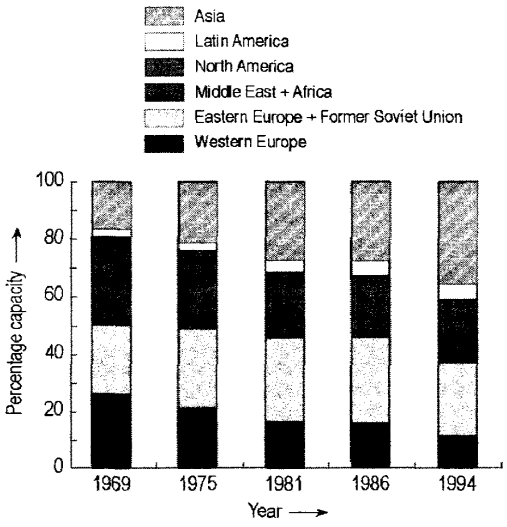


Figure 121. Geographical shift of ammonia world production capacity

development continued and in 1998 more than 40% of the world ammonia capacity is located in Asia.

The major importers of ammonia [1486] are Western Europe (1996: 3.8×10^6 t N) and the United States (1996: 3.4×10^6 t N), whereas, on account of their enormous natural gas reserves, the former Soviet Union (FSU), the Arabian Gulf, and Trinidad are dominant in ammonia export. The former FSU exported, for example, in 1996 4.1×10^6 t N, the Middle East 1.3×10^6 t, Trinidad 1.6×10^6 t N. World ammonia trade in 1996 was around 11×10^6 t N. Values for 1994 are found in [1439].

Topsoe, Inc. – EX1003
Page 379 of 1210

13.2. Feedstock Choice

Natural gas is by far the most economical feedstock for ammonia production, achieving the lowest energy consumption and requiring the lowest investment [404]. This can also be seen from Table 45, which gives an estimate of ammonia production costs in Northwest Europe for different feedstocks using state-of-the-art technological standards. The lump turn key price for the ammonia plant were assumed as $\$ 180 \times 10^6$ for steam reforming of natural gas, $\$ 270 \times 10^6$ for partial oxidation of vacuum residue and $\$ 400 \times 10^6$ for coal-based plants (Capacity 1800 mt/d).

Table 45. Ammonia production costs from various feedstocks in 1998 (600 000 t/a)

Feedstock (process)	Natural gas (steam reforming)	Vacuum residue (partial oxidation)	Coal (partial oxidation)
Feedstock price, $/10^6$ Btu	2.8	1.8	1.5
Total energy consumption, 10^6 Btu/t	27	36	45.5
Feedstock and energy costs, $/t NH_3	75.6	64.8	68.3
Other cash costs, $/t NH_3	28.5	41.0	59.0
Total cash costs, $/t NH_3	104.6	105.8	127.3
Capital related costs*, $/t NH_3	68.4	100.3	143.3
Total costs, $/t NH_3	172.5	206.1	270.6
Total capital**, 10^6 $	250	350	500

* Assumed dept/equity ratio 60:40; depreciation 6%, 8% interest on depts, 16% ROI on equity.

** Total capital (1998) includes turn-key lump sum price for plant and storage, spare parts, catalysts, clients inhouse costs, offsites, working capital (3 months), basis 1,8 DM/$.

At present there is obviously no chance for other feedstocks to compete with steam reforming of natural gas. Only under very special circumstances, for example, in cooperation with a refinery, might partial oxidation of heavy residues be economically justified. It should be noted that the average energy consumption of the steam reforming plants in operation at present is noticeably higher than the example of the most advanced concept presented in Table 45. In Western Europe the combined cost of feedstock and energy — both are actually natural gas energy — is the major determinant of the production cost. Even with most modern plants gas cost are more than 70% of the cash costs and as much as 40% of the total production costs. Gas prices are linked to a greater or lesser extent to the crude oil price but the present so-called interfuel relationship may change in the future because of the general need for less polluting fuels. Today natural gas is still favorably priced in comparison to other fossil fuels. The medium-term forecast is higher prices in Europe and USA. In the low-cost areas, such as the Middle East, Trinidad and Indonesia, where uses of natural gas competing with ammonia production are not growing to a great extent only a moderate increase of the feedstock price is expected [1444], [1445]. In these countries a certain increase in export-oriented ammonia capacity might be expected for the future.

Topsoe, Inc. – EX1003
Page 380 of 1210

Table 46. Percentage of world natural gas reserves and consumption for various geographical areas in 1997 [1442]

	% of world reserves [114.8 × 10^{12} m^3]	% of world consumption [2196.7 × 10^9 m^3 (STP)]
Former Soviet Union	39.2	22.4
(Russian Federation)	(33.2)	(15.1)
Middle East	33.7	7.3
North America	5.8	33.7
Europe (incl. North Sea)	3.8	19.0
Africa	6.8	2.3
Central and South America	4.4	3.9
Asia (incl. Australia and New Zealand)	6.3	11.4

Table 47. World Reserves and Consumption Rate of Fossil Feedstocks in 1994 [1442]

	Coal, t	Mineral oil, t	Natural gas, m^3 (STP)
Reserves	1032 × 10^9	140.9 × 10^9	141 × 10^{12}
Consumption per year	4712 × 10^6	3445 × 10^6	2136 × 10^9
Years of expected supply	219	41	66

Nearly three-quarters of world natural gas reserves (1994) are concentrated in two areas: in the former Soviet Union (39 %) and the Arabian Gulf (34 %) as may be seen from Table 46.

In the very long term, coal has prospects as can be seen from world reserves of fossil energy and their present consumption rate (Table 47).

13.3. Capital Demand for Ammonia Production

The other main contribution to the ammonia production cost are the capital related costs like interests for debts, depreciation and required return on equity. The total capital involved consists of the lump-sum turn- key price for plant and storage facility; an adequate amount of spare parts; catalysts, solvents and lubricants including some reserves; in-house costs for the client for project definition, project supervision, hazard studies, cost for project development and organization, including financing; off-sites; working capital. For non-industrialized and/or remote areas additional investments for infra structure will also be necessary. For the lump-sum turn-key price (LSTK) of a 1800 t/d steam reforming ammonia plant based on natural gas, presently a budget figure of about \$ 170 – 180 × 10^6 can be taken as a reasonable figure [1476], [1477]. Investment cost for partial oxidation plants are considerably higher. One factor is the need for a cryogenic air separation to produce the required quantity of pure oxygen and nitrogen. For a 1800 t (STP)/d ammonia plant based on heavy oil residues the investment for the air separation unit producing 100 bar oxygen and 75 bar nitrogen is around \$ 55 × 10^6 in Western Europe [1478]. Other expensive units are in the gas

Topsoe, Inc. – EX1003
Page 381 of 1210

purification, namely Rectisol for sour gas removal, Claus plant with tail gas unit and liquid nitrogen wash. Soot management, metal recovery and wastewater treatment, and in coal gasification plants the feedstock handling and preparation, are substantial cost contributions. As partial oxidation plants may differ considerably in process configuration, especially for coal feedstock, and are less frequently built — sometimes also not on a lump-sum basis — less reliable data are available. For lump-sum turn-key prices for just the ammonia plant the following figures may be used as a rule of thumb: Steam reforming natural gas 100 %, partial oxidation of heavy oil residues 150 %, coal gasification based plant 220 %.

The abovementioned budget price for the natural gas steam reforming plant consist of about 40 % of material, 30 % of labor (civil work and erection) and 30 % of other costs (transport, engineering, insurance, financing, etc.) [1476], [1477]. Geographical location of the plant may of course influence the LSTK price. Material is bought worldwide in a highly competitive market and prices are at first approximation independent of the country of destination, but the total expenditure for material might differ. For example, in a country of high natural gas prices higher investment for energy saving might be economical and vice versa. Also stricter authority regulations for safety and environmental standards in industrialized countries might cause an increase in cost as well as extreme climatic conditions. Higher material transport costs in distant locations might, for example, be compensated for by lower labor costs, e.g., NW Europe 100 %, US Gulf 90%, Trinidad 90%, the Middle East 70 %.

In conclusion it can be said that the influence of plant location on the LSTK price of the "naked" ammonia plant is often overestimated [1476]. This is not the case for the other investments. Assuming a stand-alone plant (no other ammonia plants existing at the site) the following will apply for the required storage capacity: If the capacity is intended for domestic product use only a storage capacity of about 20 days might be sufficient, if it is intended for export at least a capacity of one month would be appropriate. This is naturally different if the plant is erected at a side where already one or more ammonia plants exist and only a minor or even no increase of tank capacity is necessary. Inventory of spare parts and reserve catalysts will differ for the locations as well as the in-house costs, which will depend for example, on the technical capabilities of the client. Off-site costs can be considerable, for example, when facilities for power generation, water purification and supply, buildings for workshop, material storage and administration have to be included on a grass-root site. In some cases these additional costs might be as high as $\$ 50 \times 10^6$. For remote locations additional investments for infrastructure might be necessary, for example, harbor construction, railway tracks and roads, but this would not be justified for just one stand-alone ammonia plant even at a location with extremely low natural gas prices.

Finally an adequate working capital has to be also included in the calculation of production costs. The cash cost of three month production would be a reasonable assumption for the working capital. Keeping all these factors in mind it becomes clear that the numbers in Figure 122 have only orientating character and that each real

Topsoe, Inc. – EX1003
Page 382 of 1210

ammonia project is a custom-made solution according to the whishes and objectives of the client.

13.4. Other Production Cost Factors

Besides the capital charges, which will depend on equity/debt ratio for the involved capital, interest rates, and anticipated ROI for equity, the other major fixed costs are maintenance, labor, laboratory costs, and overheads. For the annual maintenance costs, usually a percentage of the investment is assumed, generally 3 % for steam reforming plants and 4 % for partial oxidation of heavy feedstocks and coal (this includes material and labor for maintenance). The number of operators depends to some extent on the shift schedule and operating philosophy in the individual company. The number of operators present at a plant has to be sufficient for safe continuous operation and a safe shut down, in the event of a sudden plant trip. The number need not necessarily be sufficient to restart the plant because additional people from off-duty shifts may be called in. Usually 5 – 7 operators are considered as adequate for operating a steam reforming plant; the number in partial oxidation plants is higher. Costs for consumption of catalysts, molecular sieves, inert material, solvents, and lube and seal oil are around 3 \$/t NH_3.

Catalysts have nowadays sufficient service life that change intervals can coordinated with normal turn-arounds. (Years of catalyst service life: primary reformer 2 – 4, secondary reformer > 6, HTS > 6, LTS 2 – 4 (6 with guard bed), methanation > 8, synthesis 10 – 15) (see also [1497]).

An important influence on production cost has, of course, the so-called on-stream factor, the number of production days per year. It is standard practice to assume that a well designed and operated plant should be capable to reach a minimum of 330 days per year, a value on which economic calculations are usually based. Modern plants often achieve higher on-stream factors. A beneficial effect is also that many plants achieve higher capacity than the original design. Plant outages because of operational problems or temporary shut downs for economic reasons because of unfavorable market situation can lower the profitability considerable. The on-stream factor is an average value, because plants should shut down only every 2 to 3 years for a major turn-around for repair and preventive maintenance. Only a very few short unscheduled shut-downs for repair work should occur between two turn-arounds. A start up needs between 15 to 30 hours and consumes a considerable amount of natural gas without an equivalent production (100 000 – 200 000 DM/d).

Overhead costs (administration and general services) also have to be included as cash costs.

Topsoe, Inc. – EX1003
Page 383 of 1210

13.5. Production Costs for Various Geographical Locations

Figure 122 shows an estimate of ammonia production costs at various locations. In this figure the capital-related costs are based on a debt/equity ratio of 60/40. With 6 % depreciation of fixed assets and spare material, 8 % interest on debts and 16 % ROI on equity, corresponding to a total of about 16.5 % of the total capital involved. The total capital includes the LSTK price for plant and storage, cost of the off-sites for an industrialized site, in-house project costs, spare parts and catalyst reserves, working capital.

Admittedly the picture given in Figure 122 is somewhat simplified, but nevertheless some principal conclusions can be drawn from it: The decisive cost factor is the natural gas price as the investment for the areas compared does not differ significantly for reasons discussed above. With inclusion of the high freight cost from the Arabian Gulf

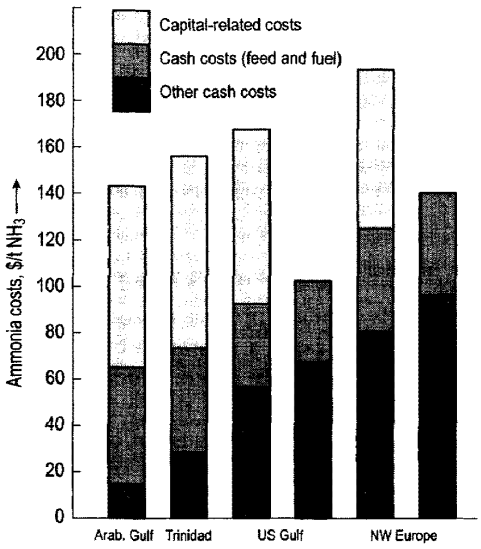


Figure 122. Ammonia production costs at various locations (capacity 600 000 t/a)

	Arab Gulf	Trinidad	US Gulf		NW Europe	
Plant	new	new	new	old	new	old
Natural gas, $/ 10^6 Btu	0.6	1.2	2.2	2.2	2.8	2.8
Feed + fuel, 10^6 Btu/t NH_3	29	28	28	32	27	32
Total capital, 10^6 $	270	250	240	-	250	-
Product use	export	export	domestic	domestic	domestic	domestic

Topsoe, Inc. – EX1003
Page 384 of 1210

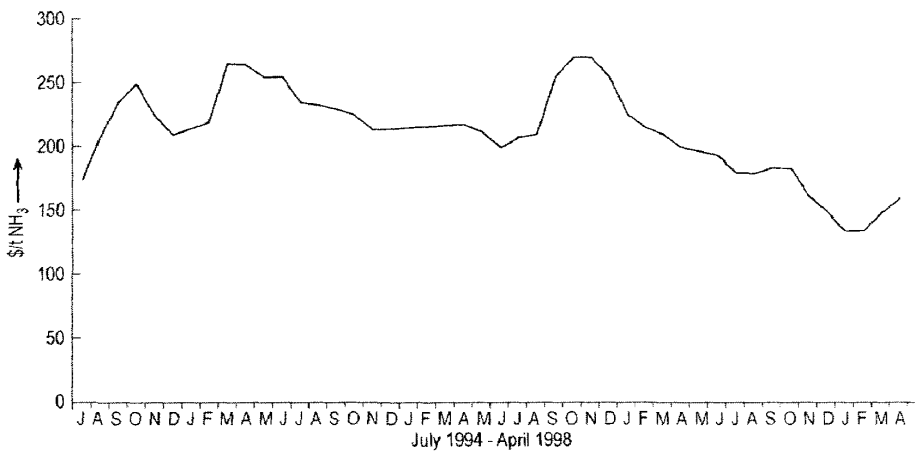


Figure 123. Development of ammonia prices in North-West Europe

a plant there is not competitive against existing world scale capacities in NW Europe and scarcely competitive against a new high efficiency plant in NW Europe. But lower freight rates and higher market prices will make the export to the Asian market out of a new Arabian Gulf plant attractive. Imports to NW Europe come mainly from former Soviet Union (FSU), which in desire of hard currency and on account of their surplus capacity (partially due to lower domestic fertilizer consumption), sell at very competitive prices. As it is rather difficult to guess how the gas will be valued internally (probably 1.6 – 2.3 $/GJ) [1440] an estimate for the production costs in the FSU former was not included in Figure 122. An account of the natural gas situation and prices is presented in [1444]. An advantage are the relatively moderate freight rates from the terminal in Ventspils at the Baltic Sea.

With inclusion of shipping costs, new plant capacities in Trinidad are, according to Figure 122, only marginally competitive against a new plant at the US Gulf, and cannot compete against existing US Gulf productions. But this simple picture might change if the plant is not intended for the free market but for long contract delivery, for example, to the owners own facilities in the United States. India and China are still net importers, Indonesia has surplus capacity, but exports to the Asian market are rather in form of urea than as ammonia. Indonesia and Malaysia together have about 3 % of the proven natural gas reserves, and a reserve/production rate of 30 and 57 respectively. Because of the present Asian financial crisis it is difficult to figure out natural gas prices, but they might range between 0.8 and 1.0 $/10^6 Btu. Production costs are a more or less calculable issue, but the prices are not. When talking of ammonia prices one has to consider that only a part of the ammonia is traded as such, the major part is directly converted by the producers in urea (about 45 %), other solid fertilizers (35 %) or chemical products. As the overseas trade represents only about 8 % of the world

Topsoe, Inc. – EX1003
Page 385 of 1210

ammonia production plant output, variations in the nitrogen fertilizer imports in Asia (mainly China and India) may at time cause substantial price variations as illustrated with the C & F prices of imports in NW Europe (Figure 123, values from Nitrogen magazine). Also of influence are, of course, the changes in the dollar exchange rates to other currencies.

Topsoe, Inc. – EX1003
Page 386 of 1210

Copyright © WILEY-VCH Verlag GmbH, 1999

14. Future Perspectives

It is difficult to venture a prognosis for the future development of ammonia production technology. As about 85% of the ammonia consumption goes into the manufacture of fertilizers, it is obvious that the future of the ammonia industry is very closely bound up with future fertilizer needs and the pattern of the world supply.

Nitrate pollution, which may become a problem in some countries, is sometimes used as an argument against the use of industrially produced "inorganic" or "synthetic" fertilizers and in favor of more "organic" or "natural" fertilizers. But this is a misconception, because degradation of biomass and manure also leads to nitrate run-off. In addition, the amount of this biological material is far to small to supply the increasing demand of the agriculture necessary to feed the growing world population. The solution to the run-off problem therefore can also not consist in cutting back fertilizer application, which would be disastrous in developing countries, but is likely to lie in a better management of the timing of fertilizer application, requiring a better understanding of the biological nitrogen cycle. Estimates of fixed nitrogen from natural sources and antropogenic activities on global basis are found in [1446], [1450].

14.1. Other Nitrogen Fixation Methods for the Future

A fundamental question is whether there are other options for the future than the present ammonia technology, which involves severe temperatures and pressures. The research for new approaches should strive for the following, admittedly rather ambitious and idealized objectives: ambient reaction conditions, less or no consumption of fossil energy, lower investment, simple application, even in remote developing areas, and wide capacity range. As the major demand is in agriculture, biological processes for in vivo conversion of molecular nitrogen into fixed nitrogen would probably be the first choice. Alternatively abiotic processes (in vitro) with homogenous catalysis under mild reaction conditions could be discussed for ammonia production. In addition there are also some reports [1017], [1451], [1452] of resumed research on direct nitrogen oxidation, as was once used in the Birkeland–Eyde process. The use of a plasma processes instead of an electric arc for radiation in a chemo-nuclear process was also discussed [1453].

Topsoe, Inc. – EX1003
Page 387 of 1210

14.1.1. Biological Processes

Certain bacteria and blue-green algae are able to absorb atmospheric nitrogen, by themselves or in symbiosis with a host plant, and transform it into organic nitrogen compounds via intermediate ammonium ions, whereby the host plant indirectly supplies the large amount of energy needed. A well known example is the symbiotic relationship between legumes (e.g., peas, beans, soybeans, lupins) and Rhizobium bacteria, which settle in their root nodules. Ammonia synthesis is performed by the enzyme nitrogenase [1455], [1456]. For the synthesis of the nitrogenase in the cell the so-called NIF gene is responsible. Apart from Rhizobium bacteria a number of other organisms have nitrogen fixation potential, living in symbiosis or providing the required energy from their own metabolism. Genetic engineering to extend biological nitrogen fixation to other plant groups pursues various routes [1457], [1458]:

1) Modifying Rhizobium to broaden its spectrum of host plants
2) Transferring the NIF gene to other bacteria which have a broader spectrum of host plants but have no natural nitrogen-fixing capability
3) Engineering soil bacteria to absorb and convert nitrogen to ammonia and release it to the soil [1459]
4) Inserting the NIF gene directly into plants

Especially the last option, to design nitrogen-fixing species of traditional crops such as wheat, rice, and corn, leads to the following questions: Would it be preferable to fix nitrogen in the leaves where energy is available or in the roots, to which carbohydrates have to be transported? If fixation is performed in the leaves, then how can the problem of the proximity of oxygen generated in the photosynthesis and oxygen-sensitive nitrogenase be dealt with? To what extent will the energy required by a plant to fix nitrogen affect overall productivity?

The last question has been discussed in some detail [1460]. For the conversion of molecular nitrogen into ammonia the following stoichiometric equation may be formulated:

$$0.5\ N_2 + 1.5\ H_2O \longrightarrow NH_3 + 0.75\ O_2 \qquad (100)$$

$$\Delta F^0_{298} = +340\ \text{kJ/mol},\ \Delta H^0_{298} = +383\ \text{kJ/mol}$$

The oxidation of glucose generates 3140 kJ/mol and with 100 % efficiency only about 0.11 mol of glucose would be required to produce one mole of ammonia. This ideal can, of course, never be achieved. In the molybdenum-containing nitrogenase a transfer of eight electrons is involved in one catalytic cycle:

$$N_2 + 8\ H^+ + 8\ e^- \longrightarrow 2\ NH_3 + H_2 \qquad (101)$$

As seen from this equation two electrons are "wasted" in forming molecular hydrogen, which also seems to be unavoidable in vivo. This stoichiometry suggests an efficiency of 75 %, but if additional functions associated with fixation are taken into

Topsoe, Inc. – EX1003
Page 388 of 1210

account, a maximum overall efficiency of 10 – 15 % is estimated for the enzyme, and even less for the bacteria as a whole [1461]. In investigations on Rizobium [1462], [1463] it was shown for the nodulated roots of peas that 12 g of glucose are consumed to produce 1 g of fixed nitrogen. Using this efficiency for the case where all the fixed nitrogen in the plant is supplied only via this route, a yield loss of 18 % would result. Nitrate, for example from a fertilizer, absorbed by the plant is transformed to ammonia involving a free energy change $\Delta F^0_{298} = +331$, which is comparable to the free energy change for converting molecular nitrogen to ammonia, as shown in the stoichiometric equation above.

This is a somewhat surprising result, which suggests that nitrogen supply with nitrate has an energetic advantage over the biological fixation process [1464]. A definite answer to this question will only be possible when genetically engineered nitrogen-fixing plants are available in sufficient amounts for field tests. There is no doubt that in the foreseeable future genetic engineering will succeed in designing nitrogen-fixing plants for agricultural crops, and that these modified plants will be used on a large scale for securing the food supply for a growing number of people in the developing countries.

But until this will become a reality, application of selected natural nitrogen-fixing microorganisms to crops would be an intermediate solution to reduce industrial fertilizer consumption. In the United States field tests with *Azospirillium* applied to corn could demonstrate a considerable increase in harvest yield [1458]. Careful directed application of blue-green algae, (*Anabaena azolla*) and water fern (*Azolla pinata*) in tropical rice fields is also very promising [1465], [1466]. Unlike most diazotropic bacteria, blue-green algae are self-sufficient in that they themselves produce the energy necessary for the nitrogen fixation by photosynthesis.

14.1.2. Abiotic Processes [1460]

Possibilities of converting molecular nitrogen into ammonia in homogeneous solution by using organometallic complexes have been studied from around 1966 onwards. Numerous investigations resulted in the laboratory-scale synthesis of ammonia , but with rather low yields. The prospects of this route are not judged to be very promising in terms of energy consumption and with respect to the costs of the rather sophisticated catalyst systems. Photochemical methods [1467], [1468] to produce ammonia at ambient temperature and atmospheric pressure conditions in presence of a catalyst have up to now attained ammonia yields which are far too low to be economically attractive.

For a detailed review of biological and abiotic nitrogen fixation, see [1469] and [1460]; additional literature references can be found in [1448] – [1450], [1454], [1455].

Topsoe, Inc. – EX1003
Page 389 of 1210

14.2. Conclusions

Based on the foregoing discussion and the evaluation of present technology (see also [404]) and research efforts one may formulate the scenario for the future development of ammonia production as follows:

1) For the major part, ammonia production in the next 15 to 20 years will rely on the classic ammonia synthesis reaction combining nitrogen and hydrogen using a catalyst at elevated temperature and pressure in a recycle process.
2) It is very likely that genetic engineering will succeed in modifying some classical crops for biological nitrogen fixation and that large-scale application will occur predominantly in areas with strongly growing populations to secure the increasing food demand. This development may be pushed by the fact that compared to the classical fertilizer route less capital and less energy would be needed. This may happen within the next 15 – 20 years, but time estimates are always difficult. But even with the introduction of this new approach, traditional ammonia synthesis will continue to operate in parallel, because it might be necessary to supplement the biological nitrogen fixation with classical fertilizers. In addition, the existing ammonia plants represent a considerable capital investment and a great number of them may reliably operate for at least another 20 to 30 years from a mere technical point of view.
3) Natural gas will remain the preferred feedstock of present ammonia production technology in the medium term (15 – 20 years) as may be assumed from the world energy balance shown in Table 47. Partial oxidation of heavy hydrocarbon residues will be limited to special cases and coal gasification might not play a major role in this period.
4) Ammonia technology will not change fundamentally, at least not in the next 10 to 15 years. Even if there are radical, unforeseeable developments, they will need some time to mature to commercial applicability. With the traditional concepts, the margins for additional improvements have become rather small after years of continuous research and development. Thus further progress may be confined to minor improvements of individual process steps, catalysts and equipment design.
5) The best energy figure so far achieved in commercial production is around 28 GJ/t NH_3. With the new ruthenium-based catalysts M. W. Kellogg claims a figure of 27.2 GJ/t NH_3. Further reduction would need an even more active catalyst to operate at a much lower synthesis pressure, for example, at around 30 bar, which is the usual pressure level of steam reforming. The probability of finding such a catalyst is rather small after all the years of intensive research. Figures between 27 and 28 GJ/t NH_3 already correspond to a rather high efficiency of around 75 % with respect to the theoretical minimum of 20.9 GJ/t NH_3 (calculated as stoichiometric methane demand, see Section 5.1.3).

Topsoe, Inc. – EX1003
Page 390 of 1210

6) The bulk of ammonia production in the near future will still be produced in world-scale plants of capacity 1000 – 2000 t NH_3/d. Small capacities will be limited to locations where special logistical, financial or feedstock conditions favor them.
7) Most newer technology developments will mainly reduce investment costs and increase operational reliability. Smaller integrated process units, such as exchanger reformers in various configurations, contribute to this reduction and will achieve additional savings by simplifying piping and instrumentation. Progress in instrumentation and computer control could reduce the effective overall energy consumption achieved over the course of a year by tuning plants continuously to optimal operating conditions.

Topsoe, Inc. – EX1003
Page 391 of 1210

Copyright © WILEY-VCH Verlag GmbH, 1999

15. References

[1] C. Bosch, Nobel price address 1933.
[2] I. Hay, G. D. Honti, in G. D. Honti (ed.): *The Nitrogen Industry, part 1,* Akademiai Kiado, Budapest 1976, pp. 68–73.
[3] F. Ritter, F. Walter in K. Winnacker, E. Weingaertner (eds.): *Chemische Technologie,* **vol. 2,** Carl Hanser, München 1950 pp. 368.
[4] J. Hess, *Chem. Ind. (Berlin)* **45** (1922) 538.
[5] *Chem. Ind. (Berlin)* **48** (1925) 718.
[6] F-W. Kampmann, W. Porz, F-K. Frorath, H. Oertel: *"Calcium Carbide",* in Ullmann's Encyclopedia of Industrial Chemistry, **vol. 4,** VCH Weinheim.
[7] G. Plumpe: *Die I. G. Farbenindustrie — Wirtschaft, Technik und Politik,* Dunker & Humblot, Berlin 1990.
[8] A. Mittasch: Chemische Grundlegung der industriellen Ammoniakkatalyse, Ludwigshafen 1953.
[9] B. Timm, W. Danz in V. Sanchelli (ed.): *"Fertilizer Nitrogen, its chemistry and production",* Reinhold, New York 1964, p. 40.
[10] A. Mittasch, W. Frankenburger, *Z. Elektrochem. Angew. Phys. Chem.* **35** (1929) 920.
[11] F. Haber, G. van Oordt, *Z. Anorg. Allg. Chem.* **43** (1904) 111; **44** (1905) 341; **47** (1905) 42.
[12] W. Nernst, *Z. Elektrochem. Angew. Phys. Chem.* **13** (1907) 521.
[13] F. Jost, *Z. Anorg. Allg. Chem.* **57** (19108) 414.
[14] M. Appl, *"The Haber-Bosch Heritage: The Ammonia Production Technology"* 50th Anniversary of the IFA Technical Conference, September 25–26, 1997, Sevilla, Spain.
[15] F. Haber, R. Le Rossignol, *Ber. Dtsch. Chem. Ges.* **40** (1907) 2144.
[16] P. Krassa, *Chem. Ztg. Chem. Appar.* **90** (1966) 104.
[17] F. Haber, *Z. Elektrochem. Angew. Phys. Chem.* **14** (1908) 181; **20** (1914) 597.
[18] R. Le Rossignol, *Naturwissenschaften* **16** (1928) 1070.
[19] B. Timm, *Chem. Ing. Tech.* **35** (1963) no. 12, 817.
[20] F. A. Henglein, *Chem. Ztg.* **75** (1951) 345–350, 389–392, 407–410.
[21] K. Holdermann: *Im Banne der Chemie – Carl Bosch,* Econ Verlag, Düsseldorf 1953.
[22] M. Appl in W. F. Furter (ed.): *A Century of Chemical Engineering,* Plenum Publ. Corp., New York, 1982 p. 29.
[23] M. Appl : *IIChE Conference,* Hyderabad, 1986; *Indian Chemical Engineer* **XXIX** (1987) no. 1, 7–29.
[24] S. A. Topham: *Catalysis, Science and Technology,* vol. 7, Springer-Verlag, Berlin–Heidelberg–New York–Tokyo pp. 1–50.
[25] A. Nagel et al.: *Stickstoff,* Schriftenreihe der BASF, 2nd ed., 1991.
[26] F. Duftschmidt, F. Markert, *Chem. Ing. Techn.* **32,** (1960), 806–811.
[27] M. Appl, *Nitrogen* **100** (1976) 47.
[28] L. Pauling: *The Nature of the Chemical Bond,* 3rd ed., Cornell University Press, Ithaca, N.Y., 1960.
L. Pauling: *Die Natur der chemischen Bindung,* 3rd ed., Verlag Chemie, Weinheim 1968.
[29] F. Hund, *Z. Phys.* **31** (1925) 95.
[30] L. Haar, *J. Phys. Chem. Ref. Data* **7** (1978) no. 3, 635–792.
[31] *VDI Forschungsh.* 1979, no. 596, VDI-Verlag Düsseldorf.
[32] F. Din: *Thermodynamic Functions of Gases,* **vol. 1,** Butterworths, London 1956.

Topsoe, Inc. – EX1003
Page 392 of 1210

[33] A. Nielsen: *An Investigation on Promoted Iron Catalysts for the Syntheses of Ammonia*, Gjellerup, Kopenhagen 1968.

[34] M. P. Wukalowitsch et al., *Teploenergetika (Moscow)* **7** (1960) no. 1, 63–69; *Chem. Ing. Tech.* **33** (1961) no. 4, 5, 291, 292.

[35] R. Döring: *Thermodynamische Eigenschaften von Ammoniak (R 717)*, Verlag C. F. Müller, Karlsruhe 1978; *Ki Klima + Kälte Ing.*, extra no. 5.

[36] *Landolt-Börnstein*, vol. 2, part 1–10, Springer Verlag, Berlin–Heidelberg–New York 1971.

[37] *Handbuch der Kältetechnik*, **vol. IV**, Springer Verlag, Berlin–Heidelberg–New York 1956.

[38] A. Kumagai, T. Toriumi, *J. Chem. Eng. Data* **16** (1971) no. 3, 293.

[39] R. Wiebe, V. I. Gaddy, *J. Am. Chem. Soc.* **60** (1938) 2300.

[40] E. P. Bartlett, H. L. Cupples, T. H. Tremearne, *J. Am. Chem. Soc.* **50** (1928) 1275.

[41] E. P. Bartlett et al., *J. Am. Chem. Soc.* **52** (1930) 1363.

[42] B. H. Sage, R. H. Olds, W. N. Lacey, *Ind. Eng. Chem.* **40** (1948) 1453.

[43] A. Michels et al., *Appl. Sci. Res.* **A3** (1953) 1.

[44] A. Michels et al., *Appl. Sci. Res.* **A4** (1954) 180.

[45] R. Plank, *Kältetechnik* **12** (1960) 282–283.

[46] W. K. Chung, *Can. J. Chem. Eng.* **55** (1977) no. 6, 707–711.

[47] G. G. Fuller, *Ind. Eng. Chem. Fundam.* **15** (1976) no. 4, 254–257.

[48] B. D. Djordjevic et al., *Chem. Eng. Sci.* **32** (1977) no. 9, 1103–1107.

[49] M. Zander, W. Thomas, *J. Chem. Eng. Data* **24** (1979) 1.

[50] L. J. Christiansen, J. Kjaer: *Enthalpy Tables of Ideal Gases*, Haldor Topsøe, Copenhagen 1982, p. 1.

[51] Dow Chemical Corp., *JANAF Thermodynamical Tables*, 2nd ed., 1971, NSRDS NBS-37.

[52] L. Haar, *J. Res. Natl. Bur. Stand. Sect. A* **72** (1968) 2.

[53] E. R. Grahl, *Pet. Process.* **8** (1953) 562.

[54] R. G. Barile, G. Thodos, *Can. J. Chem. Eng.* **43** (1965) 137–142.

[55] C. G. Alesandrini et al., *Ind. Eng. Chem. Process Des. Dev.* **11** (1972) no. 2, 253.

[56] H. Zeininger, *Chem. Ing. Tech.* **45** (1973) no. 17, 1067.

[57] H. H. Reamer, B. H. Saga, *J. Chem. Eng. Data* **4** (1959) no. 4, 303.

[58] K. V. Reddy, A. Husain, *Ind. Eng. Chem. Process Des. Dev.* **19** (1980) 580–586.

[59] H. Masuoka et al., *J. Chem. Eng. Jpn.* **10** (1977) no. 3, 171–175.

[60] A. T. Larson, C. A. Black, *J. Am. Chem. Soc.* **47** (1925) 1015.

[61] A. Michels et al., *Physica (Utrecht)* **16** (1950) 831–838.

[62] A. Michels et al., *Physica (Utrecht)* **25** (1959) 840.

[63] G. Guerreri, *Hydrocarbon Process.* **49** (1970) no. 12, 74–76.

[64] H. H. Reamer, B. H. Saga, *J. Chem. Eng. Data* **4** (1959) no. 2, 152.

[65] R. Wiebe, T. H. Tremearne, *J. Am. Chem. Soc.* **55** (1933) 975.

[66] F. Heise, *Ber. Bunsenges. Phys. Chem.* **76** (1972) 938.

[67] B. Lefrancois, C. Vaniscotte, *Genie Chim.* **83** (1960) no. 5, 139.

[68] H.-D. Müller, *Z. Phys. Chem. (Leipzig)* **255** (1974) no. 3, 486.

[69] B. I. Lee, M. G. Kesler, *AIChE J.* **21** (1975) no. 3, 510.

[70] K. Konoki et al., *J. Chem. Eng. Jpn.* **5** (1972) no. 2, 103–107.

[71] G. Sarashina, *J. Chem. Eng. Jpn.* **7** (1974) no. 6, 421–425.

[72] R. Heide, *Luft Kältetech.* **7** (1971) no. 3, 128–130.

[73] I. Durant, *J. Chem. Soc.* 1934, no. 135, 730.

[74] Yu. V. Efremov, I. F. Golubev, *Russ. J. Phys. Chem. Eng. (Engl. Transl.)* **36** (1962) no. 5, 521–522.

Topsoe, Inc. – EX1003
Page 393 of 1210

[75] J. A. Jossi et al., *AIChE J.* **8** (1962) no. 1, 59–63.
[76] H. Shimotake, G. Thodos, *AIChE J.* **9** (1963) no. 1, 63.
[77] B. K. Sun, T. S. Storwick, *J. Chem. Eng. Data* **24** (1979) no. 2, 88.
[78] I. T. Perelsatein, E. B. Parushin, *Kholod. Tekh.*, 1980, no. 6, 34–37.
[79] A. K. Pal, A. K. Barura, *J. Chem. Phys.* **47** (1967) no. 1, 216.
[80] E. A. Mason, L. Mouchik, *J. Chem. Phys.* **36** (1962) no. 10, 2746.
[81] A. B. Rakshit, C. S. Roy, A. K. Barua, *J. of Chemical Physics* **59** (1973) 3633–3688.
[82] D. P. Needham, H. Ziebland, *Int. J. Heat Mass Transfer* **8** (1965) 1387–1414.
[83] A. M. P. Tans, *Ind. Chem.* **39** (1963) no. 3, 141.
[84] R. Afshar, S. Murad, S. C. Saxna, *Chem. Eng. Commun.* **10** (1981) 1–11.
[85] D. A. Kouremenos, *Kältetechnik* **20** (1968) no. 10, 319.
[86] A. O. S. Maczek, P. Gray, *Trans. Faraday Soc.* **66** (1970) 127.
[87] P. Correia et al., *Ber. Bunsenges. Phys. Chem.* **72** (1968) 393.
[88] W. Inkofer et al., 15th AIChE Ammonia Safety Symp., Denver 1970; *Ammonia Plant Saf.* **13** (1971) 67.
[89] L. J. Gillespie, J. A. Beattie, *Phys. Rev.* **36** (1930) 743.
[90] S. Peter, H. Wenzel, *Chem. Ing. Tech.* **45** (1973) no. 9 + 10, 573.
[91] F. Haber, S. Tamaru, *Z. Elektrochem. Angew. Phys. Chem.* **21** (1915) 191.
[92] L. J. Gillespie, J. A. Beattie, *Phys. Rev.* **36** (1930) 1008.
[93] V. G. Telegin, G. M. Lutskii, *J. Appl. Chem. USSR (Engl. Transl)* **37** (1964) 2271.
[94] L. J. Christiansen in W. A. Nielsen (ed.): *Ammonia — Catalysis and Manufacture,* Springer, Heidelberg 1995 pp. 1–16.
[95] I. Granet, *Pet. Refiner* **33** (1954) no. 5, 205.
[96] I. Granet, P. Kass, *Pet. Refiner* **32** (1953) no. 3, 149.
[97] A. K. Pal, A. K. Barua, *J. Chem. Phys.* **47** (1967) 116.
[98] H. R., Christen, *Grundlagen der allgemeinen und anorganischen Chemie,* Verlag Sauerländer, Arau; Diesterweg-Salle, Frankfurt am Main, 4. Auflage, 1973, p. 482.
[99] W. G. Frankenburger, *Catalysis 1954–1960* **3** (1955) 171.
[100] R. Brill et al., *Ber. Bunsenges. Phys. Chem.* **73** (1969) 999.
[101] A. Ozaki, K. Aika: "The Synthesis of Ammonia by Heterogeneous Catalysis," in R. W. F. Hardy et al. (eds.): *A Treatise on Dinitrogen Fixation,* Sect. I and II, Wiley, New York 1979, pp. 169–247.
[102] A. Ozaki, K. Aika: "Catalytic Activation of Dinitrogen," in R. H. Anderson, M. Boudart (eds.): *Catalysis: Science and Technology,* **vol. 1**, Springer Verlag, Berlin–Heidelberg–New York 1981, pp. 87–158.
[103] P. H. Emmett in E. Drauglis, R. I. Jaffee (eds.): *The Physical Basis for Heterogenous Catalysis,* Plenum Publ., New York 1975, p. 3.
[104] K. Tamaru in J. Chatts et al. (eds.): *New Trends in the Chemistry of Nitrogen Fixation,* Academic Press, New York 1980, p. 13.
[105] G. A. Somorjai: *Chemistry in Two Dimensions: Surfaces,* Cornell Press, Ithaca 1981.
[106] G. Ertl, J. Küppers: *Low Electrons and Surface Chemistry,* 2nd ed., VCH Verlagsgesellschaft, Weinheim 1985.
[107] G. Ertl in J. R. Jennings (ed.): *Catalytic Ammonia Synthesis,* Plenum Press, New York – London 1991, pp. 109–131.
[108] P. Stolze in A. Nielsen (ed.): *Ammonia — Catalysis and Manufacture,* Springer-Verlag, Heidelberg 1995, pp. 17–102.

Topsoe, Inc. – EX1003
Page 394 of 1210

[109] G. Ertl: "Kinetics of Chemical Processes on Well-defined Surfaces," in R. H. Anderson, M. Boudart (eds.): *Catalysis: Science and Technology,* **vol. 4,** Springer-Verlag, Berlin–Heidelberg–New York 1983, pp. 257 – 282.

[110] M. Boudart, "Kinetics and Mechanism of Ammonia Synthesis," *Catal. Rev. Sci. Eng.* **23** (1981) 1 – 15.

[111] J. J. F. Scholten et al., *Trans. Faraday Soc.* **55** (1959) 2166.

[112] J. J. F. Scholten, Dissertation, Techn. Hochschule Delft 1959.

[113] P. Mars et al. in J. H. de Boer (ed.): *The Mechanism of Heterogenous Catalysis,* Elsevier, Amsterdam 1960, p. 66.

[114] K. Tanaka, A. Matsumaya, *J. Res. Inst. Catal. Hokkaido Univ.* **2** (1971) 87.

[115] M. I. Temkin, *Adv. Catal.* **28** (1979) 173.

[116] P. H. Emmett, S. Brunauer, *J. Am. Chem. Soc.* **56** (1934) 35.

[117] H. S. Taylor, *J. Am. Chem. Soc.* **53** (1931) 578.

[118] W. Frankenburger, *Z. Elektrochem.* **39** (1933) 45, 97, 269.

[119] K. T. Kozhenova, M. Y. Kagan, *Zh. Fiz. Khim.* **14** (1940) 1250.

[120] P. H. Emmett, S. Braunauer, *J. Am. Chem. Soc.* **59** (1937) 1553.

[121] L. M. Aparicio, J. A. Dumesic: *Topics in Catalysis,* vol. 1, Baltzer AG, Basel 1994, p. 233 – 252.

[122] D. R. Strongin, G. A. Somorjai in J. R. Jennings (ed.): *Catalytic Ammonia Synthesis,* Plenum Press, New York 1991, pp. 133 – 178.

[123] G. Ertl, M. Huber, S. B. Lee, Z. Paal, M. Weiss, *Appl. Surf. Sci.* **8** (1981) 373.

[124] T. Nakata, S. Matsushita, *J. Phys. Chem.* **72** (1968) 458.

[125] V. I. Shvachko et al., *Kinet. Katal.* **7** (1966) 635, 734.

[126] Y. Morikawa, A. Ozaki, *J. Catal.* **12** (1968) 145.

[127] R. Westrik, P. Zwieterring, *Proc. K. Ned. Akad. Wet. Ser. B: Palaeontol. Geol. Phys. Chem.* **56** (1953) 492.

[128] R. Brill et al., *Angew. Chem.* **79** (1967) 905.

[129] H. Taube, Dissertation, Freie Universität Berlin 1968.

[130] R. Brill, *Ber. Bunsenges. Phys. Chem.* **75** (1971) 455.

[131] J. A. Dumesic, H. Topsøe, S. Khammouma, M. Boudart, *J. Catal.* **37** (1975) 503; see also [352].

[132] F. Boszo et al., *J. Cat.* **49** (1977) 103.

[133] G. Ertl et al., *J. Vac. Sci. Technol.* **13** (1976) 314.

[134] G. Ertl et al., *Surf. Sci.* **114** (1982) 515.

[135] G. A. Somorjai et al.: *Topics in Catalysis,* vol. 1, Baltzer AG, Basel 1994, p. 215 – 231.

[136] N. D. Spencer, R. C. Schoonmaker, G. A. Somorjai, *J. Catal.* **74** (1982) 129.

[137] G. Ertl: "Plenary Lecture," in T. Seiyama, K. Tanabe (eds.): *New Horizons in Catalysis, Proc. Int. Congr. Catal. 7th 1980,* Elsevier 1981, p. 21.

[138] F. Bozso, G. Ertl, *J. Catal.* **49** (1977) 18; **50** (1977) 519.

[139] R. Schlögl: "Ammonia Synthesis," in G. Ertl, H. Knözinger, J. Weitcamp (eds.): *Handbook of Heterogeneous Catalysis,* **vol. 4,** Wiley-VCH, Weinheim 1997, pp. 1698 – 1748.

[140] B. Fastrup: *Topics in Catalysis,* **vol. 1,** Baltzer AG, Basel 1994, p. 273 – 283.

[141] L. Falicov, G. A. Somorjai, *Proc. Natl. Akad. Sci. USA* **82** (1985) 2207.

[142] G. Ertl et al., *Surf. Sci.* **114** (1982) 527.

[143] G. Ertl et al., *Surface Science* **114** (1982) 527.

[144] S. R. Bare, D. R. Strongin, G. A. Somorjai, *J. Phys. Chem.* **90** (1987) 4726.

[145] D. R. Strongin et al., *J. Catal.* **103** (1987) 289.

Topsoe, Inc. – EX1003
Page 395 of 1210

[146] M. Bowker: *Topics in Catalysis,* **vol. 1,** Baltzer AG, Basel 1994, p. 265 – 271.
[147] C. Rettner, H. Stein, *Phys. Rev. Let.* **56** (1987) 2768.
[148] C. Rettner, H. Stein, *J. Chem. Phys.* **87** (1987) 770.
[149] J. K. Norskov: *Topics in Catalysis,* **vol. 1,** Baltzer AG, Basel 1994, p. 385 – 403.
[150] M. Grunze et al., *Phys. Rev. Lett.* **53** (1984) 850.
[151] L. J. Whitman, C. E. Bartosch, W. Ho, G. Strasser, M. Grunze, *Phys: Rev. Lett.* **56** (1986) 1984.
[152] L. J. Whitman, C. E. Bartosch, W. Ho, *J. Chem. Phys.* **85** (1986) 3688.
[153] M. Grunze, G. Strasser, M. Golze, *Appl. Phys.* **A 44** (1987) 19.
[154] J. Schütze et al.: *Topics in Catalysis,* **vol. 1,** Baltzer AG, Basel 1994, p. 195 – 214.
[155] M. Boudart: *Topics in Catalysis,* **vol. 1,** Baltzer AG, Basel 1994, p. 405 – 414.
[156] R. Schlögl, *Ammonia Synthesis,* in Handbook of Heteregeneous Catalysis (ed. G. Ertl, H. Knörzinger, J. Weitkamp), **vol. 4,** VCH Weinheim, 1997.
[157] A. Nielsen, *Catal. Rev.,* **4,** (1970) no. 1, 1.
[158] W. A. Schmidt, *Angew. Chem.* **80** (1968) 151.
[159] V. I. Shvachko et al., *Kinet. Katal.* **7** (1966) 635, 734.
[160] R. Brill et al., *Z. Phys. Chem. (Wiesbaden)* **64** (1969) 215.
[161] Y. Morikawa, A. Ozaki, *J. Catal.* **12** (1968) 145.
[162] N. Takezawa, I. Toyoshima, *J. Catal.* **19** (1970) 271.
[163] S. Carra, R. Ugo, *J. Catal.* **15** (1969) 435.
[164] I. I. Tretyakov et al., *Dokl. Akad. Nauk SSSR* **175** (1967) 1332.
[165] G. Parravano, *J. Catal.* **8** (1967) 29.
[166] M. I. Temkin et al., *Kinet. Katal.* **4** (1963) 494.
[167] S. R. Logan, J. Philp, *J. Catal.* **11** (1968) 1.
[168] N. Takezawa, P. H. Emmett, *J. Catal.* **11** (1968) 131.
[169] G. Schulz-Ekloff, *Ber. Bunsenges. Phys. Chem.* **75** (1971) 110.
[170] A. Nielsen et al., *J. Catal.* **3** (1964) 68.
[171] P. E. H. Nielsen, unpublished work, Haldor Topsøe A/S, cited in [253].
[172] S. R. Tennison in J. R. Jennings (ed.): *Catalytic Ammonia Synthesis,* Plenum Press, New York and London 1991, pp. 303 – 364.
[173] K. Aika, K. Tamaru in W. A. Nielsen (ed.): *Ammonia — Catalysis and Manufacture,* Springer-Verlag, Heidelberg 1995, pp. 103 – 148.
[174] J. N. Nwalor, J. G. Goodwin jr.: *Topics in Catalysis,* **vol. 1,** Baltzer AG, Basel 1994, p. 228 – 148.
[175] K. Aika, A. Ozaki, *J. Catal.* **16** (1970) 97.
[176] D. A. King, F. Sebba, *J. Catal.* **4** (1965) 253.
[177] N. Segal, F. Sebba, *J. Catal.* **8** (1967) 105.
[178] K. Aika, A. Ozaki, *J. Catal.* **14** (1969) 311.
[179] G. E. Moore, F. C. Unterwald, *J. Chem. Phys.* **48** (1968) 5409, 5393.
[180] M. R. Hillis et al., *Trans. Faraday Soc.* **62** (1966) 3570.
[181] K. Azuma, *Nature (London)* **190** (1961) no. 4775, 530.
[182] H. Kubota, M. Shindo, *J. Chem. Eng. Jpn.* **23** (1959) 242.
[183] G. Gramatica, N. Pernicone in J. R. Jennings (ed.): *Catalytic Ammonia Synthesis,* Plenum Press, New York – London 1991, pp. 211 – 252.
[184] J. P. Hansen in A. Nielsen (ed.): *Ammonia — Catalysis and Manufacture,* Springer-Verlag, Heidelberg 1995, pp. 149 – 190.
[185] M. I. Temkin, V. Pyzhev, *Acta Physicochim. URSS* **12** (1940) 327.

Topsoe, Inc. – EX1003
Page 396 of 1210

[186] M. I. Temkin, *Zh. Fiz. Khim.* **24** (1950) 1312.
[187] R. M. Adams, E. W. Comings, *Chem. Eng. Prog.* **49** (1953) 359.
[188] P. H. Emmett, J. T. Kummer, *Ind. Eng. Chem.* **35** (1943) 677.
[189] D. Annable, *Chem. Eng. Sci (Genie Chimique)* **1** (1952) no. 4, 145.
[190] C. Bokhoven et al., *Catalysis 1954 – 1960* **3** (1955) 265.
[191] R. Brill, *J. Chem. Phys.* **19** (1951) 1047.
[192] S. Kiperman, V. S. Granovskaya, *Zh. Fiz. Khim.* **26** (1952) 1615.
[193] M. I. Temkin et al., *Kinet. Katal.* **4** (1963) 224.
[194] A. Ozaki et al., *Proc. R. Soc. London Ser. A* **258** (1960) 47.
[195] M. I. Temkin, N. M. Morozow, E. M. Shapatina, *Kinet. Catal. (Engl. Trans.)* **4** (1963) 565.
[196] ICI: *Catalyst Handbook with Special Reference to Unit Processes in Ammonia and Hydrogen Manufacture*, Wolfe Scientific Books, London 1970.
[197] K. Aika, A. Ozaki, *J. Catal.* **13** (1969) 232.
[198] A. Nielsen, J. Kjaer, B. Hansen, *J. Catal.* **3** (1964) 68.
[199] A. Ozaki, H. S. Taylor, M. Boudart, *Proc. R. Soc. London Ser. A* **258** (1960) 47.
[200] R. Brill, *J. Catal.* **16** (1970) 16.
[201] A. Cappelli, A. Collina, *Inst. Chem. Eng. Symp. Ser.* **35** (1972) 10.
[202] G. Buzzi-Ferraris et al., *Eng. Chem. Sci.* **29** (1974) 1621.
[203] U. Guacci et al., *Ind. Eng. Chem.* **16** (1977) 166.
[204] D. G. Dyson, J. M. Simson, *Ind. Eng. Chem. Fundam.* **7** (1968) 601.
[205] M. Bowker, I. Parker, K. Waugh, *Appl. Catal.* **14** (1985) 101.
[206] M. Bowker, I. Parker, K. Waugh, *Surface Science* **97** (1988) L 233.
[207] P. Stolze, J. K. Norskov, *Phys Rev. Let.* **55** (1985) 2502.
[208] P. Stolze, J. K. Norskov, *Surface Science* **189/190** (1987) 91; *Surface Science* **197** (1988) L 230; *J. Catal.* **110** (1988) 1.
[209] J. A. Dumesic, A. A. Trevino, *J. Catal.* **116** (1989) 119.
[210] P. Stolze, *Phys. Sci.* **36** (1987) 824.
[211] E. Wicke, *Z. Elektrochem.* **60** (1956) 774.
[212] A. Wheeler, *Adv. Catal.* **3** (1951) 249.
[213] T. Akehata et al., *Can. J. Chem. Eng.* **39** (1961) 127.
[214] C. Bokhoven, W. van Raayen, *J. Phys. Chem.* **58** (1954) 471.
[215] J. Hoogschagen, *Ind. Eng. Chem.* **47** (1955) 906.
[216] J. B. Hansen in A. Nielsen (ed.): *Ammonia – Catalysis and Manufacture*, Springer, Heidelberg 1995, p. 184.
[217] D. G. Dyson, J. M. Simon, *Ind. Eng. Chem. Fundam.* **7** (1968) 605.
[218] C. Chu, O. A. Hougen, *Chem. Eng. Sci.* **17** (1962) 167.
[219] C. P. P. Singh, N. D. Saraf, *Ind. Eng. Chem. Process Des. Dev.* **18** (1979) 364.
[220] A. Cappelli, A. Collina, *Inst. Chem. Eng. Symp. Ser.* **35** (1972) 10.
[221] C. Wagner, *Z. Phys. Chem. (Leipzig)* **193** (1943) 1.
[222] E. W. Thiele, *Ind. Eng. Chem.* **31** (1939) 916.
[223] J. Kjaer: *Calculation of Ammonia Converters on an Electronic Digital Computer*, Akademisk Forlag, Kopenhagen 1963.
[224] J. J. Hag, I. M. Palla, *Br. Chem. Eng.* **8** (1963) no. 3, 171.
[225] J. Kubec, J. Burianova, Z. Burianec, *Int. Chem. Eng.* **14** (1974) no. 4, 629.
[226] R. F. Baddour, R. L. T. Brian, B. A. Logeais, J. P. Eymery, *Chem. Eng. Sci.* **20** (1965) 281. R. L. T. Brian, R. F. Baddour, J. P. Eymery, *Chem. Eng. Sci.* **20** (1965) 297.
[227] M. J. Shah, *Ind. Eng. Chem.* **59** (1967) no. 1, 73.

Topsoe, Inc. – EX1003
Page 397 of 1210

[228] A. D. Stephens, *Chem. Eng. Sci.* **30** (1975) 11.
[229] L. D. Gaines, *Ind. Eng. Chem. Process. Des. Dev.* **16** (1977) no. 3, 381.
[230] T. Huberich, R. Krabetz in A. V. Slack (ed.): *Ammonia,* **part III,** Marcel Dekker, New York – Basel 1977.
[231] A. Mittasch: *Geschichte der Ammoniaksynthese,* Verlag Chemie, Weinheim 1951.
[232] A. Mittasch, *Adv. Catal.* **2** (1950) 82.
[233] C. Bosch, *Z. Elektrochem. Angew. Phys. Chem.* **24** (1918) 361.
[234] K. Aika, J. Yamaguchi, A. Ozaki, *Chem. Lett.* 1973, 161; cited in [102]
[235] S. R. Logan, C. Kemball, *Trans. Faraday Soc.* **56** (1960) 144.
[236] E. P. Perman, *Proc. R. Soc. London* **76** (1905) 167.
[237] F. Haber, G. von Oørdt, *Z. Anorg. Allg. Chem.* **43** (1905) 111.
[238] BASF, DE 249447, 1910.
[239] A. T. Larson, R. S. Tour, *Chem. Metall. Eng.* **26** (1922) 493, 555, 588, 647.
[240] J. A. Almquist, E. D. Crittenden, *Ind. Eng. Chem.* **18** (1926) 1307.
[241] G. L. Bridger et al., *Chem. Eng. Prog.* **43** (1947) 291.
[242] H. Hinrichs, *Br. Chem. Eng.* **12** (1967) 1745.
[243] Indianapolis Center for Advanced Research, US 4235749, 1980.
[244] Topsøe, GB 989242, 1961.
[245] P. D. Rabina et al., *Khim. Prom.* **5** (1969) 350.
[246] The Gas Council London, DE-OS 1931758, 1969 (T. Nicklin, D. Oyden).
[247] Chevron Res. Comp., US 3653831, 1972.
[248] J. L. Carter, C. G. Savini, US 3472794, 1969; SU 173204 (749 751) 23-4, 1961.
[249] The Lummus Comp., US 3992328, 1976; The Lummus Comp., US 3951862, 1976.
[250] Ammonia Casale, IT-A 47920 A, 1979.
[251] ICI, EP-A 7830276, 1979.
[252] Société Chimique de La Grande Paroisse, Azote et Produits Chimiques, US 3839229, 1974.
[253] A. Nielsen: "Ammonia Synthesis: Exploratory and Applied Research," *Catal. Rev. Sci. Eng.* **23** (1981) 17 – 51.
[254] D. C. Silverman, M. Boudart, *J. Catal.* **77** (1982) 208.
[255] C. Peters et al., *Z. Elektrochem.* **64** (1960) 1194.
[256] K. Schäfer, *Z. Elektrochem.* **64** (1960) 1190.
[257] P. H. Emmett, S. Brunauer, *J. Am. Chem. Soc.* **59** (1937) 310; *J. Catal.* **15** (1969) 90.
[258] S. Brunauer, P. H. Emmett, *J. Am. Chem. Soc.* **62** (1940) 1732.
[259] D. C. Silverman, Dissertation, Stanford University 1976.
[260] H. C. Chen, R. B. Anderson, *J. Colloid Interface Sci.* **38** (1972) 535; *J. Catal.* **28** (1973) 161.
[261] G. Ertl, N. Thiele, *Appl. Surf. Sci.* **3** (1979) 99.
[262] R. Hosemann, A. Preisinger, W. Vogel, *Ber. Bunsenges. Phys. Chem.* **70** (1966) 786. H. Ludwiszek, A. Preisinger, A. Fischer, R. Hosemann, A. Schönfel, W. Vogel, *J. Catal.* **51** (1977) 326.
R. Buhl, A. Preisinger, *Surf. Sci.* **47** (1975)344.
[263] W. S. Borghard, M. Boudart, *J. Catal.* **80** (1983) 194.
[264] R. Schlögl in J. R. Jennings (ed.): *Catalytic Ammonia Synthesis,* Plenum Press, New York – London 1991, pp. 19 – 108.
[265] C. Peters, K. Schäfer, R. Krabetz, *Z. Elektrochem.* **64** (1960) 1194.
[266] M. E. Dry, J. A. K. du Plessis, B. M. Leuteritz, *J. Catal.* **6** (1966) 194.
[267] R. Krabetz, C. Peters, *Angew. Chem. Int. Ed. Engl.* **4** (1965) 341.
[268] A. Kazusaka, I. Toyoshima, *Z. Phys. Chem. (Wiesbaden)* **128** (1982) 111.

Topsoe, Inc. – EX1003
Page 398 of 1210

[269] L. M. Dmitrenko et al., *Proc. Int. Congr. Catal. 4th 1968* **1** (1971) 404.
[270] K. Karaslavova, M. D. Anastasov, *Geterog. Katal. Tr. Mezhdunar. Simp. 3rd 1975,* 1978, 297.
[271] K. Z. Zakieva, P. D. Rabina, J. E. Zubova, I. E. Klaustova, N. Z. Pavlova, L. D. Kusnetzov, *Tr. Mosk. Khim. Tekhnol. Inst. im. D. I. Mendeleeva,* 1973, no. 73, 120.
[272] B. Aleksic, N. Jovanovic, A. Terlecki-Baricevic, *Geterog. Katal. Tr. Mezhdunar. Simp. 3rd 1975,* 1978, 147.
[273] M. G. Berengarten et al., *Kinet. Katal.* **15** (1974) 250.
[274] Yu. N. Artyukh, M. T. Rusov, N. A. Boldyreva, *Kinet. Katal.* **8** (1967) 1319.
[275] P. J. Smith, D. W. Taylor, D. A. Dowden, C. Kemball, D. Tayler, *Appl. Catal.* **3** (1982) 303.
[276] I. D. Kusnetsov, *Chem. Tech. (Leipzig)* **15** (1963) 211.
[277] J. Herrmann et al., *Chem. Tech. (Leipzig)* **18** (1966) 472.
[278] D. G. Ivanov, N. D. Anastasov, *Chem. Tech. (Leipzig)* **15** (1963) 229.
[279] L. Sokol, *Chem. Tech. (Leipzig)* **15** (1963) 214.
[280] U. Zardi, A. Antonini, *Nitrogen* **122** (1979) 33.
[281] M. C. Sze, *Hydrocarbon Process.* **56** (1977) no. 12, 127.
[282] N. Pernicone, G. Liberti, G. Servi in C. Eyraud, M. Escoubes (eds.): *Progress in Vacuum Mikrobalance Techniques,* **vol. 3,** Heyden, London 1975, p. 304.
[283] A. Mittasch, E. Keunecke, *Z. Elektrochem. Angew. Phys. Chem.* **38** (1932) 666.
[284] H. Uchida, I. Terao, K. Ogawa, *Bull. Chem. Soc. Jpn.* **37** (1964) 653.
[285] N. Pernicone, F. Traina: *Preparation of Catalysts,* **vol. 2,** Elsevier, Amsterdam 1979, p. 321.
[286] B. S. Clausen, S. Mørup, H. Tropsøe, R. Candis, E. J. Jensen, A. Baranski, A. Pattek, *J. Phys. (Orsay, Fr.)* **37** (1976) C6-245.
[287] P. D. Rabina, T. Y. Malysheva, L. D. Kusnetzov, V. A. Batyrev, *Kinet. Catal. (Engl. Transl.)* **11** (1970) 1030.
[288] A. Mittasch, E. Keunecke, *Z. Elektrochem. Angew. Phys. Chem.* **38** (1932) 666.
[289] R. Westrik, *J. Chem. Phys.* **21** (1953) 2049.
[290] M. E. Dry, L. C. Ferreira, *J. Catal.* **7** (1967) 352.
[291] F. Garbassi, G. Fagherazzi, M. C. Calcaterra, *J. Catal.* **26** (1972) 338.
[292] A. C. Turnock, H. P. Eugster, *J. Petrol.* **3** (1962) 533.
[293] R. Brill, *Allg. Prakt. Chem.* **17** (1966) 94.
[294] R. Hosemann et al., *Ber. Bunsenges. Phys. Chem.* **70** (1966) 769.
[295] L. v. Bogdandy et al., *Ber. Bunsenges. Phys. Chem.* **67** (1963) 958.
[296] N. Pernicone et al., *Catal. Proc. Int. Congr. 5th 1972* 1973, 1241.
[297] V. Solbakken, A. Solbakken, P. H. Emmett, *J. Catal.* **15** (1969) 90.
[298] K. C. Wough et al.: *Topics in Catalysis,* **vol. 1,** Baltzer AG, Basel 1994, p. 295–301.
[299] G. Ertl: "Zum Mechanismus der Ammoniaksynthese," *Nachr. Chem. Tech. Lab.* **31** (1983) no. 3, 178.
[300] Y. Sasa, M. Uda, I. Toyoshima, *Chem. Lett.* **no. 12,** 1982, 2011.
[301] S. K. Egeubaev et al., *Kinet. Katal.* **6** (1965) no. 4, 676; also see [9] and [269]
[302] M. M. Ivanov et al., *Kinet. Katal.* **9** (1968) 1239; **10** (1969) 349.
[303] J. G. Ommen et al., *J. Catal.* **38** (1975) 120.
[304] A. Ozaki et al., *Catal. Proc. Int. Congr. 5th 1972* **2** (1973) 1251.
[305] E. K. Enikeev, A. V. Krylova, *Kinet. Katal.* **3** (1962) 116; *Chem. Abstr.* **57** (1962) 7965.
[306] G. Ertl, M. Weiss, S. B. Lee, *Chem. Phys. Lett.* **60** (1979) 391.
[307] M. C. Tsai et al., *Surf. Sci.* **155** (1985) 387.
[308] J. A. Dumesic, Dissertation, Stanford University 1974.
[309] T. Yoshioka, J. Koezuka, I. Toyoshima, *J. Catal.* **14** (1969) 281.

Topsoe, Inc. – EX1003
Page 399 of 1210

[310] Y. E. Sinyak, Thesis, Inst. of Chemical Physics Akad. Sci. USSR, Moscow 1960; cited in [301]
[311] Haldor Topsøe, ZA 645279, 1964; also see [315]
[312] I. P. Nukhlenov et al., *J. Appl. Chem. USSR (Engl. Transl.)* **37** (1964) 248.
[313] V. N. Anokhin et al., *J. Appl. Chem. USSR (Engl. Transl.)* **35** (1962) 29.
[314] A. Baranski et al., *J. Catal.* **26** (1972) 286.
[315] V. Věk, *Chem. Ing. Tech.* **45** (1973) 608.
[316] K. Feind, *Chem. Ing. Techn.* **38** (1966) 1081.
[317] Chemie Linz, US 3965246, 1976.
[318] E. Comandini, A. Passariello, U. Zardi, *Ammonia Plant Saf.* **23** (1981) 44.
[319] Wargons Aktiebolag, Haldor Topsøe, US 3243386, 1961.
[320] Kuhlmann, GB 1080838, 1964.
[321] Kuhlmann, CH 434218, 1964.
[322] Haldor Topsøe, GB 989242, 1961.
[323] ICI, BE 576059, 1959.
[324] IG Farbenind., DE 748620, 1938.
[325] I. V. Nicolescu et al., *Genie Chim.* **82** (1959) 33.
[326] I. V. Nicolescu et al., *Chem. Tech. (Leipzig)* **15** (1963) 226.
[327] S.I.R.I. Societa Italiana Ricerche Industriali, US 4073749, 1978.
[328] ICI, GB 1484864, 1977.
[329] J. E. Jarvan, H. U. Larsen, unpublished work, (Haldor Topsøe A/S) cited in [253].
[330] A. T. Larson et al., *Chem. Trade J. Chem. Eng.* **100** (1937) 403.
[331] G. M. Schwab (ed.): *Handbuch der Katalyse,* **vol. 5: Heterogene Katalyse II,** Springer-Verlag, Wien 1957, p. 566.
[332] A. M. Rubinštejn et al., *Izv. Akad. Nauk SSSR Ser. Khim.* 1966, 1707; *Chem. Zentralbl.* 1968, 8 – 0639.
[333] A. M. Rubinštejn et al., *Kinet. Katal.* **6** (1965) 285; *Chem. Zentralbl.* 1965, 42 – 0622.
[334] P. Bussiere, R. Dutartre, G. A. Martin, J. P. Mathieu, *C. R. Hebd. Seances Acad. Sci. Ser. C* **280** (1975) 1133. R. Dutartre, M. Primet, G. A. Martin, *React. Kinet. Catal. Lett.* **3** (1975) 249.
[335] H. Topsøe, J. A. Dumesic, E. C. Derouane, B. S. Clausen, S. Mørup, J. Villadsen, N. Topsøe in: *Preparation of Catalysts,* **vol. 2,** Elsevier, Amsterdam 1979, p. 365.
H. Topsøe et al. in T. Seiyama, K. Tanabe (eds.), *New Horizons in Catalysis, Proc. Int. Congr. Catal. 7th 1980,* Elsevier 1981.
[336] M. Boudart, A. Delbouille, J. A. Dumesic,. S. Khammouna, H. Topsøe, *J. Catal.* **37** (1975) 486.
J. A. Dumesic, H. Topsøe, S. Khammouna, M. Boudart, *J. Catal.* **37** (1975) 503.
J. A. Dumesic, H. Topsøe, M. Boudart, *J. Catal.* **37** (1975) 513.
[337] The Lummus Comp., GB 1529823, 1978.
[338] IG Farbenind., DE 554855, 1928; FR 611139, 1935.
[339] N. W. Sseljakow, SU 48210, 1936; *Chem. Zentralbl.* **1937** II, 119.
[340] N. N. Pschenitzyn et al., *Zh. Prikl. Khim. (Leningrad)* **13** (1940) 76; *Chem. Zentralbl.* 1940, no. II, 1932.
[341] Österreichische Stickstoffwerke, AT 252957, 1964.
[342] M. V. Tovlin et al., *Kinet. Katal.* **7** (1966) 749; *Chem. Zentralbl.* 1966, 42 – 0597.
[343] H. Flood, D. G. Hill, *Z. Elektrochem.* **61** (1957) 18.
[344] J. Valcha, *Chem. Tech. (Leipzig)* **15** (1963) 222.
[345] Österreichische Stickstoffwerke, GB 833878, 1958.
[346] D. B. Christozvonov et al., *Int. Chem. Eng.* **9** (1969) 387.

Topsoe, Inc. – EX1003
Page 400 of 1210

[347] SU 169077, 1963.
[348] H. Uchida, N. Todo, *Bull. Chem. Soc. Jpn.* **29** (1956) 20; also see [346]
[349] Z. N. Bardik et al., *Khim. Promst. (Moscow)* **42** (1966) 351.
[350] CS 117658, 1966 (L. Sokol).
[351] P. A. Strelzov et al., *Khim. Promst. (Moscow)* **43** (1967) no. 1, 46.
[352] H. Amariglio, G. Rambeau, in G. C. Bond et al. (eds.): *Proc. Int. Congr. Catal. 6th 1976,* Chemical Society London 1977, p. 1113.
[353] T. L. Joseph, *Trans. AJME* **120** (1936) 72.
[354] P. K. Stangway, H. U. Ross, *Trans. AJME* **242** (1968) 1981.
[355] M. Moukassi et al., *Metall. Trans.* **B14** (1983) 125.
[356] Y. K. Rao et al., *Metall. Trans.* **B10** (1979) 243.
[357] J. O. Edström, *J. ISI* **175** (1953) 289.
[358] A. Baranski, M. Lagan, A. Pattek, A. Reizer, L. J. Christiansen, H. Topsøe in: *Preparation of Catalysts,* **vol. 2,** Elsevier, Amsterdam 1979, p. 353.
[359] O. Gramtica, N. Pernicone in: J. R. Jennings (ed.): *Catalytic Ammonia Synthesis,* Plenum Press, New York and London pp. 211–252.
[360] A. Baranski et al., *J. Catal.* **26** (1972), 286–294.
[361] A. I. Forster, B. J. Cromarty "Theory and practice of steam reforming" *ICI/Katalco/KTI, UOP 3rd Annual International Seminar of Hydrogen Plant Operation,* Chicago, USA (June 1995).
[362] J. R. Rostrup-Nielsen, "Catalytic steam reforming" in J. R. Anderson, M. Boudart (Eds.) *Catalytis, Science and technology,* Springer, Berlin (1984), pp. 1–130.
[363] L. Altrup, *Journal of Catalytis,* **109,** 241–251 (1988).
[364] A. Baranski et al., *Archivum Hutniktva* **25** (1980) 153.
[365] A. Baranski et al., *Appl. Catal.* **3** (1982) 207.
[366] A. Baranski et al., *Appl. Catal.* **19** (1985) 417.
[367] A. Pattek-Janczyk et al., *Appl. Catal.* **6** (1983) 35.
[368] J. A. Burnett et al., *Ind. Eng. Chem.* **45** (1953) 1678.
[369] R. Royen, G. H. Langhans, *Z. Anorg. Allg. Chem.* **315** (1962) 1.
[370] P. H. Emmett, S. Brunauer, *J. Am. Chem. Soc.* **52** (1930) 2682; **62** (1940) 1732.
[371] I. A. Smirnov et al., *Kinet. Katal.* **6** (1965) 351.
[372] I. A. Smirnov, *Kinet. Katal.* **7** (1966) 107.
[373] P. E. Højlund Nielsen, paper at the ACS meeting, Washington 1983.
[374] P. E. Højlund Nielsen inW. A. Nielsen (ed.): *Ammonia — Catalysis and Manufacture,* Springer-Verlag, Heidelberg 1995, pp. 191–199.
[375] P. E. Højlund Nielsen inJ. R. Jennings (ed.): *Catalytic Ammonia Synthesis,* Plenum Press, New York 1991, pp. 285–301.
[376] P. Stolze, *Phys. Sci.* **36** (1983) 824.
[377] P. Stolze, J. K. Nørskov, *J. Vac. Sci. Technol.* **A5** (1987) 581.
[378] T. Kirkerød, P. Skaugset, Abstracts of IV Nordic Symp. on Catalysts, Trondheim 1991.
[379] I. P. Sidorov, K. E. Istomina, *Chem. Abstr.* **54** (1960) 6049.
[380] H. Hinrichs, *Chem. Ing. Tech.* **40** (1968) 723.
[381] L. N. Marakhovets et al., *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* **15** (1972) no. 5, 735.
[382] R. Brill et al., *Ber. Bunsenges. Phys. Chem.* **72** (1968) 1218.
[383] J. D. Bulatnikova et al., *Zh. Fiz. Khim.* **32** (1958) 2717.
[384] H. J. Hansen in V. Sauchelli (ed.): *Fertilizer Nitrogen, its Chemistry and Technology,* Reinhold Publ. Co., New York 1964.

Topsoe, Inc. – EX1003
Page 401 of 1210

[385] I. Dybkjaer, E. A. Gam, AIChE Symposium on Safety in Ammonia Plants, San Francisco, Calif., 1984; *Ammonia Plant Saf.* **25** (1985) 15.
[386] A. Ozaki, *Acc. Chem. Res.* **14** (1981) 16.
[387] F. Haber, *Z. Elektrochem.* **16** (1910) 244.
[388] A. Ozaki, K. Urabe, K. Shimazaki, S. Sumiya: *Preparation of Catalysts,* **vol. 2:** Scientific Basis for the Preparation of Heterogenous Catalysts, Elsevier, Amsterdam 1979, p. 381.
[389] British Petroleum Co., US 4163775, 1979.
[390] F. F. Gadallah et al. in G. Poncelet et al. (eds.): *Preparation of Catalysts,* **vol. 3,** Elsevier, Amsterdam 1983.
[391] GB 1 468 441, 1977.
[392] GB 174 079, 1985.
[393] D. J. Lowe, B. E. Smith, R. N. F. Thornely in. P. M. Harrison (ed.): *Metalloproteins,* **Part I.** Verlag Chemie 1985 p. 207.
[394] O. Glemser, *Naturwissenschaften* **37** (1950) 539.
[395] *Nitrogen* **193** (1991) 17–21.
[396] W. K. Taylor, S. A. Hall, D. G. Heath, ICI/CFDC Technical Symp., Shanghai 1989.
[397] J. P. Shirez, J. R. LeBlanc, Kellogg Ammonia Club Meeting, San Francisco 1989.
[398] T. A. Czuppon, S. A. Knez, 41th AIChE Ammonia Safety Symp., Boston 1996; *Ammonia Plant Saf.* **37** (1997) 34.
[399] A. V. Slack, G. Russel James (eds.): *Ammonia,* part I–IV, Marcel Dekker, New York 1973/74.
[400] S. Strelzoff: *Technology and Manufacture of Ammonia,* Wiley-Interscience, New York 1981.
[401] F. J. Brykowski (ed.): *Ammonia and Synthesis Gas,* Noyes Data Corp., Park Ridge, N.J., 1981, p. 280.
[402] I. Dybkjaer in W. A. Nielsen (ed.): *Ammonia — Catalysis and Manufacture,* Springer-Verlag, Heidelberg 1995, pp. 199–327.
[403] C. W. Hooper in J. R. Jennings (ed.): *Catalytic Ammonia Synthesis,* Plenum Press, New York 1991, pp. 253–283.
[404] M. Appl: *Ammonia, Methanol Hydrogen, Carbon Monoxide — Modern Production Technologies,* CRU, London 1997.
[405] D. Wagner, J. F. Meckel, K. H. Laue in A. I. More (ed.), *Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol. 4th 1981* 1982, 471.
[406] *Nitrogen* 1975, no. 97, 35.
[407] T. Grundt, K. Christiansen in A. I. More (ed.), *Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol. 4th 1981* 1982, 73.
[408] H. Wendt, *Chem. Ing. Tech.* **56** (1984) no. 4, 265.
[409] G. A. Crawford, S. Benzimra, *Fertilizer '85 Conference (British Sulphur),* London, Feb. 1985.
[410] The Ultimate in Ammonia/Urea Studies, Fertecon 1991.
[411] K. J. Mundo, *Chem. Ing. Tech.* **45** (1973) no. 10 a, 632.
[412] T. A. Czuppon, L. J. Buividas, *Hydrocarbon Process.* **58** (1979) no. 9, 197.
[413] J. Y. Livingston, *Hydrocarbon Process.* **50** (Jan. 1971) 126.
[414] H. W. Neukermans, J. P. Schurmans, 26th AIChE Symp. Saf. Ammonia Plants, Montreal 1981.
[415] B. W. Burklow, R. L. Coleman, 21st AIChE Ammonia Safety Symp., Atlantic City, 1976; *Ammonia Plant Saf.* **19** (1977) 21.
[416] M. H. Hyman, *Hydrogen Processing, 47, 7* (1968) 131.
[417] K. Atwood, C. B. Knight, *"Reforming Kinetics and Catalysis"* in V. A. Slack, G. Russel James, Ammonia, Marcel Dekker Inc, New York, 1973, 145–174.

Topsoe, Inc. – EX1003
Page 402 of 1210

[418] J. R. Rostrup-Nielsen, *Catalysts Today*, **19**, 305–324 (1993).

[419] B. J. Cromarty, "Carbon formation and removal in the primary reforming process", *ICI/ Katalco Technical papers, ICI Group 113W/075/2 CATPREF.*

[420] H. J. Renner, F. Marschner, G. Hochgesandt, "Gas Production" in Ullmann's Encyclopedia of Industrial Chemistry, VCH, Weinheim, **vol. A 12**, p. 190.

[421] Nitrogen **166** (1987) 24–31.

[422] K. Kochloefl, "Steam reforming" in *Handbook of Heterogeneous Catalysis* (ed. G. Ertl, H. Knörzinger, J. Weitkamp), VCH Weinheim, 1997, **vol. 4**, 1819–1931.

[423] J. M. Moe, E. R. Gerhard, *56th AIChE National Meeting*, Mai 1965, Preprint 36d.

[424] D. A. Lihou, *Chem. Process Engineering*, Sept. 1965, 487.

[425] G. W. Bridger, G. C. Chinchen, "Hydrocarbon Reforming Catalysts" in, *Catalysts Handbook*, Wolfe Scientific, London 1970, 82.

[426] M. Appl, H. Gössling, *Chem. Ztg*, **96** (1972), 135.

[427] British Patents 953 877; 1 003 707; 1 040 066 (ICI).

[428] B. J. Cormarty, **Nitrogen '91:** "British Sulphur International Conference, Copenhagen (Jun 1991).

[429] *Nitrogen*, **232** (Mar-Apr 1998), 45.

[430] Nitrogen **214** (1995) 38–56.

[431] J. Thuillier, F. Pons, 22nd AIChE Ammonia Safety Symp., Aug 1977, Los Angeles; *Ammonia Plant Saf.* **20** (1978) 89.

[432] S. I. Ziolkowski, "Heat Flux and Pressure Drop", *in A. v. Slack, G. R. James (eds.), Ammonia*, Marcel Dekker, Inc. New York (1973), **Part I**, pp. 213–220.

[433] M. Leva, *Ind. Engng. Chem.* **39**, *(1947) 657.*

[434] J. Beck, Advances in Chemistry and Chemical Engineering, *3rd ed.*, Academic Press, New York (1962) p. 234.

[435] P. T. L. Brian, *AlChE J.*, **9**, 6 (1963).

[436] V. S. Beskovm V. P. Kuzin, M. G. Slinko, *Int. Chem. Engng. 5*, 2 (1965).

[437] S. Ergun, *Chem. Engng. Progress 48*, 2 (1952) 89.

[438] T. Kuen Yen, *Chem. Engng. Progress*, (March 1967) 173.

[439] B. J. Cromarty, "The use of computer simulations in primary steam reformers", *ICI Katalco Technical Paper.*

[440] F. C. Roesler, *Chem. Engng. Sci.*, 22 (1967) 1325.

[441] H. C. Hottel, E. S. Cohen, *AlChE Journ.* **4**, *1*, (1958) 3.

[442] H. C. Hottel, *J. Fuel 34*, (1961) 220.

[443] H. C. Hottel, A. F. Sarofim, *Int, J. Heat Mass Tranfer*, **8** (1965) 1153.

[444] I. Dybkjaer, *Fuel Processing Technology*, 42 (1995) 85–107.

[445] B. R. Fisher, "Failure mechanismus, Inspection techniques and repair methodes; ICI's reformer tube changing policy" *ICI Katalco Technical Papers 31 W/126/2/IMTOF.*

[446] G. Russel James, "Furnace Designs" in *A: V. Slack, G. Russel James (eds.): Ammonia*, **part I** *Marcel Dekker Inc*, New York 1973, 221–251.

[447] The Uhde Reformer, Uhde brochure Hi 118 1500 11/91.

[448] P. W. Farnell, R. J. Huges "Secondary Reforming: *Theory and Application", ICI Katalco, Technical papers, ICI Group 524/1270/0/SREF.*

[449] T. S. Christensen, I. Dybkaer, L. Hansen, I. I. Primdahl, 39th AIChE Ammonias Safety Symposium, October 3–6, 1994, Vancouver, BC, Canada; *Ammonia Plant Saf.* **35** (1995), 205.

[450] Nitrogen **217** (1995), 26–30.

Topsoe, Inc. – EX1003
Page 403 of 1210

[451] K. L. Blanchard, J. R. LeBlanc, 39th AIChE Ammonia Safety Symposium, October 3–6, 1994, Vancouver, BC, Canada; *Ammonia Plant Saf.* **35** (1995), 195.
[452] J. R. LeBlanc, R. V. Schneider, R. B. Strait, "Production of Methanol" in W.-H., Cheng, H.. H. Kung (Eds.): "Methanol Production and Use", Marcel Dekker, Inc., New York 1994, p. 91–93.
[453] P. W. Farnell, 38th AIChE Ammonia Safety Symposium, Sep. 1993, Orlando; *Ammonia Plant Saf.* **34** (1995).
[454] S. Wirtz, H. D. Marsch, M. Severin; *Nitrogen* **222** (1996) 33–35.
[455] J. M. Rhine, R. J. Tucker, "Modelling of Gas-Fired Furnaces and Boilers", McGraw-Hill in Associatione with British Gas plc London (1991), p. 191.
[456] L. Olsen, I. I. Primdahl, Institute of Energy Symposium on Modelling – Profitable Application to Industrial Processes, Birmingham, England, June 23, 1992.
[457] R. G. Cockerham, G. Percival, *Trans. Inst. Gas. Eng.* **107** (1957/58) 390/433.
[458] H. Jockel, B. E. Triebskorn, *Hydrocarbon Process.* **52** (1973) no. 1, 93.
[459] W. Rall, *Erdöl Kohle Erdgas Petrochem.* **20** (1967) no. 5, 351.
[460] H. Jockel, *GWF Gas Wasserfach* **110** (1969) no. 21, 561.
[461] T. Ishiguro, *Hydrocarbon Process.* **47** (1968) no. 2, 87.
[462] N N. Clark., W. G. S. Henson, 32rd AIChE Ammonia Safety Symp., Minneapolis; *Ammonia Plant Saf.* **28** (1987) 99.
[463] B. J. Cromatry, *Nitrogen* **191** (1991)30 – 34.
[464] R. Vannby, S. Winter-Madsen, 36th AIChE Ammonia Safety Symp., Nov. 1991, Los Angeles; *Ammonia Plant Saf.* **32** (1987) 122.
[465] B. J. Cromatry, B. J. Crewdson, *The Application of Pre-reforming in the Ammonia and Hydrogen Industries*, ICI Catalco Tech. Paper, 59W/0590/0/CAT2.
[466] K. Elkins, *Feedstock Flexibility Options*, ICI Catalco Tech. Paper, 313/035/0REF.
[467] P. W. Farnell, *Pre-Reforming — a Retrofit Case Study*, ICI Catalco Tech. Paper, 291W/025/0/IMTOF.
[468] W. D. Verduijn, 37th AIChE Ammonia Safety Symp., San Antonio 1992; *Ammonia Plant Saf.* **33** (1993) 165.
[469] S. E. Nielsen, I. Dybkaer, 41th AIChE Ammonia Safety Symp., Boston 1996; *Ammonia Plant Saf.* **37** (1997) 125.
[470] B. J. Cromarty, B. J. Crewdson, "The application of pre-reforming in the ammonia and hydrogen industries" ICI Katalco Technical Papers (59W/0590/0/CAT2).
[471] *Nitrogen* **178** (1989) 30 – 39.
[472] K. J. Elkins, I. C. Jeffery, D. Kitchen, A. Pinto, "Nitrogen '91", *International Conference (British Sulphur)*, Copenhagen, June 4 – 6, 1991.
[473] P. M. Armitage, J. Elkins, D. Kitchen, AIChE Ammonia Safety Symp., Los Angeles 1991; *Ammonia Plant Saf.* **32** (1992) 111.
[474] D. Kitchen, K. Mansfield, Eurogas 92, Trondheim 1992.
[475] R. Schneider, Kellogg Ammonia Club Meeting, San Diego 1990.
[476] J. R. LeBlanc, Asia Nitrogen: British Sulphur Intern. Conf., Singapore 1996.
[477] *Ammonia*, Kellogg brochure, HG 1/96.
[478] J. R. LeBlanc, R. Schneider, K. W. Wright, 40th AIChE Ammonia Safety Symp., Tucson [1995].
[479] M. W. Kellogg, EP-A 106076, 1983 (C. van Dijk et al.)
[480] M. Sosna, I. Bondar, B. Gunko, B. J. Grotz, 38th AIChE Ammonia Safety Symposium, Sep. 1993, Orlando, *Ammonia Plant Saf.* **34**, (1995).
[481] B. J. Grotz, Frankini, J. Magallenes, HTI Quaterly (Winter 94/95).

Topsoe, Inc. – EX1003
Page 404 of 1210

[482] *Nitrogen* **200** (1992) 39.
[483] *Nitrogen* **214** (1995) 38 – 56.
[484] R. Vannby, S. E. L. Winter Madsen "New developments in synthesis gas production", Topsoe company publication.
[485] H. D. Marsch, N. Thiagarajan, 33rd AIChE Ammonia Safety Symp., Denver 1988; *Ammonia Plant Saf.* **29** (1989) 195.
[486] H. J. Herbort, Uhde Ammonia Symp., Dortmund 1992.
[487] N. Thiagarajan, Uhde Ammonia Symp., Dortmund 1992.
[488] H. D. Marsch, N. Thiagarajan, 37th AIChE Ammonia Safety Symp., San Antonio 1992; *Ammonia Plant Saf.* **33** (1992) 108.
[489] *Chem. Eng. (N.Y.)* **73** (1966) 24.
[490] *Hydrocarbon Process.* **63** (1984) no. 4, 103.
[491] I. Dybkær, *Fuel Processing Technology* **42** (1995) 85 – 107.
[492] E. Bartholome, H. Nonnemacher, The Fifth World Petroleum Congress, May 1959..
[493] P. Degand, V. Julemont, J. P. Schurmans, 36th AIChE Ammonia Safety Symposium, Nov 1991 Los Angeles; *Ammonia Plant Saf.* **32** (1992) 129.
[494] *Nitrogen* **195** (1992) 22 – 36.
[495] T. Tomita, M. Kitugawa, *Chem. Ing. Tech.* **49** (1977) no. 6, 469.
[496] *Nitrogen* **144** (1983) 33.
[497] T. Tomita et al., Special Paper 9, 11th World Petroleum Congress, London 1983.
[498] *Nitrogen* **168** (1987) 29 – 37.
[499] *Nitrogen* **186** (1990) 21 – 30.
[500] O. J. Quartulli, *Hydrocarbon Process.* **44** (1965) no. 4, 151.
[501] J. Davies, D. A. Lihou, *Chem. Process Eng. (London)* **52** (1971) no. 4, 71.
[502] H. D. Marsch, H. J. Herbort, *Hydrocarbon Process.* **61** (1982) no. 6, 101.
[503] A. I. Forster, B. J. Cromatry, *The Theory and Practice of Steam Reforming,* ICI/Catalco/KTI/UOP, 3rd Int. Seminar on Hydrogen Plant Operation, Chicago 1995.
[504] G. W. Bridger, W. Wyrwas, *Chem. Process Eng. (London)* **48** (1967) no. 9, 101.
[505] F. Marschner, H. J. Renner, *Hydrocarbon Process.* **61** (1982) no. 4, 176.
[506] J. R. Rostrup-Nielsen, 17th AIChE Ammonia Safety Symp., Aug 1972, Minneapolis; *Ammonia Plant Saf.* **15** (1973) 82.
[507] G. W. Bridger, *Oil Gas J.* **74** (Feb. 16, 1976) 73; 20th AIChE Ammonia Safety Symp., Boston 1975; *Ammonia Plant Saf.* **18** (1976) 24. *Ammonia Plant Saf.* **18** (1976) 24.
[508] D. P. Rounthwaite, *Plant Oper. Prog.* **2** (1983) no. 2, 127.
[509] *Nitrogen* **174** (1988) 23 – 24.
[510] *Nitrogen* **166** (1987) 24 – 31.
[511] *Nitrogen* **167** (1987) 31 – 36.
[512] H. Fricke, *Chem. Ztg.* **96** (1972) 123.
[513] S. Strelzoff, *Hydrocarbon Process.* **53** (1974) no. 12, 79.
[514] E. Supp, M. Brejc, "Gas Production" in, Ullmann's Encyclopedia of Industrial Chemistry, VCH Weinheim, 5th edition, **vol. A 12,** p. 190.
[515] K. T. Lee "Partial oxidation of Hydrocarbons" in A. V. Slack, G. Russel James (ed) Ammonia, **Part I,** 293 – 294, Marcel Dekker, New York, 1973.
[516] Fertilizer Manual ed. by United Nations Industrial Development Organization (UNIDO), Vienna Austria and International Fertilizer Development Center (IFDC); Muscle Schoals, Alabama (USA) Klewer Academic Publishers, Dordrecht, The Netherlands, 1998.
[517] G. E. Weismantel, L. Ricci, *Chem. Eng. (N.Y.)* **86** (1979) no. 21, 57.

Topsoe, Inc. – EX1003
Page 405 of 1210

[518] Du Bois Eastman, "The production of synthesis gas by partial oxydation" *Fifth World Petroleum Congress, 1959, New York, Proceed, Section IV, p. 153–161.*
[519] S. C. Singer, L. W. Ter Har, *Cemical Engng. Progress,* **57,** 7 (1961), 68–74.
[520] "Shell gasification" *(Gas Processing Handbook) Hydrocarbon Processing,* **63** (4), 90 (1984).
[521] *Lurgi Gas Production Technology: The Shell Process* Lurgi comp. brochure 189e/6.92/2.20.
[522] C. Higmann, *Perspectives and Experience with Partial Oxidation of Heavy Residues,* Lurgi company brochure.
[523] *Hydrocarbon Process.* **63** (1984) no. 4, 90.
[524] *Integrated Gasification Combined Cycle Process,* Lurgi information paper, 1995.
[525] W. Liebner, N. Hauser, ERPI Conference on Power Generation and the Environment, London 1990.
[526] C. Higmann, G. Grünfelder, Conference on Gasification Power Plants, San Francisco 1984.
[527] W. Soyez, 33rd AIChE Ammonia Safety Symp., Denver 1988; *Ammonia Plant Saf.* **29** (1989) 19.
[528] G. J. van den Berg et al., *Hydrocarbon Process.* **45** (1966) no. 5, 193.
[529] L. W. ter Haar, *Ind. Chim. Belge* **33** (1968) 655.
[530] P. D. Becker et al., *Chem. Process Eng. (London)* **52** (1971) no. 11, 59.
[531] C. L. Reed, C. J. Kuhre, *Hydrocarbon Process.* **58** (1979) no. 9, 191.
[532] *Uhde's Design of the Texaco Oil Gasification,* Krupp – Uhde comp. brochure TOPG 2A/AB, 1995.
[533] *Hydrocarbon Process.* **58** (1979) no. 4, 168.
[534] H. Fricke, *Chem. Ztg.* **96** (1972) 123.
[535] E. Supp, M. Brejc, "Gas Production" in *Ullmann's Encyclopedia* of Industrial Chemistry, VCH Weinheim, **vol. A 12.**
[536] W. Liebner, *Tenth Refinery Technology Meeting,* February 11–13, Mumbay, India, 1998.
[537] R. Lohmüller, *Chem. Ing. Tech.* **56** (1984) no. 3, 203.
[538] C. I. Kuhre, C. I. Shearer, *Hydrocarbon Process.* **50** (1971) no. 12, 113.
[539] L. J. Buividas, J. A. Finneran, O. J. Quartulli, *Chem. Eng. Prog.* **70** (1974) no. 10, 21; *Ammonia Plant Saf.* **17** (1975) 4.
[540] *Nitrogen* **83** (1973) 40.
[541] C. P. Marion, J. R. Muenger, *Energy Prog.* **1** (1981) no. 1–4, 27.
[542] H. J. Madsack, *Hydrocarbon Process.* **61** (1982) no. 7, 169.
[543] *Nitrogen* **226** (1997) 47–56.
[544] *Nitrogen* **161** (1986) 23–27.
[545] E. Supp: *How to Produce Methanol from Coal,* Springer-Verlag, Heidelberg 1989.
[546] *Nitrogen* **126** (1980) 32–39.
[547] R. Reimert, G. Schaub, "Gas Production" in *Ullmann's Encyclopedia of Industrial Chemistry,* VCH Weinheim, **vol. A 12,** p. 214–236.
[548] *Nitrogen* **126** (1980) 32.
[549] L. J. Buividas, *Chem. Eng. Prog.* **77** (1981) no. 5, 44; *Ammonia Plant Saf.* **23** (1981) 67.
[550] *Ammonia from Coal,* Bull. Y-143, Tennessee Valley Authority, Muscle Shoals, Ala. 1979.
[551] D. A. Waitzman, *Chem. Eng. (N.Y.)* **85** (1978) 69.
[552] F. Brown, *Hydrocarbon Process.* **56** (1977) no. 11, 361.
[553] H. Teggers, H. Jüntgen, *Erdöl Kohle Erdgas Petrochem.* **37** (1984) no. 4, 163.
[554] V. Happe, "Partial Oxidation of Coal" in A. V. Slack, G. Russel James (eds) "Ammonia", **Part I,** 325–354, Marcel Dekker, New York, 1973.
[555] H. Staege, *Tech. Mitt. Krupp Werksber.* **40** (1982) no. 1, 1.

Topsoe, Inc. – EX1003
Page 406 of 1210

[556] *Hydrocarbon Process.* **63** (1984) no. 4, 94.

[557] H. J. Michaels, H. F. Leonard, *Chem. Eng. Prog.* **74** (1978) no. 8, 85.

[558] H. Staege, *Hydrocarbon Process.* **61** (1982) no. 3, 92.

[559] J. E. Franzen, E. K. Goeke, *Hydrocarbon Process.* **55** (1976) no. 11, 134.

[560] A. D. Engelbrecht, Tennessee Valley Authority Symposium in Muscle Shoals, Alabama 1979.

[561] *Nitrogen* 1985, no. 156, 35.

[562] H. Schmidt-Traub, H. C. Pohl, *Chem. Ing. Tech.* **55** (1983) no. 11, 850. *Hydrocarbon Process.* **63** (1984) no.no. 4, 95.

[563] W. L. E. Davey, E. L. Taylor, M. D. Newton, P. S. Larsen, P. S. Weitzel, Asia Nitrogen '98, Brit. Sulphur Internat. Conference, Kuala Lumpur, Feb. 22–24, 1998. Proceed. **vol. 2**, p. 165.

[564] T. W. Nurse, *5th International Symposium Large Chemical Plants,* Antwerpen 1982.

[565] B. Cornils et al., *Chem. Ing. Tech.* **52** (1980) no. 1, 12.

[566] *Hydrocarbon Process.* **63** (1984) no. 4, 97.

[567] W. Konkol et al., *Hydrocarbon Process.* **61** (1982) no. 3, 97.

[568] D. E. Nichols, P. C.Williamson in A. I. More (ed.), *Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol. 4th 1981* 1982, 53.

[569] B. Cornils et al., *CEER Chem. Econ. Eng. Rev.* **12** (1980) no. 6–7, 7.

[570] E. T. Child, Tennessee Valley Authority Symposium in Muscle Shoals, Alabama 1979.

[571] B. Cornils et al., *Hydrocarbon Process.* **60** (1981) no. 1, 149.

[572] *Hydrocarbon Process.* **63** (1984) no. 4, 96.

[573] M. J. van der Burgt, *Hydrocarbon Process.* **58** (1979) no. 1, 161.

[574] C. A. Bayens, 36th AIChE Ammonia Safety Symposium, Los Angeles 1991; *Ammonia Plant Saf.* **32** (1992) 268.

[575] *Clean Coal Technology,* International Power Generation, 1990.

[576] M. J. van der Burgt, J. E. Naber, *Ind. Chem. Bull.* (1983) 104–105.

[577] J. N. Mahagaokar, J. N. Phillips, A. Kreweinghaus, 10th ERPI Conf. on Coal Gasification, 1986.

[578] T. J. Pollaert, *Chem. Eng. Prog.* **74** (1978) no. 8, 95.

[579] *Hydrocarbon Process.* **60** (1980) no. 11, 130.

[580] M. K. Schad, C. F. Hafke, *Chem. Eng. Prog.* **79** (1983) no. 5, 45.

[581] H. Hiller, *Erdöl Kohle Erdgas Petrochem.* **28** (1975) no. 2, 74.

[582] P. D. Becker, Tennessee Valley Authority Symposium in Muscle Shoals, Alabama 1979.

[583] W. Schäfer et al., *Erdöl Kohle Erdgas Petrochem.* **36** (1983) no. 12, 557.

[584] *Hydrocarbon Process.* **61** (1982) no. 4, 151.

[585] *Hydrocarbon Process.* **61** (1982) no. 4, 133.

[586] K. A. Theis, E. Nitschke, *Hydrocarbon Process.* **61** (1982) no. 9, 233. *Hydrocarbon Process.* **63** (1984) no. 4, 93.

[587] P. Speich, H. Teggers, *Erdöl Kohle Erdgas Petrochem.* **36** (1983) no. 8, 376.

[588] M. Appl: *Ammonia, Methanol Hydrogen, Carbon Monoxide – Modern Production Technologies, CRU London 1994,*4. Hydrogen, p. 102–115.

[589] "Wasserstofftechnologie – Perspektiven für Forschung und Entwicklung" (Hydrogen technology – Perspectives for research and development), Dechema 1985, p. 105–133 (ISBN 3-921567-69-6).

[590] G. Sandstede, *Chemie-Ingenieur Technik,* **61,** 5, 349–361, 1989.

[591] L. Bisset, *Chemical Engineering,* **84** (21), 177 (1977).

Topsoe, Inc. – EX1003
Page 407 of 1210

[592] D. J. Bogards, J. S. Campbell, "Design and operation of CO shift, naphtha and natural gas" in *A. V. Slack, G. Russel James (eds.): Ammonia, part II, Marcel Dekker Inc,* New York 1974, p. 25–71.

[593] G. W. Bridger, G. C. Chinchen, "Hydrocarbon Reforming Catalysts" in *Catalyst Handbook, Wolf Scientific Book, London 1970, 97–125.*

[594] L. Loyd, D. E. Riddler, M. W. Twigg, Catalyst Handbook (2nd ed.), ICI. *Wolf Publ. Ltd., London, 1989.*

[595] J. R. Jennings, M. W. Twigg, in "Selected developments in catalysis" (ed. j. R. Jennings), Blackwell Sci. Publ., Oxford 1985, chapt. 4, p. 102–127

[596] P. S. Pedersen, J. H. Carstensen, J. Boghild-Hansen, 34th AIChE Ammonia Safety Symp., San Francisco 1989; *Ammonia Plant Saf.* **30** (1990) 139.

[597] R. E. Stockwell, *FINDS* **vol. V,** n. 4, fourth quater, 1990, p. 22.

[598] S. J. Catchpole et al., *Modern Catalyst Systems for Increased Ammonia Production and Efficiency,* ICI Catalco Tech. Paper.

[599] M. Schneider, K. Kochloefl, J. Pohl, O. Bock, *Europ. Pat. Appl.* o 353 453, SÜD-CHEMIE AG, München, Germany, May 17, 1984.

[600] A. Tamaru, Y. Oshima, K. Honda, *German Pat. Appl.* DE 3 835 345 A 1 *Mitsubishi Kasai Co, Tokyo, Oct. 17, 1989.*

[601] A. Andreew, V. Idakiev, D. Mihajlova, D. Shopov, Appl. Catal., 1985, 22, 385–387.

[602] D. S. Newsome, Cat. Rev.-Sci. Eng., **21,** (1980) 275–318.

[603] K. Kochloefl, "Water gas shift and COS removal in *Handbook of Heterogeneous Catalysis (ed. G. Ertl, H. Knörzinger, J. Weitkamp), VCH Weinheim,* 1997, vol. 4, 1831–1843.

[604] G. C. Chinchen, *European patent application,* A 0 062410, 1982 (ICI).

[605] D. G. Rethwisch, J. A. Dumesic, *Appl. Catal.,* 1986, 21, 97–109.

[606] F. M. Gottschalk, R. g. Copperthwaite, M. van der Riet, G. J. Hutchings, *Appl. Catal.,* 1988, 381, 103–108.

[607] F. M. Gottschalk, R. g. Copperthwaite, G. J. Hutchings, *Appl. Catal.,* 1989, 51, 103–108.

[608] C. L. Thomas, "Catalytic processes and proven catalysts" Academic Press, New York 1970, p. 104–105.

[609] D. Allen "CO conversion catalyst" in *A. V. Slack, G. Russel James (eds.): Ammonia,* **part II,** Marcel Dekker Inc, New York 1974, p. 3–23.

[610] H. Bohlbro, "An investigation on the kinetics of the conversion of CO with H_2O over iron-based catalysts, 2nd ed. *Gjellerup, Copenhagen,* 1969.

[611] M. D. Ruthven, *Canad. Chem. Eng.,* 1969, 47, 327.

[612] G. C. Cinchen, R. H. Logan, M. S. Spencer, *Appl. Catal.,* 1984, 12, 69–89, 97–103.

[613] H. Brohlo, J. Catal., 1979, 3, 207.

[614] K. Atwood, M. R. Arnold, E. G. Appel, *Ind. Eng. Chem.,* 42, 1600 (1950).

[615] R. Habermehl, FINDS, Volume VIII, no 4, Fourth Quater 1993, 25.

[616] H. Roos, H. Wanjek, 34th AIChE Ammonia Safety Symp., San Francisco 1989; *Ammonia Plant Saf.* **30** (1990) 187.

[617] D. Kitchen, W. G. Henson, J. K. Madsen, 34th AIChE Ammonia Safety Symposium, San Francisco 1989, *Ammonia Plant Saf.,* **30** (1990), 105.

[618] D. Kitchen, A. Pinto, H. van Praag, 34th AIChE Ammonia Safety Symposium, San Francisco 1989, *Ammonia Plant Saf.,* **29** (1989), 212.

[619] J. R. Rostrup-Nielsen et al., 37th AIChE Ammonia Safety Symp., San Antonio 1992; *Ammonia Plant Saf.* **33** (1993).

Topsoe, Inc. – EX1003
Page 408 of 1210

[620] J. B. Hansen, P. S. Pedersen, J. H. Carstensen, 33rd AIChE Ammonia Safety Symp., Denver 1988; *Ammonia Plant Saf.* **29** (1989) 304.
[621] W. C. Lundberg, 23rd AIChE Ammonia Safety Symp., Miami Beach, 1978, *Ammonia Plant Saf.* **21** (1979) 105.
[622] P. W. Young, B. C. Clark, 17th AIChE Ammonia Safety Symp., Minneapolis 1972; *Ammonia Plant Saf.* **15** (1973) 18.
[623] I. Dybkjaer in A. I. More (ed.), *Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol. 4th 1981* 1982, 503.
[624] T. Salmi, R. Hakkarainen, *Appl. Catal.*, 1989, 49, 285–306.
[625] T. van Herwijnen, W. A. De Jong J. Catal, 1980, 63, 83–93.
[626] R. Habermehl, *FINDS*, Volume VII, n. 4, fourth Quarter, 1992, p. 26.
[627] J. M. Stell et al., *The Operation of High, Low and Intermediate Temperature Catalysts*, ICI Catalco/KTI/UOP Hydrogen Plant Seminar, Chicago 1995.
[628] *Nitrogen* **232**, (1998), 47.
[629] J. Ilg, B. Kandziora, 41st AIChE Ammonia Safety Symp., Boston 1996; *Ammonia Plant Saf.* **37** (1997) 341.
[630] D. F. Balz, H. F. Gettert, K. H. Gründler, *Plant Oper. Prog.* **2** (1983) no. 1, 47.
[631] J. M. Moe, *Chem. Eng. Prog.* **58** (1962) no. 3, 33.
[632] *Nitrogen* **40** (1966) 28.
[633] A. P. Ting, Shen-Wu-Wan, *Chem. Eng. (N.Y.)* **76** (1969) no. 11, 185.
[634] J. F. Lombard, *Hydrocarbon Process.* **48** (Aug. 1969) 111.
[635] L. Lloyd, M. V. Twigg, *Nitrogen* **118** (1979) 30.
[636] *Nitrogen* **133** (1981) 27.
[637] P. N. Hawker, *Hydrocarbon Process.* **61** (1982) no. 4, 183.
[638] *Nitrogen* **226** (1997) 43–46.
[639] F. Lorenz, F. Wodtke, F. L. Ebenhoech, E. Giesler, H. Kirner, *German Pat*, 1 667 386, BASF AG, April 15, 1967..
[640] W. Auer, *Erdöl Kohle Erdgas Petrochem.* **24** (1971) 145.
[641] *Hydrocarbon Process.* **61** (1982) no. 4, 154.
[642] I. Dybkjaer, H. Bohlbro, 23rd AIChE Ammonia Safety Symp., Maiami Beach 1978; *Ammonia Plant Saf.* **21** (1979) 145.
[643] BASF, DE-AS 1250792, 1959.
[644] I. Dybkjaer, in: *Ammonia from Coal Symposium*, TVA Muscle Schoals Alabama, USA p. 133.
[645] C. L. Aldridge, T. Kalina *German Pat*, 2 054 946, Exxon research and engineering Co, Linden, USA November 7, 1971.
[646] J. S. Merriam, C. B. Hoog, *US Patent.* 253 941, United Catalysts Inc., Louisville, USA April 14 1981; *Europ. Pat. Appl.* 0 062 912, April 8, 1982.
[647] H. Schäfer, *FINDS*, **vol. VII,** no 4, Fourth Quater, 1992.
[648] P. Hou, D. Mecker, H. Wiese, J. Catal. 1983, 80, 280–285.
[649] V. Berispeck, "Studies on an alkali-impregnated Co-Mo catalyst for water gas shift conversion and methanation", *M. S., Thesis, Virginia Polytechnic Institute and State University, Blacksburg, VA*, USA, 1975.
[650] "Carbon monoxide production technologies", *KTI Newsletter* (Winter 1987).
[651] K. J. Stokes, *Nitrogen* **131** (1981) 35. K. J. Stokes in A. I. More (ed.): *Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol. 4th 1981* 1982, 525.
[652] K. F. Butwell et al., *Chem. Eng. Prog.* **69** (1973) no. 2, 57–61.
[653] *Nitrogen* **96** (1975) 33.

Topsoe, Inc. – EX1003
Page 409 of 1210

[654] *Nitrogen* **102** (1976) 40.
[655] K. F. Butwell, D. J. Kubek, P. W. Sigmund, 23th AIChE Ammonia Safety Symp., Miami Beach, 1978; *Ammonia Plant Saf.* **21** (1979)156; *Chem. Eng. Prog.* **75** (1979) no. 2, 75. K. F. Butwell, D. J. Kubek, *Hydrocarbon Process.* **56** (1977) no. 10, 173.
[656] J. R. Fair, D. E. Steinmeyer, W. R. Penney, B. B. Crocker, "Gas Absorption and Gas-Liquid System Design", in R: H. Perry, D. W. Green, J. O. Maloney (eds.) "Perry's Chemical Engineering Handbook ", MacGraw-Hill, New York, International edition, 1997, pp. 14-1ff.
[657] H. E. Benson, R. W. Parrish, *Hydrocarbon Process.* **53** (1974) no. 4, 81.
[658] H. E. Benson in A. V. Slack, G. J. James (eds.): *Ammonia,* **part II,** Marcel Dekker, New York 1974, p. 159.
[659] B. S. Grover, E. S. Holmes: "Nitrogen 86," *Br. Sulphur Conf.,* Amsterdam 1986, Proceedings of the Conf., p. 101.
[660] R. K. Bartoo, S. J. Ruzicka: "Fertilizer '83," *Br. Sulphur Corp. 7th Int. Conf.,* London 1983, Proceedings of the Conf., p. 129.
[661] US 4035 166, 1977 (F. C. van Hecke).
[662] L. C. Crabs, R. Pouillard, F. C. van Hecke, 24th AIChE Ammonia Safety Symp., San Francisco 1989; *Ammonia Plant Saf.* **22** (1980) 185.
[663] *Hydrocarbon Process.* **61** (1982) no. 4, 95 – 102.
[664] R. N. Maddox, M. D. Burns, *Oil Gas J.* **66** (1968) no.4 91.
[665] G. Giammarco, in A. V. Slack (ed.): *Ammonia,* **part II,** Marcel Decker New York 1974, p. 171.
[666] L. Tomasi, *Nitrogen* **199** (1992) 35.
[667] *Hydrocarbon Process.* **63** (1984) no. 4, 57 – 64.
[668] A. G. Eickmeyer in A. V. Slack, G. J. James (eds.): *Ammonia,* **part II,** Marcel Dekker, New York 1974.
[669] *Nitrogen* **180** (1989) 20 – 30.
[670] C. C. Song et al., 36th AIChE Ammonia Safety Symp., Los Angeles 1991; *Ammonia Plant Saf.* **32** (1992) 187.
[671] S. Linsmayer, *Chem. Tech. (Leipzig)* **24** (1972) no. 2, 74.
[672] K. Elberling, W. Gabriel, *Chem. Tech. (Leipzig)* **29** (1977) no. 1, 43.
[673] T. M. Gemborys, 39th AIChE Ammonia Safety Symp., Vancouver 1994.
[674] M. J. Mitariten, C. M. Wolf, T. J. DePaola, ICI Catalco/UOP Hydrogen Plant Seminar, Chicago 1995.
[675] P. Clough: "Asia Nitrogen," *Br. Sulphur Conf.,* Bali 1994, Proceedings of the Conf., p. 191 – 193.
[676] J. N. Iyengar, D. E. Keene, 38th AIChE Ammonia Safety Symp., Orlando 1993; *Ammonia Plant Saf.* **34** (1994).
[677] US 4702 898 (B. S. Grover).
[678] R. K. Bartoo, T. M. Gemborys: "Nitrogen 91," *Br.Sulphur Conf.,* Copenhagen 1991, Proceedings of the Conf., p. 127 – 139.
[679] R. K. Bartoo, *Removing Acid gas by the Benfield Process,* UOP Comp brochure, GP 5132–1M-11/93.
[680] R. K. Bartoo, *Chem. Eng. Prog.* **80** (1984) no. 10, 35
[681] *Nitrogen* **229** (Sep.-Oct 1997), 37–52.
[682] A. G. Eickmeyer, "Catacarb" in *A. V. Slack, G. Russel James (eds.): Ammonia,* **part II,** Marcel Dekker Inc, New York 1974, p. 165–169.

Topsoe, Inc. – EX1003
Page 410 of 1210

[683] G. Giammarco, "Giammarco-Vetrocoke" in *A. V. Slack, G. Russel James (eds.): Ammonia,* **part II**, Marcel Dekker Inc, New York 1974, p. 171–182.

[684] R. E. Meissner, U. Wagner, *Oil Gas J.* **81** (Feb. 7, 1983) 55.

[685] K. Volkamer, E. Wagner, F. Schubert, *Plant Oper. Prog.* **1** (1982) no. 2, 134.

[686] K. Volkamer, U. Wagner: "Fertilizer '83," *Br. Sulphur Corp. 7th Int. Conf.*, London 1983, Proceedings of the Conf., p. 139.

[687] W. Gerhard, W. Hefner, 33rd AIChE Ammonia Safety Symp., Denver 1988; *Ammonia Plant Saf.* **29** (1989) 73.

[688] D. W. Stanbridge, Y. Ide, W. Hefner, AIChE Ammonia Safety Symp., Anaheim 1984.

[689] R. Welker, R. Hugo, R. Meissner, 41st AIChE Ammonia Safety Symp., Boston 1996; *Ammonia Plant Saf.* **37** (1997) 330.

[690] R. Welker, R. Hugo, B. Büchele: "Asia Nitrogen 96", Singapore 1996.

[691] G. Ripperger, J. C. Stover, AIChE Spring National Meeting, Boston 1996.

[692] J. E. Nobles, N. L. Shay: "Nitrogen 88," *Br. Sulphur Int. Conf.*,Geneva 1988.

[693] W. Hefner, R. E. Meissner, 37th AIChE Ammonia Safety Symp., San Antonio 1992; *Ammonia Plant Saf.* **33** (1993) 101.

[694] D. K. Judd, *Hydrocarbon Process.* **57** (1978) no. 4, 122.

[695] C. G. Swanson, 23th AIChE Ammonia Safety Symp., Miami Beach, 1978; *Ammonia Plant Saf.* **21** (1979)152.

[696] C. G. Swanson, F. C. Burkhard, 23th AIChE Ammonia Safety Symp., Denver 1983; *Ammonia Plant Saf.* **24** (1984) 16.

[697] V. A. Shah, *Energy Progress* **8** (1988) 67 – 70.

[698] R. J. Hernandez, T. L. Huurdemann: "Nitrogen 88," *Br. Sulphur Int. Conf.*, Geneva 1988.

[699] T. L. Huurdemann, V. A. Shah, 34th AIChE Ammonia Safety Symp., San Franzisco 1989.

[700] V. A. Shah, *Hydrocarbon Process.* **67** (1988).

[701] R. J. Hernandez, T. L. Huurdemann, *Chem. Eng.* **5** (1989) 154 – 156.

[702] *Fertilizer Focus* **5** (1988) 27.

[703] G. C. Swanson, 23rd AIChE, Ammonia Safety Symposium, Miami Beach Nov. 1978; *Ammonia Plant Saf.* **21** (1979), 152.

[704] J. L. Lewis, H. A. Truby, M. B. Pascoo, *Hydrocarbon Process.* **58** (1979) no. 4, 112.

[705] R. W. Bucklin, R. L. Schendel, *Energy Progr.* **4** (1984) no.3, 137.

[706] J. L. Lewis, H. A. Truby, M. B. Pasco, *Oil Gas J,* 72 (June 24, 1974) 120.

[707] B. Sehrt, P. Polster, *Chem. Tech. (Leipzig)* **32** (1980) no. 7, 345.

[708] T. P. Cook, "Fluor", in *A. V. Slack, G. Russel James (eds.): Ammonia* **part II,** Marcel Dekker Inc, New York 1974, p. 249–252.

[709] "Schwefel-Rückgewinnung", in *Lurgi company brochure* 1542d/5.94/3.10.

[710] "Sulfur", Ullmann, Sed., vol 25, pp. 523–525.

[711] *The Rectisol Process for Gas Purification,* Lurgi brochure 1676 e/5.95/10.

[712] *Rectisol for Gas Treating,* Lurgi Express Information O 1051/12.72.

[713] G. Ranke, Linde Berichte aus Wissenschaft und Technik.

[714] H. Haase, *Chem. Anlagen Verfahren* **10** (1970) 59.

[715] W. Linde, G. Ranke, H. Jungfer: "Rectisol" in A. V. Slack, G. J. James (eds.): *Ammonia* **part II** Marcel Dekker, New York 1974 p. 233–241.

[716] M. Kriebel, "Gas Production" in *Ullmann's Encyclopedia of Industrial Chemistry,* VCH, Weinheim, **vol. A 12,** p. 207, 262–264.

[717] L. W. Dailey, "Purisol" in *A. v. Slack, G. Russel James (eds.): Ammonia,* **part II,** Marcel Dekker Inc, New York 1974, p. 243–248.

Topsoe, Inc. – EX1003
Page 411 of 1210

[718] M. Kriebel, "Gas Production" in *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, **vol. A 12,** p. 257.
[719] J. P. Klein, *Erdöl Kohle Erdgas Petrochem.* **23** (1970) no. 2, 84.
[720] H. W. Schmidt, H. J. Henrici, *Chem. Ztg.* **96** (1972) no. 3, 154.
[721] K. E. Zarker, "Sufinol" in A. V. Slack, G. Russel James (eds.): *Ammonia,* **part II,** Marcel Dekker Inc, New York p. 219–232.
[722] M. Kriebel, "Gas Production" in *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, **vol. A 12,** p. 261–262.
[723] K. J. Stokes, 24th AIChE Ammonia Safety Symp., San Francisco, 1979; *Ammonia Plant Saf.* **22** (1980)178.
[724] B. G. Goar, *Oil Gas J.* **69** (July 12, 1971) 75.
[725] A. L. Kohl, F. C. Riesenfeld: *Gas Purification,* Gulf Publ. Co., Houston, Tex. 1979.
[726] G. Hochgesand, *Chem. Ing. Techn.* **40** (1968) 43; *Ind. Eng. Chem.* **62** (1970), 7–37.
[727] S. Strelzoff, *Chem. Eng. (N.Y.)* **82** (1975) no. 19, 115.
[728] D. Werner, *Chem. Ing. Techn.* **53** (1981) no. 2, 73.
[729] K. G.Christensen, *Hydrocarbon Process.* **57** (1978) no. 2, 125.
[730] H. Thirkell in A. V. Slack, G. Russel James (eds.): *Ammonia,* **part II,** Marcel Dekker, New York 1974, p. 117.
[731] S. Strelzow: *Technology and Manufacture of Ammonia,* Wiley, New York 1981, p. 193.
[732] F. C. Brown, C. L. Leci, *Proc. Fertilizer Soc.* **210** (1982) 1.
[733] *Nitrogen* **180** (1989) 20.
[734] H. W. Schmidt, *Chem. Ing. Tech.* **40** (1968) 425.
[735] D. W. Allen, W. H. Yen, 17th AIChE Ammonia Safety Symp., Minneapolis, August 1972; *Ammonia Plant Saf.* **15** (1973) 96.
[736] A. J. M. Janssen, N. Siraa, J. M. Blanken, 25th AIChE Ammonia Safety Symp., Portland, 1980; *Ammonia Plant Saf.* **23** (1981)19.
[737] H. Y. Allgood, "Copper liquid scrubbing" in *A. V. Slack, G. Russel James (eds.): Ammonia* **part II,** Marcel Deckker Inc, New York 1974, p. 289–309.
[738] B. J. Cromarty, "Methanotor catalyst and operation" ICI Katalco Technical Paper, ICI Group 385W/126/0/METH.
[739] *Chemical Economy and Engineering Review,* **12** no.(6–7), 33–36, (Jun/Jul 1980).
[740] C. M. Buckthorp, *Nitrogen* **113** (1978) 34.
[741] *Nitrogen* **123** (1980) 39.
[742] J. C. Bonacci, T. G. Otchy, 22th AIChE Ammonia Safety Symp., Denver, 1977; *Ammonia Plant Saf.* **20** (1978) 165.
[743] J. H. Colby, G. A. White, P. N. Notwick, 23th AIChE Ammonia Safety Symp., Miami Beach 1978; *Ammonia Plant Saf.* **21** (1979)138.
[744] *Nitrogen* **197** (1992) 18–25.
[745] P. Soregaard-Andersen, O. Hansen, 36th AIChE Ammonia Safety Symp., Los Angeles 1991. *Ammonia Plant Safety* **32** (1992), 177.
[746] *Nitrogen* **217** (1995) 41–48.
[747] US 3442 613, 1969 (B. J. Grotz).
[748] *Nitrogen* **144** (1983) 30.
[749] B. J. Grotz, *Nitrogen* **100** (1976) 30.
[750] *Nitrogen* **182** (1989).
[751] B. J. Grotz, G. Good, *(1980) Chem. Age* (London) (November, 14), 18.
[752] C. K. Wilson et al., *Nitrogen* **151** (1984) 31.

Topsoe, Inc. – EX1003
Page 412 of 1210

[753] B. I. Grotz, *Hydrocarbon Process.* **46** (1967) no. 4, 197.
[754] W. Scholz, *DECHEMA-Monogr.* **58** (1968) 31.
[755] W. Förg, *Chem. Anlagen + Verfahren* 1970 no. (March), 33.
[756] *Nitrogen* **95** (1975) 38.
[757] S. Haseba et al., 10th AIChE Ammonia Safety Symp., Minneapolis 1965; *Ammonia Plants* **8** (1966) 14.
[758] S. R. Krolikowski, *Chem. Eng. (London)* 1965 no. 186, 40.
[759] F. Corr, F. Dropp, E. Rudelstorfer, *Hydrocarbon Process.* **58** (1979) no. 3, 119.
[760] D. H. Werner, G. A. Schlichthärle, 24th AIChE Ammonia Safety Symp., Minneapolis san Francisco, November 1979; *Ammonia Plant Saf.* **22** (1980) 12.
[761] *Nitrogen* **121** (1979) 37.
[762] J. L. Heck, *Oil Gas J.* **78** (Feb. 11, 1980) 122.
[763] P. Taffe, J. Joseph, *Chem. Age* 1978 (October) 14.
[764] P. R. Savage, *Chem. Eng. (N.Y.)* **82** (1978) no. 25, 68D.
[765] R. Rehder, P. Stead, FAI Seminar 1985, The Fertilizer Association of India, New Dehli, Tech II-2/1.
[766] W. F. van Weenen, J. Tielroy, *Nitrogen* **127** (1980) 38.
[767] *Oil Gas J.* **19** (1981) 270.
[768] W. F. van Weenen, J. Tielroy, *Chem. Age India* **31** (1980) no. 12, Dev-2/1.
[769] J. Voogd, FAI Seminar 1985, The Fertilizer Association of India, New Dehli, Tech 11–1/1.
[770] D. J. Carra, R. A. McAllister, *Chem. Eng. (N.Y.)* **70** (1963) 62.
[771] "Compressors" in *Encyclopedia of Chemical Engineering,* **vol. 10**, Marcel Dekker, New York 1979, 157–409.
[772] E. E. Ludwig, "Compressors" in *Applied Design for Chemical and Petrochemical Plants,* **vol. 3**, Gulf. Houston, 1983, pp. 251–396.
[773] C. A. Vancini: *La Sintesi dell Amoniaca,* Hoepli, Milano 1961, p. 497.
[774] J. L. Kennedy, *Oil Gas J.* **65** 1967, no. 46, 105; no. 48, 95; no. 1, 72; no. 51, 76. *Oil Gas J.* **66** 1968, no. 4, 76.
[775] G. P. Williams, W. W. Hoehing, *Chem. Eng. Prog.* **79** (1983) no. 3, 11.
[776] G. A. J. Begg, *Chem. Process Eng. (London)* **49** (1968) no. 1, 58.
[777] F. Fraschetti et al., *Quad. Pignone* 1967, no. 9, 5.
[778] *Chem. Eng. (N.Y.)* **73** (1966) no. 9, 126.
[779] P. Kerklo, *Hydrocarbon Process.* **61** (1982) no. 10, 112.
[780] H. Strassmann, Uhde Ammonia Symp., Dortmund 1992.
[781] C. Dickinson, *Why dry running gas seals?* J. Crane Inc. Comp. Publ.
[782] W. Koch, *Dry Gas Seal – Principles – Capabilities – Application,* J. Crane Inc. Comp. Publ.
[783] S. Gray, B. Baxter, G. Jones, "Magnetic Bearings can Increase Availability, Reduce Oil and Maintenance Costs," Power Engineering, 1990.
[784] R. R. Poricha, D. G. Rao, *Technology (Sindri, India)* **3** (1966) 96.
[785] H. Förster, *Chem. Tech. (Leipzig)* **23** (1971) 157.
[786] *Hydrocarbon Process. Pet. Refiner* **45** (1966) no. 5, 179.
[787] *Eur. Chem. News* **11** (1967) no. 270, 26.
[788] W. Plötner, *Chem. Tech. (Leipzig)* **24** (1972) 324.
[789] A. F. Wilck, *Energy Tech.* **23** (1971) no. 5, 161.
[790] I. M. Kalnin, *Luft Kältetech.* **8** (1972) no. 3, 142.
[791] W. L. Luther, *Ingenieur Digest* **10** (1971) no. 1, 60.
[792] H. E. Gallus, *Brennst. Wärme Kraft* **23** (1971) no. 4, 172.

Topsoe, Inc. – EX1003
Page 413 of 1210

[793] F. Fraschetti, U. Filippini, P. L. Ferrara, *Quad. Pignone* **9** (1967) 5.
[794] G. A. J. Begg, *Chem. Proc. Eng. (London)* **49** (1968) no. 1, 58.
[795] A. Vitti, *Het Ingenieursblad* **40** (1971) 619.
[796] P. L. Ferrara, A. Tesei, *Quad. Pignone* **25** (1978) 131.
[797] J. Salviani et al., in A. V. Slack, G. Russel James (eds.): *Ammonia*, **part III**, Marcel Dekker, New York 1974, p. 7.
[798] *Nitrogen* **55** (1968) 37.
[799] S. Labrow, *Chem. Proc. Eng.* (London) **49** (1968) no. 1, 55.
[800] H. Foerster, *Chem. Technol.* **23** (1971) 93.
[801] H. Foerster, *Chem. Technol.* **23** (1971) 157.
[802] W. Plötner, *Chem. Technol.* **24** (1972) 324.
[803] *Nitrogen* **181** (1981) 23.
[804] S. D. Caplow, S. A. Bresler, *Chem. Eng.* (New York) **74** (1967) no. 7, 103.
[805] F. Fraschetti, P. L. Ferrara, U. Philippini, "Centrifugal compressor arrangement and drive systems" in A. V. Slack, G. Russel James (eds.): *Ammonia* **part III**, Marcel Dekker Inc, New York 1977, p. 11–45.
[806] H. B. Hile, "Large ammonia plant centrifugal compressor operation" in *A. V. Slack, G. Russel James (eds.): Ammonia* **part III**, Marcel Dekker Inc, New York 1977, p. 47–54.
[807] K. J. Stokes, *Chem. Eng. Prog.* **75** (1979) no. 7, 88.
[808] GB 1134 621, 1968 (D. R. Twist, D. W. Stanbridge).
[809] S. Ujii, M. Ikeda, *Hydrocarbon Process.* **60** (1981) no. 7, 94.
[810] W. Rall, 35th AIChE Ammonia Safety Symp., San Diego 1990, *Ammonia Plant Saf.* **31** (1991), 247.
[811] H. Uchida, M. Kuraishi, *Bull. Chem. Soc. Jpn.* **23** (1955) 106.
[812] R. F. Baddour et al., *Chem. Eng. Sci.* **20** (1965) 281.
[813] C. van Heerden, *Ind. Eng. Chem.* **45** (1953) 1242.
[814] H. Inoue, T. Komiya, *Int. Chem. Eng.* **8** (1968) no. 4, 749.
[815] H. Bakemeier et al., *Chem. Ing. Tech.* **37** (1965) 427.
[816] I. Porubszky et al., *Br. Chem. Eng.* **14** (1969) no. 4, 495.
[817] F. Horn, *Chem. Ing. Tech.* **42** (1970) no. 8, 561.
[818] V. Hlavacek, *Ind. Eng. Chem.* **62** (1970) no. 7, 8.
[819] J. Kjaer: *Measurement and Calculation of Temperature and Conversion in Fixed-bed Catalytic Reactors*, Gjellerup, Kopenhagen 1958.
[820] G. F. Froment, *Chem. Ing. Tech.* **46** (1974) no. 9, 374.
[821] J. E. Jarvan, *Ber. Bunsenges. Phys. Chemie* **74** (1970) no. 2, 74.
[822] J. Kjaer, Computer Methods in Catalytic Reactor Calculations, Haldor Topsøe, Vedaek 1972.
[823] J. E. Jarvan, *Oil Gas J.* **76** (1978) no. 5, 178.
[824] J. E. Jarvan, *Oil Gas J.* **76** (1978) no. 3, 51.
[825] C. P. P. Singh, D. N. Saraf, *Ind. Eng. Chem. Process Des. Dev.* **18** (1979) no. 3, 364.
[826] J. Simiceanu, C. Petrila, A. Pop, *Chem. Tech.* (Leipzig) **35** (1983) no. 12, 628.
[827] K. Lukas, D. Gelbin, *Chem. Eng.* (London) **7** (1962) 336.
[828] M. J. Shah, *Ind. Eng. Chem.* **59** (1967) 72.
[829] L. D.Gaines, *Ind. Eng. Chem. Process Des. Dev.* **18** (1979) no. 3, 381.
[830] L. D. Gaines, *Chem. Eng. Sci.* **34** (1979) 37.
[831] K. V. Reddy, A. Husain, *Ind. Eng. Chem. Process Des. Dev.* **21** (1982) no. 3, 359.
[832] L. M. Shipman, J. B. Hickman, *Chem Eng. Progr.* **64** (1968) 59.
[833] R. F. Baddour et al., *Chem. Eng. Sci.* **20** (1965) 281.

Topsoe, Inc. – EX1003
Page 414 of 1210

[834] P. L. Brian, R. F. Baddour, J. P. Emery, *Chem. Eng. Sci.* **20** (1965) 297.
[835] G. A. Almasy, P. Jedlovsky, *Chem. Eng.* (London) **12** (1967) 1219.
[836] I. Porubsky, E. Simonyi, G. Ladanyi, *Chem. Eng.* (London) **14** (1969) 495.
[837] A. Murase, H. L. Roberts, A. O. Converse, *Ind. Eng. Chem. Process Des. Dev.* **9** (1970) 503.
[838] D. Balzer et al., *Chem. Technik* (Leipzig) **23** (1971) 513.
[839] D. R. Levin, R. Lavie, *Ind. Chem. Symp. Ser.* **87** (1984) 393.
[840] A. Nielsen: *Advances in Catalysis*, **vol. V**, Academic Press, New York 1953, p. 1.
[841] H. Hinrichs, J. Niedetzky, *Chem. Ing. Tech.* **34** (1962) 88.
[842] L. Fodor, *Chim. Ind. Genie Chim.* **104** (1971) 1002.
[843] *Nitrogen* **140** (1982) 30.
[844] U. Zardi, *Hydrocarbon Process.* **61** (1982) no. 8, 129.
[845] J. J. Hay, I. M. Pallai, *Br. Chem. Eng.* **8** (1963) 171.
[846] P. L. T. Brian et al., *Chem. Eng. Sci.* **20** (1965) 297.
[847] W. Hennel, *Chem. Tech. (Leipzig)* **15** (1963) 293.
[848] L. B. Hein, *Chem. Eng. Prog.* **48** (1952) no. 8, 412.
[849] N. S. Zayarnyi, *Int. Chem. Eng.* **2** (1962) no. 3, 378.
[850] A. Murase et al., *Ind. Eng. Chem. Process Des. Dev.* **9** (1970) no. 4, 503.
[851] J. B. Allen, *Chem. Process Eng. (London)* **46** (1965) no. 9, 473.
[852] Gmelins Handbuch der Anorganischen Chemie (1935), Stickstoff, nitrogen system 4, **vol. 2**, Verlag Chemie, Berlin, p. 405.
[853] C. Rumscheidt, H. H. Saenger, K. Winnacker, "Der Stickstoff und seine anorganischen Verbindungen" in K. Winnacker, E. Weingaertner (eds) "Chemische Technologie". Carl Hanser Verlag, München 1950, **vol. 2**, p. 188–190.
[854] C. A. Vancini: *Synthesis of Ammonia*, Macmillan, London 1971, p. 235.
[855] I. Hay, G. D. Honti: *The Nitrogen Industry*, **vol. 1**, Akadememiai Kiado, Budapest 1976.
[856] *Nitrogen* **72** (1971) 34.
[857] C. A. Vancini: *Synthesis of Ammonia*, Macmillian, London 1971, p. 249.
[858] US 2953 371, 1958 (A. Christensen, R. D. Rayfield).
[859] D. L. Astanovski, L. Z. Astanovski, *Nitrogen*, **232** (1998) 33–38.
[860] US 3041 151, 1962 (A. Christensen).
[861] US 3050 377, 1962 (A. Christensen).
[862] US 2861 873, 1976 (G. A. Worn).
[863] US 3032 139, 1976 (M.Vilceanu, C. Bors).
[864] H. Hinrichs et al., *DECHEMA Monogr.* **68** (1971) 493–500.
[865] P. Lesur, *Nitrogen* **108** (1977) 29.
[866] C. A. Vancini: *Synthesis of Ammonia*, Macmillan, London 1971, p. 236, 240, 244.
[867] A. V. Slack "Commercial ammonia processes"; A. V. Slack, G. J. James, *Ammonia*, **Part III** Marcel Dekker, New York 1974, p. 291–369.
[868] *Nitrogen* **75** (1972) 33.
[869] US 3475 136, 1969 (G. P. Eschenbrenner, C. A. Honigsberg).
[870] S. Strelzow: *Technology and Manufacture of Ammonia*, Wiley, New York 1981, p. 34.
[871] US 3694 169, 1972 (R. Fawcett, A. W. Smith, D. Westwood).
[872] D. E. Riddler, 16th AIChE Ammonia Safety Symp., Atlantic City 1971; *Ammonia Plant Saf.* **14** (1972), 57.
[873] US 3633 179, 1972 (D. D. Metha, E. J. Miller).
[874] I. Dybkaer inH.I. Lasa (ed.): *Chemical Reactor Design and Technology*, Nasa ASI Series E: Applied Sciences, no. 110, Nijhoff Publ., Dordrecht 1986.

Topsoe, Inc. – EX1003
Page 415 of 1210

[875] V. Vek, 7th Int. Symp. Large Chem. Plants, Brugge 1988, p. 77.
[876] V. Vek, *Chem. Ing. Tech.* **45** (1973) 608.
[877] V. Vek, *Ind Eng. Chem. Process Des. Dev.* **16** (1977) 412.
[878] DE 3334 777, 1984 (K. Ohasaki, J. Zanma, H. Watanabe).
[879] *Nitrogen* **31** (1964) 22.
[880] T. Wett, *Oil Gas J.* **69** (1971) 70.
[881] *Chem. Eng (New York)* **78** (1971) 90.
[882] US 3372 988, 1968 (H. J. Hansen).
[883] A. Nielsen, 16th AIChE Ammonia Safety Symp., Atlantic City 1971.
[884] A. V. Slack in A. V. Slack, G. J. James (eds.): *Ammonia,* **part III,** Marcel Dekker, New York 1974, p. 345.
[885] A. V. Slack in A. V. Slack, G. J. James (eds.): *Ammonia,* **part III,** Marcel Dekker, New York 1974, p. 354.
[886] US 3754 078, 1975 (H. Hinrichs et al.).
[887] US 3918 918, 1975 (H. B. Kohn, G. Friedman).
[888] O. J. Quartulli, G. A. Wagner, *Hydrocarbon Process.* **57** (1978) no. 12, 115.
[889] US 3567 404, 1971(L. C. Axelrod et al.).
[890] G. P. Eschenbrenner, G. A. Wagner, 16th AIChE Ammonia Safety Symp., Atlantic City 1971; *Ammonia Plant Saf.* **14** (1972) 51.
[891] C. A. Vancini: *Synthesis of Ammonia,* Macmillan, London 1971 p. 232.
[892] US 2898 183, 1959 (G. Fauser).
[893] S. Strelzow: *Technology and Manufacture of Ammonia,* Wiley, New York 1981, p. 27.
[894] H. W. Graeve, *Chem. Eng. Prog.* **77** (1981) no. 10, 54; *Ammonia Plant Saf.* **23** (1981) 78.
[895] *Nitrogen* **81** (1973) 29, 37.
[896] H. Hinrichs, H. Lehner, *Chem. Anlagen + Verfahren* 1972, no. 6, 55.
[897] F. Förster, *Chem. Eng. (N.Y.)* **87** (1980) no. 9, 62.
[898] *Nitrogen* **101** (1976) 42.
[899] Topsøe Topics, June 1976.
[900] I. Dybkjaer, E. A. Gam, 29th AIChE Ammonia Safety Symp., San Francisco 1994; *Ammonia Plant Saf.* **25** (1985) 15.
[901] I. Dybkjaer, E. A. Gam, *CEER Chem. Econ. Eng. Rev.* **16** (1984) 29.
[902] Haldor Topsoe US 4181 701, 1980 (E. A. Gam).
[903] Haldor Topsoe US 2710 247, 1981.
[904] I. Dybkjaer, J. E. Jarvan, Nitrogen 97, British Sulphur Conference, Geneva 1997.
[905] *Nitrogen* **169** (1987) 33.
[906] E. Commandini, U. Zardi, Fertilizer Latin America, Int. Conf. British Sulphur , Caracas 1989.
[907] L. Sutherland, B. Wallace, 33rd AIChE Ammonia Safety Symp., Denver 1988.
[908] G. Pagani, U. Zardi, FAI Seminar 1988, The Fertilizer Society of India, New Dehli, S II/1–19.
[909] K. A. Clayton, N. Shannahan, B. Wallace, 35th AIChE Ammonia Safety Symp., San Diego 1990.
[910] N. Shannahan, *Hydrocarbon Process* **68** (1989) 60.
[911] S. E. Handman, J. R. LeBlanc, *Chem. Eng. Prog.* **79** (1983) no. 5, 56.
[912] H. Stahl, *Symposium of the Fertilizer Society,* London 1982, Proceedings, p. 61.
[913] US 4452760, 1984 (R. B. Peterson, R. Finello, G. A. Denavit).
[914] US 3892 535, 1975 (W. Hennel, C. Sobolewsk).
[915] W. A. Glover, J. P. Yoars, *Hydrocarbon Process.* **52** (1973) no. 4, 165; 17th AIChE Ammonia Safety Symp., Minneapolis 1972; *Ammonia Plant Saf.* **15** (1973) 77.

Topsoe, Inc. – EX1003
Page 416 of 1210

[916] *Nitrogen* **82** (1973) 34.
[917] GB 1134 621, 1989 (D. R. Twist, D. W. Stanbridge).
[918] W. A. Glover, J. P. Yoars, *Hydrocarbon Process* **52** (1973) 165.
[919] US 3721 532, 1973 (L. E. Wright, A. E. Pickford).
[920] US 3851 046, 1975 (L. E. Wright, A. E. Pickford).
[921] US 4 744 966, 1988 (B. J. Grotz).
[922] EP 268 469, 1988 (B. J. Grotz).
[923] K. C. Wilson, B. J. Grotz, *J. Tech. Dev.* **14** (1990) 54.
[924] B. J. Grotz, L. Grisolia, *Nitrogen* **199** (1992) 39.
[925] F. Horn, L. Küchler, *Chem. Ing. Tech.* **31** (1959) 1.
[926] H. Bakemeier, R. Krabetz, *Chem. Ing. Tech.* **34** (1962) 1.
[927] R. Jackson, *Chem. Eng. Sci.* **19** (1964) no. 19, 253.
[928] D. C. Dyson et al., *Canadian J. Chem. Eng. Sci.* **45** (1967) 310.
[929] L. D. Gaines, *Ind. Eng. Chem. Process Des. Dev.* **16** (1977) no. 3, 381.
[930] I. Dybkjaer in A. Nielsen: *Ammonia — Catalysis and Manufacture*, Springer-Verlag, New York 1995, p. 251.
[931] Ammonia — Energy Integration in Ammonia Plants, Uhde Engineering News 2–91, Hi 111 9 1000 91, 1991.
[932] M. J. P. Bogart in A. I. More (ed.), *Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol. 4th 1981* 1982, 141.
[933] M. J. P. Bogart, *Plant Oper. Prog.* **1** (1982) no. 3, 147.
[934] M. J. P. Bogart, *Hydrocarbon Process.* **57** (1978) no. 4, 145.
[935] W. Malewski, *Chem. Ztg.* **95** (1971) 186.
[936] K. Bohlscheid, *Chem. Prod.* **8** (1979) no. 3.
[937] G. Holldorff, *Hydrocarbon Process.* **58** (1979) no. 7, 149.
[938] Pullman Inc., DE-OS 2741851, 1978 (C. L. Becker).
[939] G. Pagani, U. Zardi, *Hydrocarbon Process.* **51** (1972) no. 7, 106–110.
[940] F. Saviano, V. Lagana, P. Bisi, *Hydrocarbon Process.* **60** (1981) no. 7, 99.
[941] H. Hinrichs, *Chem. Ztg. Chem. Appar.* **86** (1962) 223.
[942] H. Neth et al., *Chem. Eng. Prog.* **78** (1982) no. 7, 69.
[943] *Chem. Week* **116** (Feb. 19, 1975) 29.
[944] A. Finn, *Nitrogen* **175** (1988) 25 –32.
[945] R. Harmon, W. H. Isalski, 25th AIChE Ammonia Safety Symp., Portland 1980; *Ammonia Plant Saf.* **23** (1981) 39.
[946] A. Haslam, P. Brook, H. Isalski, L. Lunde, *Hydrocarbon Process.* **55** (1976) no. 1, 103.
[947] *Nitrogen* **102** (1976) 35.
[948] R. Banks, *Chem. Eng. (N.Y.)* **84** (1977) no. 21, 90.
[949] A. A. Haslam, W. H. Isalski, 19th AIChE Ammonia Safety symp., Salt Lake City 1974; *Ammonia Plant Saf.* **17** (1975) 80.
[950] R. Harmon in A. I. More (ed.), *Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol. 4th 1981* 1982, 113.
[951] R. Banks, 22th AIChE Ammonia Safety Symp., Denver 1977; *Ammonia Plant Saf.* **20** (1978) 79.
[952] *Oil Gas J.* **77** (March 5, 1979) 182.
[953] W. H. Isalski, *Nitrogen* **152** (1984) 100.
[954] R. Harmon, W. H. Isalski, 25th AIChE Ammonia Safety Symp., Portland 1980; *Ammonia Plant Saf.* **23** (1981) 39.

Topsoe, Inc. – EX1003
Page 417 of 1210

[955] C. A. Combs, 25th AIChE Ammonia Safety Symp., Portland 1980; *Ammonia Plant Saf.* **23** (1981) 32.
[956] R. Fabian, D. Tilman, *Linde Ber. Techn. Wiss.* **59** (1986) 6.
[957] C. A. Combs, 25th AIChE Ammonia Safety Symp., Portland 1980; *Ammonia Plant Saf.* **23** (1981)32.
[958] D. L. MacLean, C. E. Prince, Y. C. Chae, *Chem. Eng. Prog.* **76** (1980) no. 3, 98; 24th AIChE Ammonia Safety Symp., San Francisco 1979; *Ammonia Plant Saf.* **22** (1980) 1.
[959] Y. C. Chae, G. S. Legendre, J. M. van Gelder in A. I. More (ed.), *Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol. 4th 1981* 1982, 457.
[960] *Nitrogen* **130** (1981) 40.
[961] *Nitrogen* **136** (1982) 29.
[962] R. L. Schendel, C. L. Mariz, J. Y. Mak, *Hydrocarbon Process.* **62** (1983) no. 8, 58.
[963] D. L. MacLean, D. J. Stockey, T. R. Metzger, *Hydrocarbon Process.* **62** (1983) no. 8, 47.
[964] H. Knieriem Jr., *Hydrocarbon Process.* **59** (1980) no. 7, 65.
[965] M. D. Rosenzweig, *Chem. Eng. (N.Y.)* **88** (1981) no. 24, 62.
[966] G. Schulz, H. Michele, U. Werner, *Chem. Ing. Tech.* **54** (1982) no. 4, 351.
[967] A. K. Fritzsche, R. A. Narayan, *CEER Chem. Econ. Eng. Rev.* **19** (1987) 19.
[968] W. A. Koros, R. A. Narayan, *Chem. Eng. Progr.* (1995) 68 - 81.
[969] *Hyrocarbon Process.* **62** (1983) 43 - 62.
[970] G. Q. Miller, M. J. Mitariten, ICI Catalco/KTI/UOP Hydrogen Plant Seminar, Chicago 1995.
[971] *Nitrogen* **121** (1979) 37 - 43.
[972] G. Low, "Revamping Ammonia Plant" (ed. K. Dunn), Supplement to *Nitrogen* **147** (1984).
[973] Union Carbide Corp., US 4077780, 1976.
[974] *Chem. Eng. (London)* 1979, no. 345, 395.
[975] K. Knoblauch et al., *Erdöl Kohle Erdgas Petrochem.* **32** (1979) 551.
[976] J. G. Santangelo, G. T. Chen, *Chemtech* **13** (1983) no. 10, 621.
[977] J. J. Sheridan, III, et al., *Less Common Met.* **89** (1983). 447.
[978] R. J. Berry, *Chem. Eng. (N.Y.)* **86** (1979) no. 15, 62.
[979] W. H. Isalski, G. J. Ashton in A. I. More (ed.), *Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol. 4th 1981* 1982, 125.
[980] S. Lynn, C. Alesandrini, 18th AIChE Ammonia Safety Symp., Vancouver 1973; *Ammonia Plant Saf.* **16** (1974) 80.
[981] I. Dybkjaer in A. Nielsen: *Ammonia — Catalysis and Manufacture*, Springer-Verlag, New York 1995, p. 231.
[982] O. J. Quartulli, J. B. Fleming, J. A. Finneran, *Hydrocarbon Process.* **47** (1968) 153.
[983] O. J. Quartulli, J. B. Fleming, J. A. Finneran, *Nitrogen* **58** (1969) 25.
[984] I. Dybkjaer in A. Nielsen (ed.): *Ammonia — Catalysis and Manufacture*, Springer-Verlag, New York 1995, p. 227, 228.
[985] H. Weber et al., *Chem. Ing. Tech.* **56** (1984) no. 5, 356.
[986] H. W. Graewe, 25th AIChE Ammonia Safety Symp., Portland 1980; *Ammonia Plant Saf.* **23** (1981) 78.
[987] H. W. Graewe, *Chem. Eng. Progr.* **77** (1981) no. 10, 54.
[988] K. Nassauer, M. Fix, AFA/Abu — Qir Ammonia/Urea Technol. Symp., 1996.
[989] "Plant and process engineering equipment – Components and plant circuitry", *Steinmüller company brochure* P 8604-06-0510/89 (1989)
[990] "Waste heat recovery for reformed gas and synthesis gas cooling in modern ammonia plants", *Borsig AG, company brochure.*

Topsoe, Inc. – EX1003
Page 418 of 1210

[991] "K. Nassauer, "Process gas waste heat boilers" *Borsig AG, company brochure* 290151 AC.
[992] *Nitrogen* **176** (1988) 25.
[993] H. Lachmann, D. Fromm, 32nd AIChE Ammonia Safety Symp., Minneapolis 1987; *Ammonia Plant Saf.* **28** (1988) 39.
[994] G.R. Prescott et al., 33rd AIChE Ammonia Safety Symp., Denver 1988; *Ammonia Plant Saf.* **29** (1989) 253.
[995] NH_3—Gas—Synthesis, Balke-Dürr comp. brochure, CBA 100o-7.91, 1991.
[996] T. Timbres et al., 34th AIChE Ammonia Safety Symp. San Francisco 1989; *Ammonia Plant Saf.* **30** (1990) 200.
[997] Balcke-Dürr, Company Leaf-let 31.07.1990.
[998] Synloop Wast Heat Boiler in Ammonia Plants — Unique Hot/Cold Tube Sheet Design, Babcock Borsig comp. brochure.
[999] M. Podhorsky et al., 40th AIChE Ammonia Safety Symp., Tucson 1995; *Ammonia Plant Saf.* **36** (1996) 321.
[1000] K. H. Deuse, *Ingenieursblad* **40** (1971) no. 21, 614 (Prospectus of Borsig: Process Gas Waste Heat Boilers).
[1001] M. Podhorski, "Hydraulic expansion of tubes", *International Conference on Expanded and Rolles Joint technology, Toronto* (1993).
[1002] J. Becker, *Verfahrenstechnik* 3, 8 (1969), 335.
[1003] Shell POX Waste heat boilers Standard Fasel-Lentjes, Company brochure 1996.
[1004] L. Silberring, *Nitrogen* **120** (1979) 35.
[1005] P. Hinchley, *Chem. Eng. (N.Y.)* **86** (1979) no. 17, 120. P. Hinchley, *Proc. Inst. Mech. Eng.* **193** (1979) no. 8.
[1006] H. Lachmann, 25th AIChE Ammonia Safety Symp., Portland 1980; *Ammonia Plant Saf.* **23** (1981) 51.
[1007] O. J. Quartulli, W. Turner, *Nitrogen* **80** (1972) 28.
[1008] O. J. Quartulli, W. Turner, *Nitrogen* **81** (1973) 32.
[1009] J. B. LeBlanc, M. N. Shah, L. J. Buividas, *Hydrocarbon Process.* **59** (1980) no. 4, 68-G.
[1010] *Hydrocarbon Process.* **62** (1983) no. 11, 81.
[1011] E. Futterer, E. Pattas, *Chem. Ztg.* **98** (1974) no. 9, 438.
[1012] K.-J. Mundo, *Chem. Anlagen + Verfahren* 1972, no. 6, 49.
[1013] J. D. Rankin, J. G. Livingstone, 25th AIChE Ammonia Safety Symp., Portland 1980; *Ammonia Plant Saf.* **23** (1981) 203.
[1014] J. S. Campbell, J. W. Marshall, *Nitrogen* 1976, no. 103, 33.
[1015] O. J. Quartulli, D. Wagener, *Erdöl Kohle Erdgas Petrochem.* **26** (1973) no. 4, 192.
[1016] U. Zardi, A. Antonini, *Nitrogen* **122** (1979) 33.
[1017] G. D. Honti, 4th Int. Conf on Fertilizer Technol., London 1981, Conf. Proc., Brit. Sulphur (ed. A. More) p. 1.
[1018] F. Saviano, W. Lagana, P. Bisi, *Hydrocarbon Process.* **60** (1981) 99.
[1019] I. Dybkjaer, ECN Europ. Chemical News: Fertilizers 83 (suppl.), 1983, p.15.
[1020] G. R. James, K. J. Stokes, *Chem. Eng. Progr.* **62** (1984)81.
[1021] J. M. Blanken, 33rd AIChE Ammonia Safety Symp., Denver 1988; *Ammonia Plant Saf.* **29** (1989) 273.
[1022] F. C. Brown, *Nitrogen* **100** (1976) 65.
[1023] K. J. Mundo, *Erdöl, Kohle, Erdgas Petrochemie* **31** (1978) 74.
[1024] *Nitrogen* **182** (1989) 25.
[1025] L. J. Buividas, *Hydrocarbon Process.* **58** (1979) no. 5, 257.

Topsoe, Inc. – EX1003
Page 419 of 1210

[1026] G. D. Honti in A. I. More (ed.), *Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol. 4th 1981* 1982, 1.
[1027] G. R. James, 31st Annual Meeting, The Fertilizer Industry Round Table, USA 1981 G. R. James, K. J. Stokes, *Chem. Eng. Prog.* **80** (1984) no. 6, 33.
[1028] I. Dybkjaer, *Eur. Chem. News* 1983, no. Feb. 21, 15 (Fertilizers '83 Suppl.).
[1029] A. Pinto, P. L. Rogerson, *Chem. Eng. Prog.* **73** (1977) no. 7, 95.
[1030] K. J. Mundo, *Erdöl Kohle Erdgas Petrochem.* **31** (1978) no. 2, 74.
[1031] J. R. LeBlanc, *Hydrocarbon Process.* **63** (1984) no. 7, 69.
[1032] A. Nielsen et al., *Plant Oper. Prog.* **1** (1982) no. 3, 186.
[1033] J. G. Livingstone, A. Pinto, *Chem. Eng. Prog.* **79** (1983) no. 5, 62.
[1034] ICI, EP-A 93502, 1983 (A. Pinto).
[1035] P. H. Brook: "Fertilizer '83," *Br. Sulphur Corp. 7th Int. Conf.*, London 1983, Proceedings of the Conf., p. 159.
[1036] G. Pagani, G. Brusasco, G. Gramatica in A. I. More (ed.), *Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol. 4th 1981* 1982, 195.
[1037] Pullman Inc., US 4079017 (D. B. Crawford, C. L. Becker, J. R. LeBlanc); US 4162290, 1979 (D. B. Crawford, C. L. Becker, J. R. LeBlanc).
[1038] S. Uji, M. Ikeda, *Hydrocarbon Process.* **60** (1981) no. 7, 94.
[1039] E. Nobles, J. C. Stover, *Chem. Eng. Prog.* **80** (1984) no. 1, 81. E. Nobles, J. C. Stover, *Ammonia Plant Saf.* **24** (1984) 41.
[1040] *Nitrogen* **162** (1986).
[1041] J. G. Livingstone, A. Pinto, 27th AIChE Ammonia Safety Symposium, Los Angeles 1982; *Chem. Eng. Progr.* **79** (1983) 62–66.
[1042] W. K. Taylor, A. Pinto, 31st AIChE Ammonia Safety Symposium, Boston 1986; *Ammonia Plant Saf.* **27** (1987) 43.
[1043] "Ammonia–Uhde's low energy technology", *Uhde engineering news 1–91 (1991).*
[1044] S. Weems, D. H. Ball, D. E. Griffin, *Chem. Eng. Prog.* **75** (1979) no. 5, 64; 23th AIChE Ammonia Safety Symp., Miami Beach 1978; *Ammonia Plant Saf.* **21** (1979) 39.
[1045] G. Collier, J. D. Voelkers, D. E. Griffin, *Ammonia Plant Saf.* **22** (1980) 206.
[1046] F. Yazhari, *Hydrocarbon Process.* **61** (1982) no. 5, 187.
[1047] P. Tjissen, 21nd AIChE Ammonia Safety Symp., Atlantic City 1976; *Ammonia Plant Saf.* **19** (1977) 155.
[1048] G. R. Nieman, L. C. Daigre, III, 18th AIChE Ammonia Safety Symp., Vancouver 1973; *Ammonia Plant Saf.* **16** (1974) 45.
[1049] C. C. Yost, C. R. Curtis, C. J. Ryskamp, 24th AIChE Ammonia Safety Symp., San Francisco 1979; *Ammonia Plant Saf.* **22** (1980) 200.
[1050] *Nitrogen* **65** (1970) 32.
[1051] T. L. Huurdeman, 33rd AIChE Ammonia Safety Symp., Denver 1988; *Ammonia Plant Saf.* **29** (1989) 234.
[1052] R. L. Allen, jr., G. A. Moser, 36th AIChE Ammonia Safety Symp., Los Angeles 1991; *Ammonia Plant Saf.* **32** (1992) 170.
[1053] D. Dekmush et al., 37th AIChE Ammonia Safety Symp., San Antonio 1992; *Ammonia Plant Saf.* **33** (1993)278.
[1054] S. Madhaven, *Plant /Oper. Progr.* **3** (1984) no. 1, 14.
[1055] S. M. Solomon, 29th AIChE Ammonia Safety Symp., San Francisco 1984; *Ammonia Plant Saf.* **25** (1985) 129.

Topsoe, Inc. – EX1003
Page 420 of 1210

[1056] S C. Moore, T. M. Piper, C. C. Chen,30th AIChE Ammonia Safety Symp., Seattle 1985; *Ammonia Plant Saf.* **26** (1986) 56.
[1057] *Nitrogen* **169** (1987) 35.
[1058] S. Mani, S. K. Shoor, H. S. Pedersen, 33rd AIChE Ammonia Safety Symp., Denver 1988; *Ammonia Plant Saf.* **29** (1989) 244; *Plant /Oper. Progr.* **8** (1989) 33.
[1059] G. Grossman, J. Dejaeger, 37th AIChE Ammonia Safety Symp., Los Angeles 1991; *Ammonia Plant Saf.* **32** (1992) 164.
[1060] I. Dybkjaer in A. Nielsen (ed.): *Ammonia Catalysis and Manufacture* Springer, New York 1995 p. 263.
[1061] I. Dybkjaer in A. Nielsen (ed.): *Ammonia Catalysis and Manufacture* Springer, New York 1995 p. 258–261; 269–271 .
[1062] P. Radke, *Nitrogen* **225** (1997) 27.
[1063] *Oilweek (Calgary, Alberta)* (May 23, 1983) 12.
[1064] *Chem. Week* **134** (March 21, 1984) 15.
[1065] *Nitrogen* **189** (1989) 25.
[1066] J. R. LeBlanc, *Chem. Econ. Eng. Rev.* **18** (1986) no. 5, 22.
[1067] *Fertilizer Focus* **4** (1987) no. 10, 40.
[1068] J. R. LeBlanc, *Energy Prog.* **5** (1985) no. 1, 4.
[1069] M. Appl: *Ammonia, Methanol, Hydrogen, Carbon Monoxide — Modern production Technologies* CRU Publ., London 1997, p. 44, 45.
[1070] J. R. LeBlanc, 29th AIChE Symposium on Safety in Ammonia Plants, San Francisco, Calif., 1984; *Ammonia Plant Saf.* **25** (1985) 29.
[1071] *CEER Chem. Econ. Eng. Rev.* **11** (1979) no. 5, 24.
[1072] I. Dybkjaer in A. Nielsen (ed.): *Ammonia Catalysis and Manufacture* Springer, New York 1995 p. 288, 289.
[1073] I. Dybkjaer, Fertilizer Latin America Int. Conf., Caracas 1989; Brit. Sulphur Corp. Proc., vol. 1, p. 77.
[1074] I. Dybkjaer, FAI Seminar 1990, The Fertilizer Assoc. of India, New Delhi, p. SIII–1.
[1075] T. Bajpai, *Nitrogen 88, Brit. Sulphur 12th Int. Conf.*, Geneva 1988.
[1076] T. S. Hariharan, *J. Tech. Dev.* **7** (1987) no. 4, 42.
[1077] S. R. Sahore, T. S. Krishnan, *Fertilizer News* **15** (1989).
[1078] I. Dybkjaer, *Fertilizer Industry Ann. Rev.* **XIII** (1990) 42a.
[1079] I. Dybkjaer, IFA Technical Conf., The Hague 1992.
[1080] I. Dybkjaer, IFA – FADINAP Regional Conf. for Asia and Pacific, Bali 1992
[1081] *Hydrocarbon Process.* **62** (1983) no. 11, 79.
[1082] F. Brown, Proceedings no. 218, The Fertilizer Society, London 1983.
[1083] *Hydrocarbon Process.* **60** (1981) no. 11, 132.
[1084] *The Uhde Reformer: High Pressure, High Temperature Service* Uhde Brochure Hi 18 1500 11/ 1991.
[1085] Energy Efficient Ammonia Production*Uhde Eng. News.***3** (1991)
[1086] Ammonia Plant – Energy Integration*Uhde Eng. News.***2** (1991).
[1087] *Uhde's Ammonia Technology* Uhde Brochure Hi 18 1500 11/1991; RRD, 1992.
[1088] Ammonia, Uhde's Low Energy Technology*Uhde Eng. News.***1** (1991).
[1089] R. Hakmann,FAI Seminar 1990, The Fertilizer Assoc. of India, New Delhi, p. SIII–3.
[1090] J. Dejaeger, E. Das, 38th AIChE Ammonia Safety Symp., Orlando 1993; *Ammonia Plant Saf.* **34** (1994) 145.

Topsoe, Inc. – EX1003
Page 421 of 1210

[1091] F. C. Brown in A. I. More (ed.), *Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol. 4th 1981* 1982, 39.
[1092] P. A. Ruziska, C. C. Song, 29th AIChE Ammonia Safety Symp., San Francisco 1984; *Ammonia Plant Saf.* **25** (1985) 22.
[1093] P. A. Ruziska, P. Dranze, C. C. Song, Nitrogen 86, Brit. Sulphur conf., Amsterdam 1986.
[1094] *Chem. Eng. (N.Y.)* **86** (1979) no. 26, 88.
[1095] L. J. Ricci, *Chem. Eng. (N.Y.)* **86** (1979) no. 3, 50, 54.
[1096] *Oil Gas J.* **76** (1978) no. 49, 34.
[1097] P. Taffe, *Chem. Age (London)* **117** (Dec. 15, 1978) 8.
[1098] V. Pachaiyappan, *Fertilizer News* 1979, 41.
[1099] V. Lagana, *Chem. Eng. (N.Y.)* **85** (1978) no. 1, 37.
[1100] B. J. Grotz, *Nitrogen* **100** (1976) 71.
[1101] B. Grotz, G. Good, *Chem. Age* (London) **121** (Nov. 14, 1980) p. 18.
[1102] *Nitrogen* **144** (1983) 30.
[1103] K. C. Wilson et al., *Nitrogen* **151** (1984) 31.
[1104] K. C. Wilson, B. J. Grotz, J.Richez, Nitrogen 86, Brit. Sulphur Conf., Amsterdam 1986.
[1105] B. J. Grotz, *Nitrogen* **217** (1995) 41 - 48.
[1106] K. G. Christensen, B. J. Grotz, K. G. Gosnell, *Nitrogen* **181** (1989) 31 - 36.
[1107] W. Glover, J. P. Yoars, *Hydrocarbon Process.* **52** (1973) no.no. 4, 165.
[1108] W. Glover, J. P. Yoars, 17th AIChE Ammonia Safety Symp., Minneapolis 1972; *Ammonia Plant Saf.* **15** (1973) 77.
[1109] K. G. Christensen, B. J. Grotz, K. G. Gosnell, Fertilizer Latin America Int. Conf., Caracas 1989; Brit. Sulphur Corp. Proc., vol. 1.
[1110] B. J. Grotz, L. Grisolia, *Nitrogen* **199** (1992) 39.
[1111] ICI, EP-A 49967, 1982 (A. Pinto).
[1112] *Chem. Week* **132** (Jan. 5, 1983) 23.
[1113] *Hydrocarbon Process.* **62** (1983) no. 11, 80.
[1114] J. G. Livingstone, A. Pinto, 27th AIChE Ammonia Safety Symp., Los Angeles 1982; *Chem. Eng. Progr.* **79** (May 1983) 62 – 66.
[1115] Fertilizer Industry Annual Review, vol. XI, 1988
[1116] S. A. Topham, S. A. Hall, D. G. Heath, ICI/CFDC Tech. Symp., Shanghai 1989.
[1117] W. K. Taylor, A. Pinto, *Commisioning C–I–Ls Ammonia Plant*, 31st AIChE Ammonia Safety Symp., Boston 1986; *Ammonia Plant Saf.* **27** (1987) 43; *Plant/Operations Prog.* **6** (1987) 106 – 111.
[1118] M. P. Robert, C. W. Hooper, ICI/CFDC Tech. Symp., Shanghai 1989.
[1119] K. J. Elkins et al., Asia Nitrogen, Int. Conf., (Brit. Sulphur) Bali 1994.
[1120] K. J. Elkins et al., *ICIs AMV Ammonia Technology* ICI Catalco tech. paper 246W/126/3/AMM.
[1121] *Nitrogen* **162** (1989) 32 - 37.
[1122] J. G. Livingstone, A. Pinto, Fertilizer 83, Int. Conf. (Brit. Sulphur), London 1988.
[1123] D. L. Banquy, 24th AIChE Ammonia Safety Symp., Denver 1983; *Ammonia Plant Saf.* **24** (1984) 8.
[1124] F. C. Brown, *Eur. Chem. News* 1982, no. 15, 10 (Process Review Suppl.).
[1125] Humphreys & Glasgow Ltd., GB-A 2126208 A, 1983 (C. L. Winter).
[1126] F. C. Brown, C. Topham, Proc. Europ. Conf. on Energy Efficient Prod. of Fertilizers, Bristol 1990, p. 1.
[1127] *Jacobs Ammonia Technology*, Jacobs company brochure, 1996.

Topsoe, Inc. – EX1003
Page 422 of 1210

[1128] *Chem. Eng. (N.Y.)* **88** (1981) no. 10, 33.
[1129] P. Conolly, *Chem. Age (London)* **122** (Feb. 6, 1981) 12. *Eur. Chem. News* **36** (1981) no.no. 967, 16.
[1130] Pullman Inc., US 4148866, 1979 (C. L. Becker); US 4153673, 1979 (C. L. Becker).
[1131] *Nitrogen* **178** (1989) 30–39.
[1132] J. M. Halstead, A. Pinto, FAI Seminar, Delhi 1988.
[1133] S. P. Sergeev, *Nitrogen*, **233** (1998) 31–34
[1134] A. Pinto, J. M. S. Moss, T. C. Hicks, 34th AIChE Ammonia Safety Symp., San Francisco 1989; *Ammonia Plant Saf.* **30** (1990) 152.
[1135] K. Elkins, I. R. Barton, 39th AIChE Ammonia Safety Symp., Vancouver 1994; *Ammonia Plant Saf.* **35** (1995) 276; *Operational Performance of the ICI Leading Concept Ammonia (LCA) Process*, ICI Catalco tech. paper 274W/126/3/LCA.
[1136] T. C. Hicks, A. Pinto, *Fertilizer News* (1989) 37.
[1137] T. Miyasugi et al., *Chem. Eng. Prog.* **80** (1984) no. 7, 41. T. Miyasugi et al., *Ammonia Plant Saf.* **24** (1984) 64.
[1138] W. F. van Weenen, J. Tielroy, *Nitrogen* **127** (1980) 38.
[1139] *Oil Gas J.* **79** (1981) no. 18, 270.
[1140] S. Ratan, K. S. Jungerhans, KTI Symp., Scheveningen 1991.
[1141] J. J. Westenbrink, J. Voogd, Nitrogen 86, Brit. Sulphur Int. Conf., Amsterdam 1986.
[1142] J. J. Westenbrink, J. Voogd, FAI Seminar, New Delhi 1995.
[1143] W. F. van Weenen, J. Tielroy, *Proc. Fertilizer Soc.* (London) (1980) no. 191, 1.
[1144] W. F. van Weenen, J. Tielrooy, *32nd Ann. Meet., The Fertilizer Industry Round Table*, USA 1982, p. 268.
[1145] *Nitrogen* **208** (1994) 44–49.
[1146] M. Lembeck, Asia Nitrogen 96: Brit. Sulphur Int. Conf., Singapore 1996.
[1147] M. Lembeck, *Fertilizer News* (1993) 15.
[1148] *The Linde Ammonia Concept*, Linde Comp. publ. 1995.
[1149] J. Ilg, B. Kandziora, 41st AIChE Ammonia Safety Symp., Boston 1996; *Ammonia Plant Saf.* **37** (1997) 341.
[1150] M. Spear, *Chem. Eng. (London)* 1979, no. 340, 29.
[1151] P. R. Savage, *Chem. Eng. (N.Y.)* **85** (1978) no. 25, 68 D.
[1152] *ECN Euro Chem News* **20** (1978) 39.
[1153] F. C. Brown, Proc. Dev. Symp. 1978, The Inst. of Engineers, p. 1.
[1154] W. Armbruster, *Erdöl Kohle Erdgas Petrochem.* **33** (1980) no. 3, 118.
[1155] G. Kammholz, G.-A. Müller, *Erdöl Kohle Erdgas Petrochem.* **26** (1973) no. 12, 695.
[1156] H. E. Butzert, *Chem. Eng. Prog.* **72** (1976) no. 1, 56; 20th Ammonia Safety Symp., Boston 1975; *Ammonia Plant Saf.* **18** (1976) 78.
[1157] E. Supp, *Nitrogen* **109** (1977) 36.
[1158] J. Morrison, *Oil Gas J.* **67** (Feb. 24, 1969) 76.
[1159] *CEER Chem. Econ. Eng. Rev.* **12** (1980) no. 6–7, 33.
[1160] J. Dybkjaer, J. Hansen *Chem. Age India* **31** (1980) no. (12): DEV. 3/1
[1161] T. Sueyama, T. Tsujino, Fertilizer 85: Brit. Sulphur Int. Conf., London 1985.
[1162] G. F. Skinner in A. I. More (ed.), *Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol. 4th 1981* 1982, 491.
[1163] Humphreys & Glasgow Ltd., GB-A 2126573 A, 1983 (F. C. Brown).
[1164] R. A. Sharpe, *Hydrocarbon Process.* **55** (1976) no. 11, 171.

Topsoe, Inc. – EX1003
Page 423 of 1210

[1165] L. J. Partridge, *Chem. Eng. Prog.* **72** (1976) no. 8, 57; 20th AIChE Ammonia Safety Symp., Boston 1975; *Ammonia Plant Saf.* **18** (1976) 73.
[1166] S. McQueen, *Chem. Eng. (N.Y.)* **85** (1978) no. 25, 68 H.
[1167] Lurgi Express Information Ö 1323/5.79, Ammonia Plant Based on Coal.
[1168] *Chem. Eng. News* **57** (1977) no. 23, 27.
[1169] G. W. Alves, D. A. Waitzmann, *Erdöl Kohle Erdgas Petrochem.* **35** (1982) no. 2, 70.
[1170] D. Netzer, J. Moe, *Chem. Eng. (N.Y.)* **84** (1977) no. 23, 129.
[1171] D. A. Waitzman et al., Fall Annual Meeting of the AIChE, Washington, D.C., Oct. 30, 1983.
[1172] T. Matsunami, paper presented to the Internat.Fertilizer Industry Assoc., Johannesburg, South Africa, March 1983.
[1173] *Ubes Texaco Process Coal Gasification Plant,* Ube comp. brochure 1984.
[1174] D. C. Thomson, 4th Int. Conf. on Fertilizer Technol., London 1991, Conf. Proc., part 1, p. 1.
[1175] J. A. Tonna, F. C. Brown, T. W. Nurse, *Nitrogen 91: Brit. Sulphur Conf.*, Copenhagen 1991, p. 127 – 139.
[1176] S. Madhavan, B. Landry, *Nitrogen 91: Brit. Sulphur Conf.*, Copenhagen 1991, p. 127 – 139.
[1177] R. W. Parrish, *Process Improvements,* Gulf Coast Ammonia Producers Meeting, Baton Rouge 1991.
[1178] J. R. LeBlanc, *Hydrocarbon Process.* **65** (1986) no. 8, 39 – 44.
[1179] M. Jung, *Nitrogen* **191** (1991) 42 – 52.
[1180] *Nitrogen* **141** (1983) 38.
[1181] F. C. Brown, *ECN Europ. Chem. News, Proc. Rev.* **8** (1982).
[1182] I. Dybkjaer, Fertilizer Latin America, Int. Conf. Brit Sulphur, Caracas 1989.
[1183] A. Nielsen et al., *Plant/Oper. Progr.* **1** (1982) no. 3, 186.
[1184] H. Graewe, *Nitrogen 88: 12th Int. Conf. Brit. Sulphur,* Geneva 1988, p. 77.
[1185] A. M. Dark, E. A. Stallworthy, *Nitrogen* **153** (1985) 25
[1186] D. Singh, *Process Plant Eng.* **73** (1986) Jan–March.
[1187] J. R. LeBlanc, *Hydrocarbon Process.* **63** (1984) no. 7, 69..
[1188] R. Darjat, J. R. LeBlanc, Nitrogen 88: 12th Int. Conf. Brit. Sulphur, Geneva 1988, p. 77.
[1189] C. L. Becker in A. I. More (ed.), *Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol. 4th 1981* 1982, 537.
[1190] J. R. LeBlanc, *Hydrogen Process.* **63** (1984) no. 7, 69.
[1191] S. I. Wang, N. M. Patel, 28th Ammonia Safety Symp., Denver 1983; *Ammonia Plant Saf.* **24** (1984) 1. S. I. Wang, N. M. Patel, *Plant Oper. Prog.* **3** (1984) no. 2, 101.
[1192] G. Low, *Nitrogen* **147** (1984)1 – 32 (Suppl. "Revamping Ammonia Plants").
[1193] Foster Wheeler, US 4296 085, 1981 (D. L. Banquy).
[1194] D. Kitchen, A. Pinto, 35th AIChE Ammonia Safety Symp., San Diego 1990; *Ammonia Plant Saf.* **31** (1991) 219.
[1195] *Nitrogen* **214** (1996) 46.
[1196] H. Bendix, L. Lenz, 33rd AIChE Ammonia Safety Symp., Denver 1988; *Ammonia Plant Saf.* **29** (1989) 221.
[1197] D. L. MacLean, C. E. Prince, Y. C. Chae, 24th AIChE Ammonia Safety Symp., San Francisco 1979; *Ammonia Plant Saf.* **22** (1980) 1, *Chem. Eng. Progr.* 1980, 98 – 104.
[1198] R. G. Howerton, 24th AIChE Ammonia Safety Symp., San Francisco 1979; *Ammonia Plant Saf.* **22** (1980) 9.
[1199] N. W. Patel, S. I. Wang, K. J. Kittelstad, 33rd AIChE Ammonia Safety Symp., Denver 1988; *Ammonia Plant Saf.* **29** (1989) 33.

Topsoe, Inc. – EX1003
Page 424 of 1210

[1200] M. Tsujimoto et al., 34th AIChE Ammonia Safety Symp., San Francisco 1989; *Ammonia Plant Saf.* **30** (1990) 167.
[1201] M. Tsujimoto et al., *Nitrogen 91: Brit. Sulphur Conf.*, Copenhagen 1991, p. 127–139.
[1202] R. L. Newland, J. D. Pierce, D. M. Borzik, 32nd AIChE Ammonia Safety Symp., Minneapolis 1987; *Ammonia Plant Saf.* **28** (1988) 53.
[1203] U. Zardi, E. Commandini, C. Gallazzi in A. I. More (ed.), *Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol. 4th 1981* 1982, 173.
[1204] Ammonia Casale, DE-OS 3146778, 1981 (U. Zardi, E. Commandini).
[1205] E. Commandini, U. Zardi: "Fertilizer '83", *Br. Sulphur Corp. 7th Int. Conf.*, London 1983, Proceedings of the Conf., p. 179.
[1206] *Fertilizer News* (1987) (December) 19.
[1207] F. C. Brown, U. Zardi, G. Pangani, *Nitrogen 88: 12th Brit. Sulphur Int. Conf.*, Geneva 1988, p. 1159–139.
[1208] The M. W. Kellogg ammonia converter retrofit, Kellogg company brochure HG/2.5M/3–88 (1988)
[1209] R. G. Howerton, S. A. Noe, *33rd AIChE Ammonia Safety Symposium*, Denver, Oct 1988; *Ammonia Plant Saf.* **29** (1989) 157.
[1210] T. Czuppon et al., 38th AIChE Ammonia Safety Symp., Orlando 1993; *Ammonia Plant Saf.* **34** (1994).
[1211] B. Szantay, E. Jahab in G. D. Honti (ed.): *The Nitrogen Industry*, Akademiai Kiado, Budapest 1976, p. 701–706.
[1212] C. A. Vancini: *La Sintesi dell Amoniaca*, Hoepli, Milano 1961, p. 769.
[1213] *Nitrogen* **16** (1962) 48.
[1214] H. Jungfer, "Synthesegas aus Raffinerie-Rückständen, Konzeption und Betriebsergebnisse von Lindeanlagen zur Partiellen Oxidation", *Linde-Bericht aus Technik und Wissenschaft*, Nr. 57 (1985), 15–20 (ISBN 0024-3728).
[1215] Lurgi, References – *Gas- and Synthesis gas Technology, Lurgi Brochure* 1569e/9.93/4.10.
[1216] M. Appl: *Ammonia, Methanol Hydrogen, Carbon Monoxide – Modern Production Technologies*, CRU London 1997, 3. Methanol, p. 98–99.
[1217] D. Claes, N. Frisse, R. Hakman "Methanol co-production as a revamp otopn for an ammonia plant" *FAI Symposium "Advances in Fertilizer Production"*, New Delhi (April 1995).
[1218] I. Dybkjaer "Ammonia Production Processes" in W. A. Nielsen (ed.): *Ammonia – Catalysis and Manufacture*, Springer, Heidelberg, 1995, p. 300–302.
[1219] *Nitrogen* **43** (1966) 26.
[1220] *Nitrogen* **64** (1970) 17.
[1221] O. J. Quartulli, L. C. Axelrod, R. Randall, (1971) Het Ingenieursblad, 40 (21), 642.
[1222] V. Lagana, U. Zardi, Proc. Fert., Soc. London, (1977), 167, 1.
[1223] V. Lagana, Chem. Eng. (NY) (1978), 85 (1), 167, 1.
[1224] G. Farinola, V. Lagana, Hydrocarbon Processing (1979), 58 (9), 202.
[1225] W. Hausmann et al., *Stahl Eisen* **107** (1987) no. 12, 45–53.
[1226] W. A. Bonner, *Hydrocarbon Process.* (1951) no. 5, 165.
[1227] B. Granville, *Welding in the World* **31** (1993) no. 5, 308.
[1228] API Publication 941, 2nd ed., American Petroleum Institute, Washington, D.C., June 1977; last ed. April 1990.
[1229] G. A. Nelson, *Transactions of ASME* **56** (1977) 205–213.
[1230] I. Class, *Stahl Eisen* **80** (1960) no. 11, 17.
[1231] I. Class, *Stahl Eisen* **85** (1965) 149.

Topsoe, Inc. – EX1003
Page 425 of 1210

[1232] G. R. Prescott, *Plant Oper. Prog.* **1** (1982) no. 2, 94.
[1233] A. Heuser, 36th AIChE Ammonia Safety Symp., Los Angeles 1991; *Ammonia Plant Saf.* **32** (1992) 243.
[1234] G. R. Prescott, 37th AIChE Ammonia Safety Symp., Los Angeles 1991; *Ammonia Plant Saf.* **32** (1992) 217.
[1235] G. H. Wagner, A. Heuser, G. Heinke, 36th AIChE Ammonia Safety Symp., Los Angeles 1991; *Ammonia Plant Saf.* **32** (1992) 252.
[1236] G. R. Prescott, B. J. Grotz, 39th AIChE Ammonia Safety Symp., Vancouver 1994; *Ammonia Plant Saf.* **35** (1995) 116.
[1237] H. D. Marsch, *Plant Oper. Prog.* **1** (1982) no. 3, 152.
[1238] U. Jäkel, W. Schwenk, *Werkst. Korros.* **22** (1971) no. 1, 1.
[1239] S. Y. Sathe, T. M. O'Connor 32nd AIChE Ammonia Safety Symp., Minneapolis 1987; *Ammonia Plant Saf.* **28** (1988) 115.
[1240] C. A. van Grieken, 33rd AIChE Ammonia Safety Symp., Denver 1988; *Ammonia Plant Saf.* **29** (1989) 145.
[1241] Y. Murakami, T. Nomura, J. Watanabe, *MPC/ASTM Symposium on the Application of 2 1/4 Cr-1 Mo Steel for Thick Wall Pressure Vessels*, Denver, Col. 1980. J. Watanabe et al., *29th Petroleum Mechanical Engineering Conf.*, Dallas, Tex. 1974. G. Grote, *Chem. Ing. Tech.* **55** (1983) no. 2, 93.
[1242] R. Bruscato, *Weld. J. (Miami)* **49** (1970) no. 4, 148.
[1243] J. A. Richardson, *Nitrogen* **205** (1993) 49–52.
[1244] H. Stahl, S. G. Thomson, 40th AIChE Ammonia Safety Symp., Tucson 1995; *Ammonia Plant Saf.* **36** (1996) 180.
[1245] T. Shibasaki et al., 40th AIChE Ammonia Safety Symp., Tucson 1995; *Ammonia Plant Saf.* **36** (1996) 165.
[1246] R. J. Gommans, T. L. Huurdeman, 39th AIChE Ammonia Safety Symp., Vancouver 1994; *Ammonia Plant Saf.* **35** (1995) 145.
[1247] J. DeJaeger, L. Guns, J. Korkhaus, 39th AIChE Ammonia Safety Symp., Vancouver 1994; *Ammonia Plant Saf.* **35** (1995) 134.
[1248] J. A. Richardson, Boudouard Carbon and Metal Dusting, ICI Catalco Tech. paper.
[1249] O. J. Dunmore, *Proc. of UK Corrosion Conf.*, 1982.
[1250] H. Grabke, R. Krajak, J. C. Nava Paz, *Corrosion Science* **35** (1993) 1141.
[1251] R. F. Hochmann, 4th Int. Congr. on Metal Corrosion, Nat. Corr. Engineers, 1972.
[1252] A. W. Loginow, E. H. Phelps, *Corrosion (Houston)* **18** (1962) 299.
[1253] L. Lunde, 28th AIChE Ammonia Safety Symp., Denver 1983; *Ammonia Plant Saf.* **24** (1984) 154. J. M. Blanken, 28th AIChE Ammonia Safety Symp., Denver 1983; *Ammonia Plant Saf.* **24** (1984) 140.
[1254] *Plant Oper. Prog.* **2** (1983) no. 3, 247.
[1255] Dechema-Werkstoff-Tabelle/Chem. Beständigkeit, keyword "Ammoniak," sheet 4, Nov. 1978.
[1256] I. Class, K. Gering, *Werkst. Korros.* **25** (1974) no. 5, 314.
[1257] A. W. Loginow, *Mater. Perform.* **15** (1976) no. 6, 33.
[1258] B. E. Wilde, *Corrosion-NACE* **37** (1981) no. 3, 131.
[1259] R. S. Brown, *Plant Oper. Prog.* **1** (1982) no. 2, 97.
[1260] T. Kawamoto et al., *IHI Eng. Rev.* **10** (1977) no. 4, 17.
[1261] N. K. Roy, *Fert. Technol.* **18** (1981) no. 1+2, 1.
[1262] P. B. Ludwigsen, H. Arup, *Corrosion (Houston)* **32** (1976) no. 11, 430.
[1263] E. H. Phelps, *Ammonia Plant Saf.* **16** (1974) 32.

Topsoe, Inc. – EX1003
Page 426 of 1210

[1264] E. H. Phelps, 18th AIChE Ammonia Safety Symp., Vancouver 1973; *Ammonia Plant Saf.* **16** (1974) 32.
[1265] E. A. Olsen, 13th AIChE Ammonia Safety Symp., Montreal 1968; *Ammonia Plant Saf.* **11** (1969) 46.
[1266] W. v. d. Heuvel, G. v. d. Lindenbergh, *Ingenieursblad* **43** (1974) no. 18, 540–546.
[1267] C. C. Hale, *Nitrogen* **119** (1979) 30–36.
[1268] C. C. Hale, *Nitrogen* **125** (1980) 5.
[1269] T. Huberich, *Plant Oper. Prog.* **1** (1982) no. 2, 117–122.
[1270] I. K. Suri, R. K. Bohla, *Fertilizer News* (1986) (May), 52
[1271] E. H. Phelps, 16th AIChE Ammonia Safety Symp., Atlantic City 1971; *Ammonia Plant Saf.* **14** (1972) 109.
[1272] H. Arup, 21st AIChE Ammonia Safety Symp., Atlantic City 1976; *Ammonia Plant Saf.* **19** (1977) 73.
[1273] L. Lunde, R. Nyborg, 27th AIChE Ammonia Safety Symp., Vancouver 1994; *Ammonia Plant Saf.* **35** (1995) 50; *Plant/Oper. Progr.* **6** (1967) 11–16.
[1274] J. D. Stephens, F. Vidalin, 32nd AIChE Ammonia Safety Symp., Minneapolis 1987; *Ammonia Plant Saf.* **28** (1988) 9.
[1275] L. Lunde, R. Nyborg, 34th AIChE Ammonia Safety Symp., San Francisco 1989; *Ammonia Plant Saf.* **30** (1990) 60.
[1276] J. Blanken, 22nd AIChE Ammonia Safety Symp., Denver 1983; *Ammonia Plant Saf.* **20** (1978) 32.
[1277] L. Lunde, R. Nyborg, The Fertilizer Society, London 1991, Proc. no. 307.
[1278] H. Arup, 21st AIChE Ammonia SAfety Symp., Atlantic City 1976; *Ammonia Plant Saf.* **19** (1977) 73.
[1279] J. R. Byrne, F. E. Moir, R. D. Williams, 33rd AIChE Ammonia Safety Symp., Denver 1988. *Ammonia Plant Saf.* **29** (1989) 122.
[1280] M. Appl et al., 34th AIChE Ammonia Safety Symp., San Francisco 1989; *Ammonia Plant Saf.* **30** (1990) 22.
[1281] R. A. Selva, A. H. Heuser, 21st AIChE Ammonia Safety Symp.; *Ammonia Plant Saf.* **30** (1990) 39.
[1282] K. A. van Krieken, 20th AIChE Ammonia Safety Symp., Boston 1976; *Ammonia Plant Saf.* **18** (1976) 15.
[1283] A. Cracknell, 24th AIChE Ammonia Safety Symp., San Francisco 1979; *Ammonia Plant Saf.* **22** (1980) 63.
[1284] R. S. Brown, *Plant/Oper. Progr.* **1** (1982) 97.
[1285] D. C. Guth, D. A. Clark, 29th AIChE Ammonia Safety Symp., San Francisco 1994; *Ammonia Plant Saf.* **25** (1984) 60.
[1286] D. C. Guth, D. A. Clark, *Plant/Oper. Progr.* **4** (1985) 16.
[1287] S. Hewerdine, The Fertilizer Society, London 1991, Conf. Proc. no. 308, p. 1.
[1288] B. G. Burke, D. E. Moore, 21st AIChE Ammonia Safety Symp., San Francisco 1989; *Ammonia Plant Saf.* **30** (1990) 91.
[1289] M. J. Conley, S. Angelsen, D. Williams, 35th AIChE Ammonia Safety Symp., San Diego 1990; *Ammonia Plant Saf.* **31** (1991) 159.
[1290] C. C. Hale, 18th AIChE Ammonia Safety Symp., Vancouver 1978; *Ammonia Plant Saf.* **16** (1974)23; 23th AIChE Ammonia Safety Symp., Miami Beach 1978; **21** (1979) 61; 28th AIChE Ammonia Safety Symp., Denver 1983; **24** (1984) 181; C. C. Hale, *Nitrogen* **150** (1984) 27.

Topsoe, Inc. – EX1003
Page 427 of 1210

[1291] J. J. Aarts, D. M. Morrison, 25th AIChE Ammonia Safety Symp., Portand 1980; *Ammonia Plant Saf.* **23** (1981) 124.
[1292] N. A. Hendricks, 23rd AIChE Ammonia Safety Symp., Miami Beach 1978; *Ammonia Plant Saf.* **21** (1979)69.
[1293] J. M. Shah, *Plant Oper. Prog.* **1** (1982) no. 2, 90.
[1294] K. Feind, 22nd AIChE Ammonia Safety Symp., Denver 1977; *Ammonia Plant Saf.* **20** (1978) 46.
[1295] Code of Practice for the Large Scale Storage of Fully Refrigerated Anhydrous Ammonia in the UK, Chemical Industries Association, London 1975.
[1296] J. R. Thomson, 34th AIChE Ammonia Safety Symp., San Francisco 1989; *Ammonia Plant Saf.* **30** (1990) 241.
[1297] J. R. Thomson, R. N. Carnegie, 33rd AIChE Ammonia Safety Symp., Denver 1988; *Ammonia Plant Saf.* **29** (1989) 116.
[1298] C. C. Hale, *Plant Oper. Prog.* **1** (1982) no. 2, 107.
[1299] E. T. Comeau, M. L. Weber, 21st AIChE Ammonia Safety Symp., Atlantic City 1976; *Ammonia Plant Saf.* **19** (1977) 63.
[1300] K. A. Wick, J. B. Withaus, H. C. Mayo, 22nd AIChE Ammonia Safety Symp., San Francisco 1979; *Ammonia Plant Saf.* **22** (1980) 54.
[1301] O. A. Martinez, S. Madhavan, D. J. Kellett, 31th AIChE Ammonia Safety Symp., Boston 1986; *Ammonia Plant Saf.* **27** (1987) 162; *Plant Oper. Prog.* **6** (1967) 129
[1302] C. C. Hale, J. A. Josefson, D. E. Mattick, 29th AIChE Ammonia Safety Symp., San Francisco 1984; *Ammonia Plant Saf.* **25** (1985) 172.
[1303] P. N. Arunachalam, *Fertilizer News* **57** (1986).
[1304] I. Dayasagan, *Fertilizer News* **60** (1986) no.
[1305] P. P. Briggs, J. M. Richards, III, E. G. Fiesinger, 30th AIChE Ammonia Safety Symp., Seattle 1985; *Ammonia Plant Saf.* **26** (1986) 89.
[1306] F. Prasek, 32nd AIChE Ammonia Safety Symp., Minneapolis 1987; *Ammonia Plant Saf.* **28** (1988) 66.
[1307] R. C. A. Wiltzen, 35th AIChE Ammonia Safety Symp., San Diego 1990; *Ammonia Plant Saf.* **31** (1991) 28.
[1308] R. H. Squire, 35th AIChE Ammonia Safety Symp., San Diego 1990; *Ammonia Plant Saf.* **31** (1991) 131.
[1309] S. B. Ali, R. E. Smallwood, 35th AIChE Ammonia Safety Symp., San Diego 1990; *Ammonia Plant Saf.* **31** (1991) 142.
[1310] V. V. Kharlamov, Yu. M. Tsymbal, *Zh. Vses. Khim. Ova.* **28** (1983) no. 4, 433–438.
[1311] G. Schlichthärle, T. Huberich, *Plant Oper. Prog.* **2** (1983), no. 3, 165–167.
[1312] A. A. Arseneaux, 29th Ammonia Safety Symp., San Francisco 1984; *Ammonia Plant Saf.* **25** (1985) 150.
[1313] W. R. Southard et al., Interstate Commerce Comission, U.S. Govt., Informal Study of Freight Rate Structure Fertilizer and Fertilizer Products, **vol. II**.
[1314] R. F. Schrader, *Nitrogen* **117** (1979) 26.
[1315] T. P. Hignett, *Transportation and Storage of Ammonia,* Fertilizer Industry Round Table, Washington 1979.
[1316] C. C. Hale, *Nitrogen 88: 12th Brit. Sulphur Int. Conf.,* Geneva 1988.
[1317] *Nitrogen* **140** (1982) 20.
[1318] G. V. Rohleder, 13th Ammonia Safety Symp., Montreal 1968; *Ammonia Plant Saf.* **11** (1967) 35.

Topsoe, Inc. – EX1003
Page 428 of 1210

[1319] W. A. Inkofer, 13th Ammonia Safety Symp., Montreal 1968; *Ammonia Plant Saf.* **11** (1967) 40.
[1320] W. A. Inkofer, G. M. Wilson, J. E. Adams, 15th Ammonia Safety Symp., Denver 1970; *Ammonia Plant Saf.* **13** (1971) 67.
[1321] T. F. Kohlmeyer, *Gas Wärme Int.* **19** (1970) no. 1, 15–20.
[1322] R. Leschbaer, H. Schumann, *DECHEMA-Monogr.* **80** (1976) no. 1639–1669, part 2, 747–748.
[1323] *Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry*, Booklet 1: Production of Ammonia, European Fertilizer Manufacturers Assoc., 1995.
[1324] Fertilizer Manual ed. by United Nations Industrial Development Organization (UNIDO), Vienna Austria and International Fertilizer Development Center (IFDC), Muscle Schoals, Alabama (USA) Klewer Academic Publishers, Dordrecht, The Netherlands, 1998.
[1325] C. C. Hale, W. H. Lichtenberg, 32nd AIChE Ammonia Safety Symposium; Minneapolis, 1987, *Ammonia Plant Saf.* **28,** (1980) 76.
[1326] D. Eckhold et al., *Chem. Tech. (Leipzig)* **24** (1972) no. 2, 92.
[1327] L. V. Caserta, *Chem. Eng. Prog.* **68** (1972) no. 5, 41.
[1328] T. Dear, 18th AIChE Ammonia Safety Symp., Vancouver 1973; *Ammonia Plant Saf.* **16** (1974) 108.
[1329] R. Werchan, 20th AIChE Ammonia Safety Symp., Boston 1975; *Ammonia Plant Saf.* **18** (1976) 87.
[1330] J. G. Seebold, *Hydrocarbon Process.* **51** (1972) no. 3, 97.
[1331] E. E. Allen, *Gas World* **172** (1970) no. 4501, 431.
[1332] TA, Technische Anleitung zur Reinhaltung der Luft vom Dezember 1983.
[1333] *Environmental Quality of Life*, Technical Note on the best Available Technology not Entailing Excessive Costs for Ammonia Production, EC Report *EUR 13002 EN, 1990.*
[1334] R. F. Griffiths, G. D. Kaiser, *J. Hazard Mater* **6** (1982) 197.
[1335] C. Charp, Agricult. Anhydrous Ammonia Technol. Use Proc. Symp., San Louis 1966, p. 21.
[1336] G. F. P. Harris, P. E. MacDermott, *Inst. Chem. Eng. Symp. Ser.* **49** (1977) 29.
[1337] Association des Producteurs Europeens d'Azote (APEA), Sekretariat Schweizerische Treuhandgesellschaft, St. Jakobstraße 25, Basel, Postfach, 1974.
[1338] W. J. De Coursey et al., *Can. J. Chem. Eng.* **40** (1962) 203.
[1339] C. D. Swann, M. L. Preston, *Loss Prev. Proc Ind.*, **vol. 8.** No. 6, 349–353, 1995, Elsevier Science Ltd.
[1340] R. D. Turney, *TransChem.*, **vol. 68.** Part B, Feb 1990, 12–16.
[1341] R. A. McConnel, 36th AIChE Ammonia Safety Symposium, Nov 1991, Los Angeles; *Ammonia Plant Saf.* **32** (1992), 104.
[1342] A. L. Ormond, *J. ChemE Loss Prev. Bulletion, Issue 126, Dec 1995.*
[1343] E. Banik, *Explosivstoffe* **5** (1957) no. 2, 29.
[1344] J. M. Blanken, 24th Ammonia Safety Symp., San Francisco 1979. *Chem. Eng. Progr.* **76** (1980) 89–104.
[1345] *Oil Gas J.* **70** (Sep. 4, 1972) 86.
[1346] Hauptverband der gewerblichen Berufsgenossenschaften: *Technische Regelwerke*, Carl Heymanns Verlag, Köln.
[1347] DIN Deutsches Institut für Normung e.V., Deutsches Informationszentrum für techn. Regeln (DITR), Berlin.
[1348] Binnenschiffahrtsverlag GmbH, 4100 Duisburg-Ruhrort, Haus Rhein, Dammstraße 15–17.
[1349] IMO, International Maritime Organization, London.

Topsoe, Inc. – EX1003
Page 429 of 1210

[1350] Bundesanzeigerverlag GmbH, Postfach, 5000 Köln 1.
[1351] Chemical Industries Association Limited, Alembic House, 93 Albert Embankment, London SE 1 7 TU.
[1352] Agricultural Nitrogen Institute, 703 Dupont Building, 22 South Second Str., Memphis, Tennessee.
[1353] Manufacturing Chemists Association, 1825 Connecticut Avenue, N.W., Washington, D.C.
[1354] W. L. Ball, 14th AIChE Ammonia Safety Symp., Portland 1969; Ammonia Plant Saf. **12** (1970), 1.
[1355] A. Resplandy, *Chim. Ind. Genie Chim.* **102** (1969) 691.
[1356] H. C. Goldwire, *Chem. Eng. Progr.* **82** (1986) 35.
[1357] P. K. Raj, J. H. Hagopian, A. S. Kalekar, 19th AIChE Ammonia Safety Symp., Salt Lake City 1969; *Ammonia Plant Saf.* **17** (1970) 102.
[1358] J. C. Statharas et al., *Process Safety Progr.* **10** (1993) 118.
[1359] K. P. Raj, R. C. Reid, *Environ. Sci. Technol.* **12** (1978) 1422.
[1360] National Research Council Panel on Response to Causalities Involving Shipborne Hazards, AD-A075203, 1979, p. 1.
[1361] H. v. Bell, *Chem. Eng. Prog.* **78** (1982) no. 2, 74–77.
[1362] K. A. Vick, J. B. Witthaus et al., *Chem. Eng. Prog. Techn. Man.* **22** (1980) 54–62.
[1363] B. H. Winegar, *Chem. Eng. Prog. Tech. Man.* **22** (1980) 226–230.
[1364] F. J. Heller, *Chem. Eng. Prog. Tech. Man.* **23** (1981) 132–145.
[1365] R. J. Eiber, *Chem. Eng. Prog. Tech. Man.* **23** (1981) 146–156.
[1366] J. J. O'Driscol, 19th AIChE Ammonia Safety Symp., Salt Lake City 1974; *Ammonia Plant Saf.* **17** (1975) 119–122.
[1367] R. F. Griffiths, G. D. Kaiser, *J. Hazard. Mater.* **6** (1982) no. 1/2, 197–212.
[1368] P. P. K. Raj, R. C. Reid, *Environ. Sci. Technol.* **12** (1978) no. 13, 1422–1425.
[1369] M. L. Greiner, *Plant Oper. Prog.* **3** (1984) no. 2, 66; 28th AIChE Ammonia Safety Symp., Denver 1984; *Ammonia Plant Saf.* **24** (1984) 109.
[1370] J. E. Lessenger, *Plant Oper. Prog.* **4** (1985) no. 1, 20.
[1371] A. Nielsen: *Ammonia — Catalysis and Manufacture*, Springer, New York 1995, 329–346.
[1372] C. C. Hale, W. H. Lichtenberg, 24th AIChE Ammonia Safety Symp., San Francisco 1979; *Ammonia Plant Saf.* **22** (1980) 35.
[1373] P. J. Baldock, *Chem. Eng. Prog. Loss Prev.* **13** (1980) 35–42.
[1374] M. Y. Nuttonson, PB–209478, 1 (1972)
[1375] M. B. Jacobs: *The analytical Toxicology of Industrial Inorganic poisons*, **509** Interscience, Wiley N.Y. (1967).
[1376] National Inst. for Occupational Safety and Health, Rockville 1974, PB-246669, p. 1.
[1377] National Research Council, Committee on Toxicology, Washington, PB-244336, p. 1.
[1378] L. Legters, (1980), AD-A094501 p. 1
[1379] I. M. Alpator, *Prom. Toksikol. i. Klinika Prof. Zabol. Khim. Etiol.* **200** (1962).
[1380] L. Matt, *Med. Inaugural Diss*, Würzburg (1889).
[1381] A. C. S. Fieldner, S. H. Katz, S. P. Kinney, *in Noxious Gases*, **125** 2nd rev. ed. Reinhold, N.Y. (1943).
[1382] L. Silvermaur, L. Whittenberger, I. Muller, *I. Industr. Hyg.* **31** (1949) 74.
[1383] J. E. Lessenger, *Plant/Oper. Progr.* **4** (1985) 20.
[1384] R. A. Michaels, Nitrogen **228** (1997) 27–31.
[1385] J. C. Barber, 22nd AIChE Ammonia Safety Symp., Denver 1977; *Ammonia Plant Saf.* **20** (1978) 5.

Topsoe, Inc. – EX1003
Page 430 of 1210

[1386] J. E. Ryer-Powder, 35rd AIChE Ammonia Safety Symposium, San Diego 1990; *Ammonia Plant Saf.* **31** (1991) 93.
[1387] M. Coplin, *Lancet* **241** (1949) 95.
[1388] W. M. Grant, *Arch. Ophthal.* **44** (1950) 399.
[1389] T. Sollmann, *A Manual of Pharmacology*, 6th ed., Saunders, Philadelphia 1944.
[1390] R. C. Wands, in G. D. Clayton, F. E. Clayton: *Patty's Industrial Hygiene and Toxicology*, **vol. 2 B**, Wiley Interscience, New York 1981, p. 3045–3052.
[1391] K. B. Lehmann, *Arch. Hyg.* **17** (1893) 329.
[1392] P. Trendelenburg in A. Heffter: *Handbuch der experimentellen Pharmakologie*, **vol. I**, p. 470, Springer, Berlin 1923.
[1393] I. M. Alpator, *Gig. Tr. Prof. Zabol.* **2** (1964) 14.
[1394] D. P. Stombaugh, H. S. Teague, W. L. Roller, *J. Anim. Sci.* **6** (1969) 844.
[1395] H. F. Smith, *Amer. Industr. Hyg. Quart.* **17** (1956) 145.
[1396] C. P. Carpenter, H. F. Smith Jr., U. C. Pozzani, *J. Industr. Hyg.* **31** (1949) 343.
[1397] V. I. Mikhailow, *Probl. Kosmich. Biol. Akad. Nauk SSSR* **4** (1965) 531.
[1398] E. M. Boyd, M. L. McLachlin, W. F. Perry, *J. Industr. Hyg.* **26** (1944) 29.
[1399] S. D. Silver, F. P. McGrath, *J. Industr. Hyg.* **30** (1948) 7.
[1400] K. B. Lehmann, *Arch. Hyg.* **5** (1886) 68.
[1401] I. H. Weatherby, *Proc. Soc. Exp. Biol.* **81** (1952) 300.
[1402] R. A. Coon, R. A. Jones, L. J. Jenkins, I. Siegel, *Toxicol. Appl. Pharmacol* **16** (1970) 646.
[1403] K. S. Warren, S. Schenker, *J. Lab. Clin. Med.* **64** (1964) 442.
[1404] W. D. Lotspeich, *Amer. J. Physiol.* **206** (1965) 1135.
[1405] P. Vinay, E. Alignet, C. Pichette, M. Watford, G. Lemieux, A. Gougoux, *Kidney Intern.* **17** (1980) 312.
[1406] D. Z. Levine, L. A. Nash, *Amer. J. Physiol.* **225** (1973) 380.
[1407] K. S. Warren, *J. Clin. Invest.* **37** (1958) 497.
[1408] J. Oliver, E. Bourke, *Clin. Sci. Molec. Med.* **48** (1975) 515.
[1409] J. Yoshida, K. Nakame, R. Nakamura, *Nippon Chikusangakukaiko* **28** (1957) 185.
[1410] D. C. Topping, W. J. Visek, *J. Nat.* **106** (1976) 1583.
[1411] B. Toth, *Int. J. Cancer* **9** (1972) 109.
[1412] Litten Bionetics, *NTIS, PB-245*, 506 (1975) Washington D.C.
[1413] K. A. Hofmann: *Anorganische Chemie*, 20th ed., Vieweg & Sohn, Braunschweig 1969.
[1414] J. Jander: *Chemie in wasserfreiem flüssigem Ammoniak*, Vieweg & Sohn, Braunschweig – Interscience, New York 1963.
[1415] J. P. Lenieur et al., *C. R. Acad. Sci. Ser. C* **268** (1969) no. 20, 1791.
[1416] E. Weiss, W. Buchner cited in [1413]
[1417] F. W. Bergstrom, *Ind. Eng. Chem.* **24** (1932) 57.
[1418] P. Barton et al., *Ind. Eng. Chem. Process Des. Dev.* **7** (1968) no. 3, 366.
[1419] Michael Thiemann et al.: *"Nitric Acid, Nitrous Acid, and Nitrogen Oxides"*, in Ullmann's Encyclopedia of Industrial Chemistry 5ed., **vol. A 17**, pp. 293–340.
[1420] G. D. Honti "Nitric Acid" in G. D. Honti (ed.): The Nitrogen Industry, Akademiai Kiado, Budapest 1976.
[1421] C. Keleti, "Nitric Acid and Fertilizer Nitrates" (Fertilizer Science and Technology Series, **vol. 4**) Marcel Dekker, New York, 1985.
[1422] J. H. Meesen, H. Petersen: *"Urea"* in Ullmann's Encyclopedia of Industrial Chemistry 5ed., **vol. A 27**, pp. 333–366.

Topsoe, Inc. – EX1003
Page 431 of 1210

[1423] H. Müller: *"Sulfuric Acid and Sulfur Trioxide"* in Ullmann's Encyclopedia of Industrial Chemistry, 5ed., **vol. A 25,** pp. 635–704.
[1424] K. Schrödter et al.: *"Phosphoric Acid and Phosphates"* in Ullmann's Encyclopedia of Industrial Chemistry , 5ed., **vol. A 19,** pp. 465–504.
[1425] U. Müller, A. Greiner, *Chem. Tech. (Leipzig)* **18** (1966) no. 6, 327.
[1426] P. W. Langvardt: *"Acrylonitrile"* in Ullmann's Encyclopedia of Industrial Chemistry, 5ed., **vol. A 1,** pp. 177 – 187.
[1427] T. Wakabayashi, *Ammonia Plant Saf.* **20** (1978) 17.
[1428] *Erdöl Kohle Erdgas Petroch.* **37** (1984) no. 4, 143. *Chem. Ing. Tech.* **56** (1984) no. 8, A 407.
[1429] H. J. Bomelburg, *Plant Oper. Prog.* **1** (1982) no. 3, 175.
[1430] *Chem. Ing. Tech.* **56** (1984) no. 4, A 154.
[1431] K. Dietrich, *Kältetech. Klim.* **22** (1970) no. 6, 184.
[1432] H. L. v. Cube, *Kältetechnik* **16** (1964) no. 3, 76.
[1433] F. Özvegyi, *Kälte (Hamburg)* **23** (1970) no. 6, 298.
[1434] A. Miller, *Kälte (Hamburg)* **20** (1967) no. 6, 275.
[1435] H. Borrmann, *Chem. Ing. Tech.* **40** (1968) 1192.
[1436] C. Hollmann, *Gas Wärme* **9** (1960) 267.
[1437] G. Kurz, *Proc. Eng.* (1976) no. Oct., 97.
[1438] M. N. Park., *Nitrogen 88: Brit. Sulphur International Conference,* Geneva Mar 1988.
[1439] "World Ammonia Production, Consumption and Trade", Statistical supplement, *Nitrogen* **217** (1995) 22.
[1440] "Five year outlook for Ammonia 1995 – 2000", British Sulphur.
[1441] M. Appl, *Ammonia, Methanol, Hydrogen, Carbon monoxide – Modern Production Technologies* CRU Publishing Ltd, London 1997 63 – 65.
[1442] "BP Statistical Review of the world Energy", British Petroleum Co., June 1995.
[1443] "Hydrogen" in Ullmann's Encyclopedia of Industrial Chemistry, VCH Weinheim, **vol A 13,** p. 358.
[1444] F. J. Wollmer, *Ammonia Casale's 75th Anniversary Symposium,* Lugano, Switzerland, Nov. 1996.
[1445] B. Brentnall, "Nitrogen Projects: Gas, Capital, and What Else? *Asia Nitrogen '98, British Sulphur International Conference. Kuala Lumpur.* Feb 22–24, 1998.
[1446] K. Isermann in A. I. More (ed.), *Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol. 4th 1981* 1982, 571.
[1447] Nitrex Statistik 1991, Nitrex AG, Zürich.
[1448] A. Quispel: *The Biology of Nitrogen Fixation,* Elsevier/North Holland Publ. Comp., Amsterdam – Oxford – New York 1974.
[1449] Emerging Technologies no. 1: Nitrogen Fixation. An Analysis of Present Research and Implications for the Future. Technical Insights Inc., Fort Lee, New Jersey.
[1450] R. W. F. Hardy, U. D. Havelka, *Science (Washington, D.C.)* 1975, no. 4188, 633.
[1451] G. J. Leigh in A. I. More (ed.), *Proc. Br. Sulphur Corp. Int. Conf. Fert. Technol. 4th 1981* 1982, 662.
[1452] R. F. Baddour, R. S. Timmins: *The Application of Plasmas to Chemical Processing,* Mass. Inst. Technol. Press, Cambridge 1967.
[1453] D. R. Safrany, *Chem. Eng. Prog. Symp. Ser.* **67** (1971) no. 112, 91, 103.
[1454] *Nitrogen* **144** (1983) 32.
[1455] *The Energetics of Biological Nitrogen Fixation,* Workshop Summaries I, Plant, Physiology, Am. Soc. of Plant Physiologists, Rockville, Maryland, USA.

Topsoe, Inc. – EX1003
Page 432 of 1210

[1456] D. F. Shanmugam, F. O'Gara, D. Andersen, R. C. Valentine: "Biological Nitrogen Fixation," *Am. Rev. Plant Physiol.* **29** (1978) 263.

[1457] H. J. Rehm: "Beiträge der modernen Biotechnologie und Biochemie zur Ernährung," *VCI-Schriftenreihe Chemie + Fortschritt* 1983, no. 3, 18.

[1458] *Nitrogen* **146** (1983) 24.

[1459] J. R. Postgate: "Fertilizer '83," *Br. Sulfur Corp. 7th Int. Conf.*, London 1983, Proceedings of the Conf., p. 119.

[1460] G. J. Leigh, in *Catalytic Ammonia Synthesis*, ed. by J. R. Jennings, Plenum Press New York and London 1991, 365–387.

[1461] J. S. Pathe, C. A. Atkins, R. M. Rumbird, in A. H. Gibson, W. E. Newton (eds.): *Current Perspectives in Nitrogen Fixation*, Australian Academy of Science, Canberra 1981.

[1462] V. P. Gutschick, Long term strategies for supplying nitrogen to crops; Informal report LA-6700–19S, Los Alamos Scientific Laboratory, Los Alamos, NM, USA, 1977.

[1463] R. F. Michin, S. J. Pate, *J. Exp. Bot.* **24** (1973) 259.

[1464] M. J. Merrik, *J. R. Agric. Soc. Engl.* **147** (1986) 202.

[1465] M. Tamaguchi: "Biological Nitrogen Fixation in Flooded Rice Fields," in Nitrogen and Rice, International Rice Research Institute, Manila, Philippines, 1979, p. 193–204.

[1466] K. Gopalakrishna Pillai, D. B. B. Chaudary, K. Krishnamurty: "Bio-Fertilizers in Rice Culture – Problems and Prospects for Large Scale Adaptation", *Fert. News* **25** (1980) 40–45.

[1467] *Chem. Eng. News* **55** (1977) no. 40, 19.

[1468] G. N. Schrauzer, T. D. Guth, *J. Am. Chem. Soc.* **99** (1977) 7189.

[1469] "Nitrogen Fixation" in Ullmann's Encyclopedia of Industrial Chemistry, **vol. A 18**, VCH Weinheim.

[1470] C. Gleitzner, *Solid State Ionics*, **38** (1990) 33–141.

[1471] M. Et-Tabiru, B. Dupré, C. Gleitzner, *Metallurgical Trans*, **19B** (1988) 311–371.

[1472] H. Schenck, H. P. Schulz, *Arch. Eisenhüttenwesen*, **31** (1960) 691–702.

[1473] J. Schütze, W. Mahdi, B. Herzog, R. Schlögl, *Top. Catal.* 230 (1994), 95–96.

[1474] B. Brentnall, "The investment climate of nitrogen fertilizers", Krupp-Uhde Fertilizer Symposium 1998, Dortmund, June 11–13, 1998.

[1475] L. Connock, *Nitrogen*, **226**, (1997) 47–56.

[1476] Krupp-Uhde, private communication.

[1477] R. Saure, "Ammonia from hydrogen-rich off-gases", Krupp-Uhde Fertilizer Symposium 1998, Dortmund, June 11–13, 1998.

[1478] Linde AG, Juliy 1998, private communication.

[1479] P. L. Louis, *66th IFA Annual Conference*, 1998, May 11–14, Toronto.

[1480] L. Maene, "The nitrogen fertilizer markets of Asiain global context – status and outlook", *Asia Nitrogen '98, British Sulphur International Conference*, Kuala Lumpur, 1998, Feb 22–24.

[1481] Capacity statistics by Factories, Situation May 1998, *Nitrex-Complex*.

[1482] K. P. Wang, "The People's Republic of China". US Bureau of Mines, Washington, D. C., 1975.

[1483] "American Rural Small-Scale Industry Delegation", 1977. Rural Rural Small-Scale Industry in the People's Republic of China, Chapter VI, University of California Press, Berkley and Los Angeles, CA, USA.

[1484] G. Heinke, G. H. Wagner, Mat.-Wiss. und Werkstofftechnik, **27** (1996) 259–266.

[1485] S. Fritsch, "Synthesis Gas Production, Comparison of four Synthesis Gas Routes: Steam Reforming, Combined Autothermal Reforming and Partial Oxidation", Krupp-Uhde Fertilizer Symposium 1998, Dortmund, June 11–13, 1998.

Topsoe, Inc. – EX1003
Page 433 of 1210

[1486] *Nitrogen* **232** (1998) 12.
[1487] J. Richardson, FINDS, X (2) 28 (Second Quarter 1995).
[1488] M. W. Kellogg Press release, Houston July 28, 1998; "Trinidad KAAP Ammonia Plants", M. W. Kellogg presentation September 3, 1998 at Charleston Place Hotel, Charleston, SC.
[1489] J. Xu, G. F. Froment, *AIChE J* **35** (1989). 88–86.
[1490] T. Mohri, K. Takamura, T. Shibasaki, 37th AIChE Ammonia Safety Symposium, San Antonio (Sep-Oct 1992); *Ammonia Plant Saf.* **33** (1993). 86–100.
[1491] B. J. Cromarty, 36th AIChE Ammonia Safety Symposium, Los Angeles (Nov 1991); *Ammonia Plant Saf.* **32** (1992), 197–208.
[1492] "Paralloy H39WM (25/35 Cr/Ni + Nb Microalloy)" Paralloy Technical Paper.
[1493] Schmidt + Clemens, Data Sheets for "Märker G 4852 Micro" and "Märker ET 45 Micro".
[1494] *H. Smith "Organic Reactions in Liquid Ammonia", Vieweg & Sohn, Braunschweig – Interscience*, New York 1963.
[1495] T. Takagi, *Jap. Chem. Q* **4** (4) (1968) 47.
[1496] S. K. Mukherjee, Nitrogen 188, Brit. Sulphur Conf., Geneva, March 27–29, 1988.
[1497] R. Habermehl, *FINDS* **vol. IX**, number 3, Third Quater 1994, 24.
[1498] R. Lavie, *Plant/Oper. Prog.* **6 (2)** (1987) 118; *Chem. Eng. Sci.* **40 (11)** (1985), 2019.
[1499] R. US Pat 4537760 (R. Lavie).

Topsoe, Inc. – EX1003
Page 434 of 1210

Copyright © WILEY-VCH Verlag GmbH, 1999

Index

Advanced control 182
AIChE Ammonia safety Symposia V, 65
Air separation 138, 201, 239
Alternative synthesis gas supply
  Electrolysis 111f
  Hydrogen from waste gases 111f
Amine formation 118
Ammonia catalyst poisons
  Chlorine compounds 59
  Oxygen compounds 56ff
  Reversible (temporary) poisoning 56, 58
  Sulfur 57
Ammonia history
  BASF 5ff
  BERTHOLLET 5
  BIRKELAND-EYDE 5
  FRANK-CARO 5
  HABER's recycle idea 6
  ICI 8
  Leuna 7
  M. W. KELLOGG 8
  MITTASCH 5, 36
  NERNST's preocupation 6
  NORSK HYDRO 5
  Oppau 7
  OSTWALD's iron catalyst patent application 6
  SCHOENHERR 5
Ammonia plant emmission 223
Ammonia plant, general considerations 65f, 177
Ammonia reaction kinetics
  Effectiveness factor 34
  Experimental kinetics 30f
  Mathematical expressions 31f
  Surface science based kinetics 32
  Transport phenomena 33ff
Ammonia recovery from synthesis loop
  Absorption refrigeration 164
  Adsorption on solids 165
  Condensation 163
  Flash gas 164
  Water scrubbing 164
Ammonia spills
  Ammonia vapor dispersion 226, 228
  Evaporation rate 228
  Explosion hazard/inflamability 226
  Incidents 228
  Spill experiments 228
Ammonia storage and loading terminal 214
Ammonia vapor dispersion 226
Argon recovery from purge gas 169
Autothermal reforming 96
Auxiliary boiler 90, 178ff, 183
Auxiliary burners 178
Capacity (ammonia)
  By feedstocks 67
  Geographical distribution of world capacity 236f
  Geographical shift of ammonia capacity 237
  Number of ammonia plants 236
  Special situation in China 236
  World supply/demand balance 236
Capital investment costs 67, 239f
Catalyst life 59, 117, 241
Catalyst stability, synthesis
  Abrasion resistance 48, 51
  Catalyst life 59
  Thermal stability 44
Classification of steam reforming plants 186f
CO_2 removal by scrubbing
  Chemical solvents 122f
  Corrosion inhibitor 126
  Ethanolamine systems 128
  Foaming 125
  Heat requirement 125
  Hot potash systems 126
  Physical solvents 122f
  Process configuration 123
  Column packings 123
  Solvents 124
Coal gasification
  See partial oxidation of coal
Commercial ammonia converters
  C. F. Braun converter system 160f
  Casale quench converter 155
  Casale's axial-radial flow principle 157f
  Chemico converter 153
  Claude converter 152
  Fast Engineering Ltd. Converter 152f
  Fauser (old) converter 152
  Fauser-Montecatini converter 159
  Grand Paroisse quench converter 155
  Haber-Bosch converters 152
  Hot wall converter 161
  ICI lozenge converter 155, 157
  ICI opposed flow converter 155f
  ICI tube cooled converter 152
  Kellogg horizontal indirect cooled converter 160
  Kellogg horizontal, quench, converter 157
  Kellogg KAAP converter 162
  M. W. Kellogg quench converter 155f
  Mont Cenis converter 152
  NEC converter 153
  Topsøe S100 quench converter, radial flow 156, 158
  Topsøe S200 converter 159f
  Topsøe S300 converter 160
  Topsøe three bed/two vessel system (S250) 161
  TVA converter 151

Topsoe, Inc. – EX1003
Page 435 of 1210

- Uhde quench converter 155
- Uhde three bed/two vessel system 161, 171
- Uhde-Chemie Linz converter 159

Commercial CO_2 removal processes
- ACT-1 activator (UOP) 126
- BASF aMDEA process 129f
- Benfield LoHeat System (UOP) 126f
- Carbosolvan process 128
- Catacarb process 127
- Exxon Flexsorb process 128
- Fluor Solvent Process 131
- Giammarco-Vetrocoke process 127
- LRS 10 (British Gas) 127
- MEA process/Amine Guard 128f
- Purisol (Lurgi) process 133
- Rectisol (Lurgi/Linde) 132
- Selexol process (UOP) 130, 132
- Sepasolv MPE process (BASF) 131
- SPIC process 128
- Sulfinol process 134

Compressor drivers
- Gas turbines 144, 181
- Steam turbines 144

Compressors, centrifugal
- Bearings 142
- Control 143
- Couplings 141
- Dry seals 143
- Four-nozzle compressor 145f
- Integrated geared centrifugal compressors 143
- Introduction to ammonia plants 140
- Magnetic bearings 143
- Minimum flow rate 140
- Minimum load without efficiency loss 143
- Minimum plant capacity 140
- Number of impellers 141
- Oil seals 142
- Recycle compression 141
- Surge 143

Compressors, reciprocating 139
- Gas engine drive 139
- Linear arrangement 139
- Multifunction compressor 140
- Parallel arrangement 139

Converter design 148ff

Converter performance parameters
- Blow-out point 147
- H/N ratio 147f
- Inert gas 146, 148
- Oxygen content of make up-gas 146, 148
- Pressure 146f
- Space velocity 147f

Converter types
- Axial radial flow 157f
- Cocurrent tube cooled converters 153
- Counter current tube cooled converters 151
- Cross flow 157
- Direct cooled multibed converters 154
- Indirect cooled multibed converters 157
- Principal configurations 150f
- Quench converters 154
- Radial flow 156
- Temperature profiles 152, 154f, 159

Co-Production of other products
- Carbon monoxide 207
- Hydrogen 207
- Methanol 207f
- Urea 207

Cost factors in addition to feedstock and capital 241

Cryogenic methods for gas purification
- Braun Purifier process 137
- Cryogenic hydrogen recovery 166
- Liquid nitrogen wash 137f

Dirty shift catalyst 120f

Dryers for make-up gas 137

Electric arc process
- Birkeland-Eyde 5
- Energy consumption 5
- Schönherr furnace 5

Energy consumption in ammonia plants
- Development 1940-1998 185
- Energy export 183f
- Energy surplus in steam reforming plants 183
- Exergy analysis (steam reforming) 185f
- Influence of cooling medium and temperature 185
- Influence of design criteria 185
- Influence of physical state of ammonia product 185
- POX plants 199, 203f
- Steam reforming 180
- Theoretical Minimum for steam reforming plants 182ff

Energy integration 177ff

Environmental aspects
- Best Available Technique 225
- EFMA Booklet Production of Ammonia 225
- Emmission limits and guidelines 224
- IPPC Directive of the EU commission 225
- Noise 224f
- NO_x emmissions 223f
- SO_2 emmissions 224

Exchanger reformer
- AGHR (ICI Synetics) 94f
- CAR (Uhde) 96f
- GHR (ICI Synetics) 93ff
- KRES (Kellogg) 94ff
- TANDEM Reformer (GIAP) 95

Feedstock and gasification technology 67f

Feedstock choice
- Advantage of natural gas 67f, 238
- Coal gasification 108

Topsoe, Inc. – EX1003
Page 436 of 1210

Geographical distribution of natural gas reserves 239
Influence on technology selection 68
Reserves and consumption of fossil feedstocks 239
Feedstock distribution of ammonia capacity 67
Feedstock price
Coal 238
Fuel oil 238
Influence on ammonia costs 238
Natural gas 238, 242 ff
Frank-Caro calcium cyanamide process 1, 5

HABER's recycle concept 6
Health aspects in ammonia production
General considerationy 228
Human exposure 228
Toxicology 229
Heat exchange reforming
See exchanger reformer
HT shift conversion
Catalyst 113
Chromium free catalyst 114
Fischer-Tropsch reaction 114
Kinetics 115
Manufacture 114
Over-reduction of HTS catalyst 113 f
Radial flow 119
Reaction mechanism 114 ff
Hydrodesufurisation 69, 121
Cobalt molybdenum catalyst 69
Zinkoxide 69, 121
Hydrogen attack
Chemical 209
Dissimilar welds 210
Hydrogen attack in hot wall ammonia converter 210
Hydrogen embrittlement 210
Mechanism 209 f
Metal Carbides 209
Nelson Diagram 209
Physical 209
Post weld heat treatment 210
Soaking 210
Hydrogen recovery from purge gas
Cryogenic methods 166
Membrane separation 167
Metal hydrides 169
Pressure swing adsorption 168
Secondary synthesis loop 166
Hydrogen sulfide corrosion 212

Industrial synthesis loop (example) 171

Loading terminal (ammonia) 214
LT Shift conversion
Amine formation 118
Catalyst 117 f
Catalyst manufacture 117
Catalyst service life 117
Chlorine poisoning 118
Equilibrium 117
Guard bed 117
Kinetics LT 118 f
Methanol formation 118
Radial flow 119
Reaction mechanism 119
Sulfur poisoning 117 f

Magnetite ammonia catalysts
Ammonia iron 54
Chemical composition 39
Cobalt promoted catalyst (ICI) 62
Commercial catalysts 40
Influence of promotors 42 ff
Manufacture 49 ff
Mechanism of promoter effect 44 ff
Particle shape 48 f
Particle size and activity 47, 49
Pre-reduced catalysts 54
Pressure drop 49
Price 50
Promoter distribution 41
Reduction 52
Reduction mechanism 53 ff
Spherical catalyst 48, 50
Surface 39
Maintenance 241
Material questions 209 ff
Membrane Separation 167 f
Metal dusting
Aluminium coating 212
Carbon activity 211
Inhibition by H_2S 212
Materials to reduce metal dusting 212
Mechanism 211
Methanation
Application in POX plants 136
Catalyst 135
CO_2 breakthrough 136
Kinetics 135
Nickel carbonyl formation 136
Methanol formation 118
Methanolation (Topsøe) 136
Minimum energy for steam reforming 182
MT shift conversion 119

Natural gas prices 238, 242 ff
Nickel carbonyl formation 136
Nitriding of steels 211
Nitrogen cycle 1
Nitrogen fixation abiotic 247
Nitrogen fixation, biological 246
Blue-green algae 246 f
Energetic efficiecy 246 f

Topsoe, Inc. – EX1003
Page 437 of 1210

Mechanism 246
Nitrogenase 246
Options for genetic engineering 246
Rhizobium bacteria 246
Water fern 247
Nitrogen magazine (British Sulphur, CRU Publishing) V, 65, 219, 244
Non-iron ammonia catalysts
Alkali promoter 61
Ammonia inhibition 63
Commercial Ruthenium catalyst 62
Criteria for support material 60
Effect of H/N ratio 63
Graphite stability 61
Graphite support 61
Kellogg/BP catalyst 62
Low pressure potential 63
Nitride formation and effectivity 61
Osmium 61
Rate determining step 62
Search criteria 60
Search program of Mittasch 60
Structure sensitivity 62
NO_x emmission 91, 223f

On-stream factor 241
Operational variables of the synthesis loop 169f
Options for production schemes 66

Partial oxidation (POX)
Chemical reactions 98f
Reaction conditions 99f
Soot formation 99ff
Soot recycle 102ff
Soot removal 102ff
Vanadium recovery 103, 106
Partial oxidation of coal
Abstich generator 8
Advanced Coal Gasification Process 109
British Gas/Lurgi Slagging Gasifier 110
Classic Winkler Gasifier 7, 110
Dow Process 108
Energy consumption 203f
HTW Process 110
Koppers-Totzek Process 108
Lurgi Dry Gasifier 110f
PRENFLOW Process 108
Shell Coal Gasification Process 110
Suitable feedstocks 108
Texaco Coal Gasification Process 109
Water gas process 7, 107
Partial oxidation of hydrocarbons
Energy consumption 199
Lurgi SVZ MPG process 105ff
Principle flow diagrams 200
Raw gas composition 101f
Shell Process 102
Soot and ash removal 102ff, 106
Soot recycle 102, 104
Texaco process 103
Vanadium recovery 103, 106
Waste water treatment 103
Physical properties (ammonia)
Caloric data 10
Important data 11
Molecular configuration 9
p-V-T data 10
Solubility in water 17
Solubility of H_2, N_2, Ar, CH_4 11, 15f
Specific heat 10, 13f
Surface tension 14
Thermal conductivity 16
Vapor pressure 14
Viscosity 14
Plants based on heavy hydrocarbons
Foster Wheeler 200
Foster Wheeler POX Process 201
Linde flowsheet 202
Lurgi 199
Shell POX 199
Texaco POX 200
Topsøe Process 201
Linde 200
Uhde 200
Plants with conventional steam reforming
Exxon Chemical Process 190
Fluor Process 190
Haldor Topsøe Process 187
Jacobs (formerly H&G) LEAD Process 190
Kellogg-Low Energy Ammonia Plant 187
Krupp-Uhde Process 183, 188
Lummus Process 190
Snamprogetti Ammonia/Urea concept 190
Plants with reduced primary reforming
Braun Purifier process 190
Foster Wheeler AM2 Process 193
GIAP concept 194
ICI AMV Process 192
Jacobs (formerly H&G) BYAS Process 193
Jacobs Plus Ammonia Technology 193
Kellogg LEAP Process 194
Montedison Low-Pressure Process 193
Plants without a fired reformer
Chioda Process 197
ICI LCA Process 194
Kellogg Ammonia 2000 Process 197
Plants without a secondary reformer
Jacobs (formerly H&G) MFD Process 198
KTI PARC Process 197
Linde LAC Process 198
Prices (ammonia) 243
Primary reformer
Auxiliary burners 178
Bottom-fired reformer 84, 86

Topsoe, Inc. – EX1003
Page 438 of 1210

Burner disposition 84
Combustion air preheat 180
Convection section 90, 178
Flue gas duct 90, 178
Foster-Wheeler reformer 87
Furnace design 80, 82f
Heat flux and heat transfer 83
Heat recovery from flue gas 90
ICI REFORM computer program 82
Insulatiaton of fire box 87
Isolation of ruptured tube 87
M. W. Kellogg reformer 88
Mechanical features 86ff
Pig-tails 86f
Radiant box insulation 87
Reformer configurations 84
Side-fired reformer 85f
Terraced wall reformer 86f
Top-fired reformer 85
Tube suspension 86
Tunnels 88
Uhde manifold concept 88
Uhde reformer 89
Primary reformer by-passing 91, 193
Primary reformer catalysts
Acidity of support 76
Alkalized catalysts 75f
Carbon formation tendency 76
Composition 74ff
Manufacture 75
Reducibility 75
Shape 76f
Splitloading 78
Process condensate 118
Process control 182
Process optimization 182
Process simulation 182
Processes based on coal
Historic coke plant 8
Koppers-Totzek 203
Lurgi Dry Bottom Gasifier 203
Texaco Coal Gasification process 204
Ube Industries Texaco Ammonia plant 204
Production (ammonia)
Geographical distribution of world capacity 236f
Geographical shift of ammonia capacity 237
Number of ammonia plants 236
Special situation in China 236
World population and ammonia production 235
World supply/demand balance 236
Production costs
At various locations 242f
Capital costs 239ff
Cash costs 238, 241
Feedstock costs 238, 242ff
From various feedstocks 238
Labor 241
Maintenance 241f
Purification by Pressure Swing Adsorption 138, 168, 196, 198

Reaction kinetics
Ammonia synthesis 29ff
HT shift 114f
LT shift 118f
Methanation 135
Steam reforming 72f
Reaction mechanism
Ammonia synthesis 24ff
HT shift 115f
LT shift 119
Methanation 135
Steam reforming 73
Reactions of ammonia
Ammonium hydroxide 231
Chemistry in liquid ammonia 232
Metal amides and imides 231
Nitride formation 232
Nitrogen-halogen compounds 232
Organic reactions 233f
Oxidation 231
Salt formation 231
Reduced primary reforming 91, 190
Reformer tubes
Creep 79f
Heat flux 83
Hot spots 84
Influences shortening tube life 84
Larson-Miller parameter 79
Micro alloys 80
Tube length 79
Tube materials 79ff
Wall temperature 83
Wall thickness 79, 84
Regate process 97
Revamp of ammonia plants
General considerations 205
Objectives 205
Options 180ff, 205f
Rich gas process 74
(*see* also pre-reformer)

Safety
Ammonia evaporation in spills 228
Ammonia spills 228
Ammonia storage 226
Flamability limits of ammonia 226
HAZOP studies 225f
Incidents 228
Regulations and guidelines 226ff
Toxicity 228f
Secondary reformer
Burner 89f
CFD simulation 91

Topsoe, Inc. – EX1003
Page 439 of 1210

Combustion chamber 91
Operation with air surplus 94, 190 ff
Operation with enriched air 94
Secondary reformer catalysts 78
Selectoxo process (Engelhard) 136
Shift conversion in POX plants
Alkalized dirty shift catalysts 120
Catalyst 120
COS 120
Isothermal converter (Linde) 121
Minimum sulfur for dirty shift catalyst 120 f
Single train ammonia plant concept 8, 177
Sour gas removal from POX gases
Purisol 133
Rectisol configurations 132 f
Selexol 132, 134
Specifications (ammonia) 221
Steam reforming
Carbon formation 71, 75
Chemical equilibrium 70
General 68 f
Influence of pressure 70 f
Kinetics 72 f
Naphtha reforming 74 f
Reaction mechanism 73
Steam/carbon ratio 69, 71
Steam system 184
Steam reforming 184
POX plants 199, 203
Storage of aqueous ammonia 218
Storage of liquid ammonia
Capacity 213, 215 f
Double integrity tank design 216
Double wall tanks 216
Foundation 217
Investment cost 215, 217
Low temperature storage 215
Pressurized storage 214
Refrigeration 216
Single-wall tanks 216
Underground storage 218
Stress corrosion cracking in liquid ammonia
Al and Zn spraying 215
Atmospheric storage tanks 215
General aspects 212
Pressure vessels 215
Prevention 215
Water addition 215
Stress corrosion in POX plants 212
Sulfur recovery
Claus process 132
Stratford-Holmes process 132 f
Synthesis gas generation
General considerations 65 ff
Hydrogen by water electrolysis 111 f
Hydrogen-rich gases 112
POX Coal 107 ff
POX heavy hydrocarbons 100 ff
Steam reforming of natural gas 68 ff
Synthesis loop, example 171
Synthesis loop configurations 145
Synthesis loop variables 146 ff, 169 f
Synthesis loop waste heat recovery
Boiler feed water preheat 163
Feed-effluent heat exchanger 162 f
Steam raising 162 f, 173
Temperature enthalpy diagram (example) 164
Waste heat boilers 173 ff
Synthesis mechanism on magnetite catalyst
Crystal surface orientation 24 ff, 28
Dissosiative nitrogen adsorption 26 ff
Energy profile 27
Reaction scheme 26
Synthesis pressure (optimal) 170
Synthesis reaction
Chemical Equilibrium 19
Entropie change 19
Equilibrium concentrations 20 f
Free Energy 19
Heat of reaction 22
Thermodynamic data 19

Temper embrittlement 211
Trade of ammonia 237
Transportation of ammonia
Accidents 228
Loading capacities 219
Ocean vessel and river barges 219
Pipeline 219
Shipping prices 219
Trucks and railcars 218
Turn-around 241

Uses of ammonia
Acid amides 234
Amines 233 f
Ammonium salts 234
Fertilizer 233
Melamine 233
Nitric acid 234
Nitriles by ammonoxidation 234
Polyamides, polyurethans, polyacrylnitrile, resins 233
Production of hydrogen nitrogen-mixtures 234
Refrigerant 234
SRC for NO_x removal 234
Technical nitrogen 233
Urea 234

Waste heat boilers
Babcock-Borsig 173, 175
Balcke-Dürr AG 174 f
Boiler for POX gas 175 f
Fasel-Lentjes 175

Topsoe, Inc. – EX1003
Page 440 of 1210

Fire tube boilers 172
M. W. Kellogg 172
Steinmüller 173, 175 f
Struthers 173
Thick tube sheet boilers 174
Thin tube sheet concepts 173
Uhde 173 f
Water tube boilers 172
Waste heat recovery 162, 172 ff, 178
Water electrolysis 111 f

Topsoe, Inc. – EX1003
Page 441 of 1210

(19) Deutsches Patent- und Markenamt

(10) **DE 10 2015 210 803 A1** 2016.12.15

(12) # Offenlegungsschrift

(21) Aktenzeichen: **10 2015 210 803.1**
(22) Anmeldetag: **12.06.2015**
(43) Offenlegungstag: **15.12.2016**

(51) Int Cl.: ***C01B 3/36*** (2006.01)

(71) Anmelder:
ThyssenKrupp AG, 45143 Essen, DE;
ThyssenKrupp Industrial Solutions AG, 45143 Essen, DE

(74) Vertreter:
Kutzenberger Wolff & Partner Patentanwaltspartnerschaft mbB, 50668 Köln, DE

(72) Erfinder:
Gorval, Evgeni, Dr., 44135 Dortmund, DE;
Johanning, Joachim, Dr., 46045 Oberhausen, DE; Keil, Bernd, Dr., 44141 Dortmund, DE;
Poschlad, Katja, Dr., 45529 Hattingen, DE;
Potthoff, Christiane, 44265 Dortmund, DE

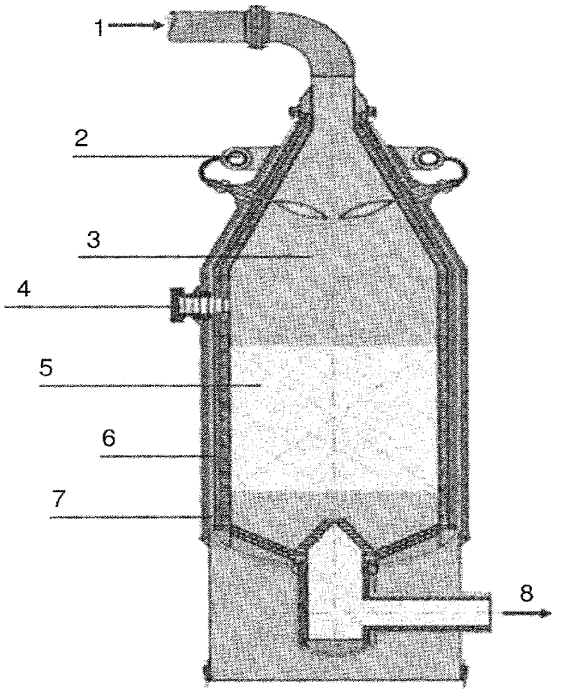
(56) Ermittelter Stand der Technik:

US	6 689 294	B1
US	2001 / 0 008 621	A1
US	4 822 521	A

Prüfungsantrag gemäß § 44 PatG ist gestellt.

Die folgenden Angaben sind den vom Anmelder eingereichten Unterlagen entnommen

(54) Bezeichnung: **Festlegung von Druck, Temperatur und S/C-Verhältnis für einen rußfreien ATR-Betrieb**



(57) Zusammenfassung: Die Erfindung betrifft ein Verfahren zur Festlegung von Druck, Temperatur und Dampf/Kohlenstoff-Verhältnis (S/C-Verhältnis) für einen rußfreien Betrieb eines autothermen Reformers (ATR).

Beschreibung

[0001] Die vorliegende Erfindung betrifft ein Verfahren zur Festlegung von Druck, Temperatur und Dampf/Kohlenstoff-Verhältnis (S/C-Verhältnis) für einen rußfreien Betrieb eines autothermen Reformers (ATR).

[0002] Die Produktion von Synthesegas ist ein wichtiger Schritt bei der Herstellung einer Vielzahl von Stoffen wie Ammoniak, Methanol und auch von synthetischen Kraftstoffen aus kohlenwasserstoffhaltigen Einsatzstoffen. Die Reformierung von kohlenwasserstoffhaltigen Einsatzstoffen, insbesondere Erdgasen, mit Wasserdampf ist heute das vorherrschende Verfahren zur Herstellung von Synthesegasen. Als Synthesegase werden Gasgemische mit den Hauptbestandteilen H_2 und CO bezeichnet, je nach Technologie und Anwendung beinhalten sie ggf. weitere Komponenten wie z.B. Anteile an H_2O, CO_2, N_2, CH_4 und Argon. Synthesegase sind die Basis für die großtechnische Herstellung von Ammoniak, Reinwasserstoff, Methanol und synthetischen Kraftstoffen.

[0003] Die Reformierung von kohlenwasserstoffhaltigen Einsatzstoffen kann üblicherweise entweder in einem Spaltofen mit externer Beheizung (Dampfreformer) oder in einem autothermen Reformer (ATR) mit einer inneren Beheizung erfolgen. Welche der beiden Reformierungstechnologien die wirtschaftlichste ist, hängt in jedem einzelnen Fall von vielen Parametern ab, wie z.B. dem gewünschten Verhältnis von H_2 zu CO, der Anlagenkapazität, der Produkt- und Eduktpreise etc. Kohlenwasserstoffhaltige Einsatzstoffe umfassen dabei Erdgas, Flüssiggas, Biogas, Butan, Benzin oder eine andere Art von Kohlenwasserstoff.

[0004] Die autotherme Reformierung ist eine Kombination aus partieller Oxidation und Dampfreformierung von kohlenwasserstoffhaltigen Einsatzstoffen, wobei sowohl die partielle Oxidation als auch die Dampfreformierung innerhalb eines Reaktors erfolgen. Der Vorteil der autothermen Reformierung liegt im Wegfall der externen Wärmequelle. Die exotherme partielle Oxidationsreaktion (1) und die exotherme Wassergas-Shift-Reaktion (3) decken dabei teilweise den Energiebedarf für die endotherme Dampfreformierungsreaktion (2). Der weitere Energiebedarf wird zumindest teilweise durch die Verbrennungsreaktionen (4) und (5) gedeckt. Diese Reaktionen sind beispielhaft für die Reformierung von Methan formuliert:

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \quad (1)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad (2)$$

$$CO + H_2O \rightarrow H_2 + CO_2 \quad (3)$$

$$CO + 1/2O_2 \rightarrow CO_2 \quad (4)$$

$$H_2 + 1/2O_2 \rightarrow H_2O \quad (5)$$

[0005] Die Reaktionen laufen katalytisch bei Betriebstemperaturen von 500–1250°C und Drücken bis 70 bar abs ab.

[0006] Das Verbrennen der kohlenwasserstoffhaltigen Einsatzstoffe erfolgt mit einer unterstöchiometrischen Menge an Sauerstoff mit Hilfe einer Flammenreaktion in der Verbrennungszone eines Reaktors. Die Dampfreformierungsreaktion erfolgt anschließend in demselben Reaktor im Festbett eines Dampfreformierungskatalysators.

[0007] Die Anwendung der autothermen Reformierung hat viele Vorteile im Vergleich zur Dampfreformierung mit ausschließlich externer Beheizung. Sie zeichnet sich aus durch eine kompakte Bauweise des Reformers, durch deutlich geringere Baukosten und bessere Regelbarkeit im Vergleich zur Dampfreformierung, ist mechanisch verhältnismäßig einfach durchführbar und erlaubt ein rasches An- und Abfahren des Reformers.

[0008] Die Verbrennung von kohlenwasserstoffhaltigen Einsatzstoffen bei unterstöchiometrischen Mengen an Sauerstoff kann jedoch zur Bildung von Ruß führen, insbesondere im Bereich der Teiloxidation oberhalb des Katalysators (POX-Zone). Der sich bildende Ruß deaktiviert dabei den darauffolgenden Katalysator durch Belegung und chemische Veränderung. Die Rußbildung hängt dabei hauptsächlich von den Betriebsparametern Druck, Temperatur und dem Dampf/Kohlenstoff-Verhältnis (S/C) ab. Einerseits wirken ein steigender Druck, eine steigende Temperatur und ein steigendes S/C-Verhältnis der Rußbildung entgegen, andererseits erhöht jede Steigerung von Temperatur, Druck und S/C-Verhältnis die Betriebskosten. Außerdem verschlechtert sich mit steigendem Druck der Umsatz der Dampfreformierungsreaktion (2) und darüber hinaus ist eine Tempera-

tursteigerung wegen der Belastbarkeit des Katalysators nur sehr begrenzt möglich. Beispielsweise kann der Ruß bei der Unterschreitung eines kritischen Dampf/Kohlenstoff-Verhältnisses (S/C) gebildet werden.

[0009] Beispiele der Betriebsbedingungen, welche nicht zu einer Rußbildung führen, sind in T. S. Christensen et al., Hydrocarbon Processing, 1994, S. 39ff zusammengefasst. In dieser Druckschrift sind beispielhaft verschiedene Wertepaare für die Temperatur, den Druck und das S/C-Verhältnis angegeben, bei denen ein rußfreier Betrieb eines ATR-Reformers gewährleistet werden kann.

[0010] US 6,143,202 offenbart ein Verfahren zur rußfreien autothermen Reformierung einer Kohlenwasserstoffeinspeisung.

[0011] Die aus dem Stand der Technik bekannten Verfahren zur Festlegung von Druck, Temperatur und S/C-Verhältnis für einen rußfreien Betrieb eines autothermen Reformers sind jedoch nicht in jeder Hinsicht zufriedenstellend und es besteht ein Bedarf an verbesserten Verfahren und Vorrichtungen.

[0012] Der Erfindung liegt die Aufgabe zugrunde, die Rußgrenze beim Betrieb eines autothermen Reformers zu ermitteln, d.h. eine Kombinations-Matrix von Druck, Temperatur und S/C-Verhältnis zu bestimmen, bei der gerade noch kein Ruß gebildet wird.

[0013] Diese Aufgabe wird durch den Gegenstand der Patentansprüche gelöst.

[0014] Die Erfindung betrifft ein Verfahren zur Reformierung eines Gasgemischs, welches Kohlenwasserstoffe, Sauerstoff und Wasser und ggf. weitere Komponenten umfasst, in einem autothermen Reformer

- bei einem Dampf/Kohlenstoff-Verhältnis $\frac{S}{C}$ [mol/mol] am Eintritt des autothermen Reformers im Bereich von 0,1 bis 2,5, und
- bei einer adiabatischen Temperatur T [°C] am Austritt des autothermen Reformers von mindestens 500 °C, und
- bei einem Druck P [bar abs] im autothermen Reformer im Bereich von 10 bar abs bis $73{,}5 - 18 \cdot \frac{S}{C}$ bar abs,

wobei eine der folgenden Bedingungen (a), (b) oder (c) erfüllt ist:

(a) für $\frac{S}{C} < 1{,}38$ und $P\,[\text{bar abs}] \leq 47 - 34 \bullet \frac{S}{C}$: $1779{,}548 \bullet Z - 231{,}076 \bullet \frac{S}{C} - 13{,}280 \bullet Q - 273{,}15 > T[°C] \geq \frac{78 - Q - 34 \bullet \frac{S}{C}}{0{,}04} - 273{,}15$

(b) für $\frac{S}{C} < 1{,}38$ und $P\,[\text{bar abs}] > 47 - 34 \bullet \frac{S}{C}$: $1779{,}548 \bullet Z - 231{,}076 \bullet \frac{S}{C} - 13{,}280 \bullet Q - 273{,}15 > T[°C] \geq 500$

(c) für $\frac{S}{C} \geq 1{,}38$: $1779{,}548 - 231{,}076 \bullet \frac{S}{C} - 13{,}280 \bullet Q - 273{,}15 > T[°C] \geq 500$,

wobei für Z jeweils gilt:

$$Z = 0.958 + Q^3 \bullet 1.83^{-6} \text{ für } 22.101 < \left[\frac{Q}{(S/C)}\right]^{-0,1} < 26.311, \text{ sonst } Z=1,$$

und wobei Q jeweils der dimensionslose Zahlenwert des Drucks P [bar abs] ist.

[0015] Es wurde überraschend gefunden, dass bei Erfüllung einer der Bedingungen (a), (b) oder (c) ein rußfreier Betrieb eines autothermen Reformers möglich ist, und dass mit Hilfe der genannten Bedingungen der autotherme Reformer ganz gezielt im rußfreien Bereich bei gleichzeitig wirtschaftlich günstigen Betriebsbedingungen gefahren werden kann, was eine Verbesserung der Wirtschaftlichkeit von autothermen Reformern bedeutet.

[0016] Die Rußgrenze im Betrieb eines autothermen Reformers wird dabei vorzugsweise bestimmt durch die Werte für Druck, Temperatur und Dampf/Kohlenstoff-Verhältnis (S/C), bei denen im Betrieb des autothermen Reformers gerade noch kein Ruß gebildet wird, deren geringfügige Unterschreitung jedoch eine Rußbildung nach sich zieht. Bezüglich der Temperatur bedeutet geringfügige Unterschreitung eine Unterschreitung um höchstens 50°C, bevorzugter höchstens 45°C, höchstens 40°C, höchstens 35°C, höchstens 30°C, höchstens 25°C oder höchstens 20°C. Bezüglich des Drucks bedeutet geringfügige Unterschreitung eine Unterschreitung um höchstens 1bar, bevorzugter höchstens 0,9bar, höchstens 0,8bar, höchstens 0,7bar, höchstens 0,6bar,

höchstens 0,5bar, höchstens 0,4bar, höchstens 0,3bar, höchstens 0,2bar oder höchstens 0,1bar. Bezüglich des Dampf/Kohlenstoff-Verhältnisses (S/C) bedeutet geringfügige Unterschreitung eine Unterschreitung um höchstens 0,5, bevorzugter höchstens 0,45, höchstens 0,4, höchstens 0,35, höchstens 0,3, höchstens 0,25, höchstens 0,2, höchstens 0,15 oder höchstens 0,1, oder höchstens 0,05.

[0017] Das Dampf/Kohlenstoff-Verhältnis (S/C) ist das Stoffmengenverhältnis von Molekülen Wasserdampf zu Atomen Kohlenstoff im Gasgemisch, wobei allerdings nur diejenigen Kohlenstoffatome von Verbindungen eingerechnet werden, welche reine Kohlenwasserstoffe, d.h. frei von Sauerstoff sind; Kohlenstoffatome von Alkoholen, Aldehyden, etc. werden entsprechend nicht eingerechnet. Das Dampf/Kohlenstoff-Verhältnis (S/C) hat die Einheit [mol/mol] und ist dementsprechend dimensionslos.

[0018] Das Gasgemisch, welches im erfindungsgemäßen Verfahren reformiert wird (Prozessgas), umfasst Kohlenwasserstoff, Sauerstoff und Wasser und ggf. Kohlenmonoxid, ggf. Kohlendioxid, ggf. Stickstoff, ggf. Wasserstoff und ggf. Argon. Der Kohlenwasserstoff umfasst kohlenwasserstoffhaltige Energieträger, welche Erdgas, Leichtbenzin, Methanol, Biogas und Biomasse umfassen. Bevorzugt umfasst der Kohlenwasserstoff Erdgas, welches bevorzugt Methan umfasst. Bevorzugt umfasst das Gasgemisch einen Oxidator, der bevorzugt der Sauerstoff ist. Das Gasgemisch kann weitere, inerte Komponenten umfassen. Inerte Komponenten im Sinne der Erfindung sind im Hinblick auf die Reformierung und die Wassergas-Shift-Reaktion inert.

[0019] Die Komponenten des Gasgemischs können alle an derselben Position oder als Teilströme an verschiedenen Positionen in den Reformer geleitet werden. Bevorzugt erfolgt die Einleitung aller Komponenten des Gasgemischs einschließlich des Oxidatorstroms in das obere Ende des Reformers. Der Oxidatorstrom umfasst dabei bevorzugt Sauerstoff, er kann aber ggf. auch weitere Komponenten wie Stickstoff, Wasser, Kohlendioxid und/oder Argon umfassen. In einer anderen bevorzugten Ausführungsform werden die Komponenten an verschiedenen Positionen in den Reformer geleitet. Bevorzugt werden alle Komponenten mit Ausnahme des Oxidatorstroms an einer Position und der Oxidatorstrom an einer anderen Position in den Reformer geleitet. Die Komponenten des Gasgemischs durchströmen anschließend den Reformer von oben nach unten. Nach Durchströmen des Reformers erfolgt der Austritt des Gasgemischs aus dem Reformer am unteren Ende.

[0020] Das S/C-Verhältnis liegt am Eintritt des autothermen Reformers im Bereich von 0,1 bis 2,5, bevorzugter im Bereich von 0,2 bis 2,4, bevorzugter im Bereich von 0,3 bis 2,3, im Bereich von 0,4 bis 2,2, im Bereich von 0,5 bis 2,1, im Bereich von 0,6 bis 2,0, im Bereich von 0,7 bis 1,9, im Bereich von 0,8 bis 1,8, im Bereich von 0,9 bis 1,7, im Bereich von 1,0 bis 1,6 im Bereich von 1,1 bis 1,5 oder im Bereich von 1,2 bis 1,4.

[0021] Die adiabatische Temperatur T [°C] am Austritt des autothermen Reformers beträgt mindestens 500 °C, bevorzugter mindestens 550°C, mindestens 600°C, mindestens 650°C, mindestens 700°C, mindestens 750°C, mindestens 800°C, mindestens 850°C oder mindestens 900°C.

[0022] Der Druck P [bar abs] im autothermen Reformer liegt im Bereich von 10 bar abs bis 73,5 – 18·(S/C) bar abs. In einer bevorzugten Ausführungsform liegt der Druck P [bar abs] im autothermen Reformer im Bereich von 10 bar abs bis 73,5 bar abs, bevorzugter im Bereich von 10 bar abs bis 71,7 bar abs, im Bereich von 10 bar abs bis 70 bar abs, im Bereich von 10 bar abs bis 60 bar abs, im Bereich von 10 bar abs bis 50 bar abs, im Bereich von 10 bar abs bis 40 bar abs, im Bereich von 10 bar abs bis 30 bar abs oder im Bereich von 10 bar abs bis 28,5 bar abs.

[0023] Die Variable Z kann jeden Wert einer rationalen Zahl annehmen, wobei für Z jeweils gilt:

$$Z= 0{,}958 + Q^3 \cdot 1{,}83^{-6} \text{ für } 22{,}101 < \left[\frac{Q}{S/C}\right]^{0,1} < 26{,}311, \text{ sonst } Z=1.$$

[0024] In einer bevorzugten Ausführungsform ist $Z \leq 0{,}99$, bevorzugter ist $Z \leq 0{,}985$, noch bevorzugter ist $Z \leq 0.98$, $Z \leq 0.978$, $Z \leq 0.975$, $Z \leq 0.972$, $Z \leq 0.969$, $Z \leq 0.966$, $Z \leq 0.963$ und am bevorzugtesten ist $Z \leq 0{,}960$.

[0025] In einer bevorzugten Ausführungsform des erfindungsgemäßen Verfahrens weist der autotherme Reformer mindestens einen Oxidatorstromeinlass auf, welcher dazu vorgesehen ist, den Oxidatorstrom in einer definierten Richtung in den autothermen Reformer zu leiten.

[0026] In einer bevorzugten Ausführungsform erfolgt der Oxidatorstromeinlass derart, dass sich innerhalb des autothermen Reformers ein Strömungsregime bildet, welches sich spiralförmig von oben nach unten abwärts bewegt. Die Komponenten des Gasgemischs mit Ausnahme des Oxidatorstroms werden dabei bevorzugt axial

von oben in den Reformer geleitet. Bevorzugt entsprechen die Richtung des Oxidatorstromeinlasses und das damit verbundene Strömungsregime dem Aufbau eines Drallbrenners, bei dem die Zuführung des Oxidatorstroms bevorzugt außer einer Axial- auch eine Radial- und eine Tangentialkomponente (Verdrallung) besitzt.

[0027] In einer bevorzugten Ausführungsform ist der Oxidatorstromeinlass eine Diffusionslanze. Bevorzugt wird über die Diffusionslanze der Oxidatorstrom in den Reformer geleitet. Bevorzugt werden der Oxidatorstrom und die restlichen Komponenten des Gasgemischs im Reformer gemischt und mindestens ein Teil des Oxidators und ein Teil der Kohlenwasserstoffe des Gasgemischs unter Flammenbildung verbrannt. Bevorzugt werden mindestens 5 Vol.-% des Oxidators am Oxidatorstromeinlass verbrannt, bevorzugter mindestens 10 Vol.-%, mindestens 20 Vol.-%, mindestens 30 Vol.-%, mindestens 40 Vol.-%, mindestens 50 Vol.-%, mindestens 60 Vol.-%, mindestens 70 Vol.-%, mindestens 80 Vol.-% oder mindestens 90 Vol.-%. Bevorzugt werden mindestens 5 Vol.-% der Kohlenwasserstoffe des Gasgemischs am Oxidatorstromeinlass verbrannt, bevorzugter mindestens 10 Vol.-%, mindestens 20 Vol.-%, mindestens 30 Vol.-% oder mindestens 40 Vol.-%.

[0028] In einer anderen bevorzugten Ausführungsform werden höchstens 90 Vol.-% des Oxidators des Gasgemischs am Oxidatorstromeinlass verbrannt, bevorzugter höchstens 80 Vol.-%, höchstens 70 Vol.-%, höchstens 60 Vol.-%, höchstens 50 Vol.-%, höchstens 40 Vol.-%, höchstens 30 Vol.-%, höchstens 20 Vol.-% oder höchstens 10 Vol.-%.

[0029] Bevorzugt werden höchstens 40 Vol.-% der Kohlenwasserstoffe des Gasgemischs am Oxidatorstromeinlass verbrannt, bevorzugter höchstens 30 Vol.-%, höchstens 20 Vol.-% oder höchstens 10 Vol.-%. Das Verhältnis O/C im ATR beträgt typischerweise < 0,8.

[0030] In einer bevorzugten Ausführungsform umfasst das erfindungsgemäße Verfahren
- die Messung der adiabatischen Temperatur T, des Drucks P und/oder des Dampf/Kohlenstoff-Verhältnisses (S/C) und
- die Regelung des Gehalts an Sauerstoff im Gasgemisch und/oder des Dampf/Kohlenstoff-Verhältnisses im Gasgemisch unter Einhaltung einer der Bedingungen (a), (b) oder (c) gemäß dem erfindungsgemäßen Verfahren, so dass das Verfahren praktisch ohne Rußbildung erfolgt.

[0031] Bevorzugt erfolgen die Regelung des Gehalts an Sauerstoff im Gasgemisch und/oder die Regelung des Dampf/Kohlenstoff-Verhältnisses (S/C) im Gasgemisch in Abhängigkeit der gemessenen adiabatischen Temperatur T und/oder in Abhängigkeit des gemessenen Drucks P und/oder in Abhängigkeit der Messung des Dampf/Kohlenstoff-Verhältnisses (S/C). Dabei wird der Gehalt an Sauerstoff im Gasgemisch und/oder das Dampf/Kohlenstoff-Verhältnis (S/C) derart geregelt, dass eine der Bedingungen (a), (b) oder (c) gemäß dem erfindungsgemäßen Verfahren eingehalten wird und das Verfahren praktisch ohne Rußbildung erfolgt. Unterschreitet beispielsweise das Dampf/Kohlenstoff-Verhältnis (S/C) den durch eine bestimmte Temperatur und einen bestimmten Druck vorgegebenen minimalen Grenzwert, wird das Dampf/Kohlenstoff-Verhältnis so lange reguliert, bis eine der Bedingungen (a), (b) oder (c) des erfindungsgemäßen Verfahrens eingehalten wird. Bevorzugt erfolgen die Regelung des Gehalts an Sauerstoff im Gasgemisch und die Regelung des Dampf/Kohlenstoff-Verhältnisses (S/C) kontinuierlich, sie können aber auch nur zeitweise erfolgen.

[0032] In einer bevorzugten Ausführungsform wird ein autothermer Reformer zur Reformierung von Kohlenwasserstoffen entsprechend dem erfindungsgemäßen Verfahren verwendet.

[0033] **Fig.** 1 illustriert schematisch und beispielhaft das erfindungsgemäße Verfahren zum Betrieb eines autothermen Reformers, ist jedoch nicht einschränkend auszulegen.

[0034] Bei dem in **Fig.** 1 dargestellten autothermen Reformer erfolgt sowohl der Eintritt des Prozessgases (**1**) als auch der Eintritt des Oxidatorstroms (**2**) im oberen Bereich des Reformers. Bevorzugt wird der Oxidatorstrom über Diffusionslanzen in den autothermen Reformer geleitet und zumindest ein Teil des Oxidators wird in der Brennkammer (**3**) unter Flammenbildung verbrannt. Die Flammenrichtung weist dabei neben einer axialen auch eine radiale und eine tangentiale Komponente auf. Der autotherme Reformer umfasst ein Mannloch (**4**), der den Zugang zum Innenraum des Reformers gewährleistet. Die Reformierung des Prozessgases erfolgt im Katalysatorbett (**5**). Nach Durchströmen des Katalysatorbetts (**5**) tritt das Prozessgas am unteren Ende aus dem autothermen Reformer aus (**8**). Der autotherme Reformer umfasst zusätzlich eine Feuerfestauskleidung (**6**) und einen Wassermantel (**7**).

Bezugszeichenliste

1 Eintritt Prozessgas
2 Eintritt Oxidatorstrom
3 Brennkammer
4 Mannloch
5 Katalysatorbett
6 Feuerfestauskleidung
7 Wassermantel
8 Austritt Prozessgas.

ZITATE ENTHALTEN IN DER BESCHREIBUNG

Diese Liste der vom Anmelder aufgeführten Dokumente wurde automatisiert erzeugt und ist ausschließlich zur besseren Information des Lesers aufgenommen. Die Liste ist nicht Bestandteil der deutschen Patent- bzw. Gebrauchsmusteranmeldung. Das DPMA übernimmt keinerlei Haftung für etwaige Fehler oder Auslassungen.

Zitierte Patentliteratur

- US 6143202 [0010]

Zitierte Nicht-Patentliteratur

- T. S. Christensen et al., Hydrocarbon Processing, 1994, S. 39ff [0009]

Patentansprüche

1. Ein Verfahren zur Reformierung eines Gasgemischs, welches Kohlenwasserstoffe, Sauerstoff und Wasser und ggf. weitere Komponenten umfasst, in einem autothermen Reformer
– bei einem Dampf/Kohlenstoff-Verhältnis $\frac{S}{C}$ [mol/mol] am Eintritt des autothermen Reformers im Bereich von 0,1 bis 2,5, und
– bei einer adiabatischen Temperatur T [°C] am Austritt des autothermen Reformers von mindestens 500 °C, und
– bei einem Druck P [bar abs] im autothermen Reformer im Bereich von 10 bar abs bis $73{,}5 - 18 \cdot \frac{S}{C}$ bar abs, wobei eine der folgenden Bedingungen (a), (b) oder (c) erfüllt ist:

(a) für $\frac{S}{C} < 1{,}38$ und $P[\text{bar abs}] \leq 47 - 34 \bullet \frac{S}{C}$: $1779{,}548 \bullet Z - 231{,}076 \bullet \frac{S}{C} - 13{,}280 \bullet Q - 273{,}15 > T[°C] > \frac{78 - Q - 34 \bullet \frac{S}{C}}{0{,}04} - 273{,}15$

(b) für $\frac{S}{C} < 1{,}38$ und $P[\text{bar abs}] > 47 - 34 \bullet \frac{S}{C}$: $1779{,}548 \bullet Z - 231{,}076 \bullet \frac{S}{C} - 13{,}280 \bullet Q - 273{,}15 > T[°C] \geq 500$

(c) für $\frac{S}{C} \geq 1{,}38$: $1779{,}548 - 231{,}076 \bullet \frac{S}{C} - 13{,}280 \bullet Q - 273{,}15 > T[°C] \geq 500$,

wobei für Z jeweils gilt:

$$Z = 0{,}958 + Q^3 \bullet 1{,}83^{-6} \text{ für } 22{,}101 < \left[\frac{Q}{S/C}\right]^{0{,}1} < 26{,}311, \text{ sonst } Z = 1,$$

und wobei Q jeweils der dimensionslose Zahlenwert des Drucks P [bar abs] ist.

2. Das Verfahren nach Anspruch 1, wobei $Z \leq 0{,}978$ ist.

3. Das Verfahren nach Anspruch 1, wobei $Z \leq 0{,}975$ ist.

4. Das Verfahren nach Anspruch 1, wobei $Z \leq 0{,}972$ ist.

5. Das Verfahren nach Anspruch 1, wobei $Z \leq 0{,}969$ ist.

6. Das Verfahren nach Anspruch 1, wobei $Z \leq 0{,}966$ ist.

7. Das Verfahren nach Anspruch 1, wobei $Z \leq 0{,}963$ ist.

8. Das Verfahren nach Anspruch 1, wobei $Z \leq 0{,}960$ ist.

9. Das Verfahren nach einem der vorstehenden Ansprüche, umfassend
– die Messung der adiabatischen Temperatur T, des Drucks P und/oder des Dampf/Kohlenstoff-Verhältnisses (S/C) und
– die Regelung des Gehalts an Sauerstoff im Gasgemisch und/oder des Dampf/Kohlenstoff-Verhältnisses im Gasgemisch unter Einhaltung einer der Bedingungen (a), (b) oder (c) gemäß Anspruch 1, so dass das Verfahren praktisch ohne Rußbildung erfolgt.

10. Das Verfahren nach einem der vorstehenden Ansprüche, wobei der autotherme Reformer mindestens einen Oxidatorstromeinlass aufweist, welcher dazu vorgesehen ist, einen Oxidatorstrom in einer definierten Richtung in den autothermen Reformer zu leiten.

11. Das Verfahren nach Anspruch 10, wobei der Oxidatorstromeinlass eine Diffusionslanze ist.

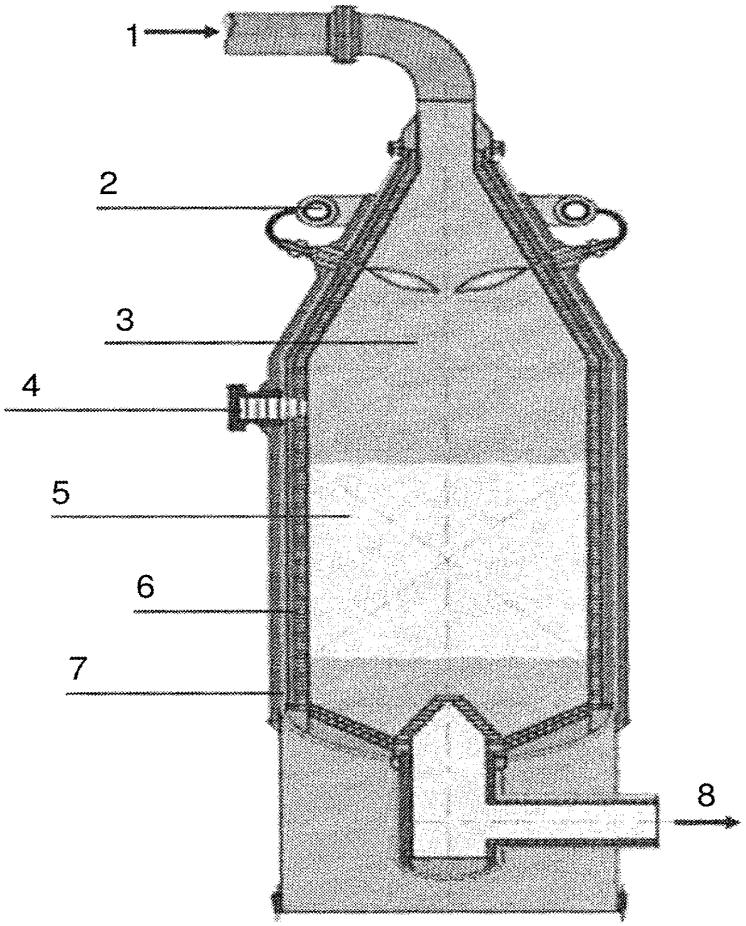
12. Das Verfahren nach einem der Ansprüche 10 oder 11, wobei der Oxidatorstromlass derart erfolgt, dass sich innerhalb des autothermen Reformers ein Strömungsregime bildet, welches sich spiralförmig von oben nach unten abwärts bewegt.

13. Verwendung eines autothermen Reformers zur Reformierung von Kohlenwasserstoffen nach einem der Ansprüche 1 bis 12.

Es folgt eine Seite Zeichnungen

Anhängende Zeichnungen

Figur 1



Patents

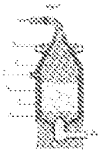
Determination of pressure, temperature and S / C ratio for a soot-free ATR operation

Abstract

translated from German

The invention relates to a method for determining pressure, temperature and steam / carbon ratio (S / C ratio) for a soot-free operation of an autothermal reformer (ATR).

Images (1)



Classifications

- C01B3/382 Multi-step processes

View 5 more classifications

DE102015210803A1

Germany

Download PDF Find Prior Art Similar

Other languages: German

Inventor: Evgeni Gerval, Joachim Johanning, Bernd Keil, Katja Peschlad, Christiane Potthoff

Current Assignee : ThyssenKrupp AG , ThyssenKrupp Industrial Solutions AG

Worldwide applications

2015 DE 2016 WO

Application DE102015210803.1A events

2015-06-12 Application filed by ThyssenKrupp AG, ThyssenKrupp Industrial Solutions AG

2015-06-12 Priority to DE102015210803.1A

2016-12-15 Publication of DE102015210803A1

Status Ceased

Info: Patent citations (4), Non-patent citations (1), Cited by (2), Legal events, Similar documents, Priority and Related Applications

External links: Espacenet, Global Dossier, DPMA, Discuss

Claims (13)

Hide Dependent

translated from German

A process for reforming a gas mixture comprising hydrocarbons, oxygen and water and optionally other components in an autothermal reformer - at a steam / carbon ratio S / C [mol / mol] at the inlet of the autothermal reformer in the range of 0.1 to 2.5, and - at an adiabatic temperature T [° C] at the outlet of the autothermal reformer of at least 500 ° C, and - at a pressure P [bar abs] in the autothermal reformer in the range of 10 bar abs to 73.5 - 18 · S / C bar abs, wherein one of the following conditions (a), (b) or (c) is satisfied.

(a) für $\frac{S}{C} < 1{,}38$ und $P[\text{bar abs}] \leq 47 - 34 \bullet \frac{S}{C}$: $1779{,}548 \bullet Z - 231{,}076 \bullet \frac{S}{C} - 13{,}280 \bullet Q - 273{,}15 > T[°C] > \frac{78 - Q - 34 \bullet \frac{S}{C}}{0{,}04} - 273{,}15$

(b) für $\frac{S}{C} < 1{,}38$ und $P[\text{bar abs}] > 47 - 34 \bullet \frac{S}{C}$: $1779{,}548 \bullet Z - 231{,}076 \bullet \frac{S}{C} - 13{,}280 \bullet Q - 273{,}15 > T[°C] \geq 500$

(c) für $\frac{S}{C} \geq 1{,}38$: $1779{,}548 - 231{,}076 \bullet \frac{S}{C} - 13{,}280 \bullet Q - 273{,}15 > T[°C] \geq 500$,

where for each of Z applies:

$Z = 0{,}958 + Q^3 \bullet 1{,}83^{-6}$ für $22{,}101 < \left|\frac{Q}{S/C}\right|^{0{,}1} < 26{,}311$, sonst $Z = 1$,

and Q is the dimensionless numerical value of the pressure P [bar abs]. The method of claim 1, wherein Z ≤ 0.978. The method of claim 1, wherein Z ≤ 0.975. The method of claim 1, wherein Z ≤ 0.972. The method of claim 1, wherein Z ≤ 0.969. The method of claim 1, wherein Z ≤ 0.966. The method of claim 1, wherein Z ≤ 0.963. The method of claim 1, wherein Z ≤ 0.960. The method according to any one of the preceding claims, comprising The measurement of the adiabatic temperature T, the pressure P and / or the steam / carbon ratio (S / C) and - The regulation of the content of oxygen in the gas mixture and / or the vapor / carbon ratio in the gas mixture in compliance with one of the conditions (a), (b) or (c) according to claim 1, so that the process takes place practically without soot formation. The method of any one of the preceding claims, wherein the autothermal reformer has at least one oxidant stream inlet intended to direct an oxidizer stream in a defined direction into the autothermal reformer. The method of claim 10, wherein the oxidant stream inlet is a diffusion lance. The method of any one of claims 10 or 11, wherein the oxidant flow inlet is such that within the autothermal reformer, a flow regime is formed which spirally descends from top to bottom. Use of an autothermal reformer for the reforming of hydrocarbons according to one of claims 1 to 12.

Description

translated from German

The present invention relates to a method of determining pressure, temperature and steam / carbon ratio (S / C ratio) for soot-free operation of an autothermal reformer (ATR).

The production of synthesis gas is an important step in the production of a variety of substances such as ammonia, methanol and also of synthetic fuels from hydrocarbonaceous feedstocks. The reforming of hydrocarbonaceous feedstocks, especially natural gas, with steam is today the predominant process for the production of synthesis gas. As synthesis gases, gas mixtures are designated with the main components H_2 and CO, depending on the technology and application, they may contain

other components such as, for example, H_2O, CO_2, N_2, CH_4 and argon. Synthesis gases are the basis for the large-scale production of ammonia, pure hydrogen, methanol and synthetic fuels.

The reforming of hydrocarbonaceous feedstocks can usually be carried out either in a cracking furnace with external heating (steam reformer) or in an autothermal reformer (ATR) with an internal heating. Which of the two reforming technologies is the most economical depends on many parameters in each case, such as the desired ratio of H_2 to CO, plant capacity, product and educt prices, etc. Hydrocarbon-containing feedstocks include natural gas, LPG, biogas, butane , Gasoline or another type of hydrocarbon.

Autothermal reforming is a combination of partial oxidation and steam reforming of hydrocarbonaceous feedstocks, with both partial oxidation and steam reforming occurring within a reactor. The advantage of autothermal reforming is the elimination of the external heat source. The exothermic partial oxidation reaction (1) and the exothermic water gas shift reaction (3) partially cover the energy requirements for the endothermic steam reforming reaction (2). The additional energy requirement is at least partially covered by the combustion reactions (4) and (5). These reactions are exemplary for the reforming of methane formulated: $CH_4 + 1/2\,O_2 \rightarrow CO + 2H_2$ (1)

$CH_4 + H_2O \rightarrow CO + 3H_2$ (2) $CO + H_2O \rightarrow H_2 + CO_2$ (3) $CO + 1/2\,O_2 \rightarrow CO_2$ (4) $H_2 + 1/2\,O_2 \rightarrow H_2O$ (5)

The reactions proceed catalytically at operating temperatures of 500-1250 ° C and pressures up to 70 bar abs.

The combustion of the hydrocarbon-containing feedstocks takes place with a substoichiometric amount of oxygen by means of a flame reaction in the combustion zone of a reactor. The steam reforming reaction is then carried out in the same reactor in the fixed bed of a steam reforming catalyst.

The application of autothermal reforming has many advantages compared to steam reforming with external heating alone. It is characterized by a compact design of the reformer, by significantly lower construction costs and better controllability compared to steam reforming, is mechanically relatively easy to carry out and allows a quick startup and shutdown of the reformer.

The combustion of hydrocarbonaceous feedstocks at substoichiometric amounts of oxygen, however, can lead to the formation of soot, especially in the region of partial oxidation above the catalyst (POX zone). The forming carbon black deactivates the subsequent catalyst by occupancy and chemical change. The formation of soot depends mainly on the operating parameters of pressure, temperature and the steam / carbon ratio (S / C). On the one hand, increasing pressure, rising temperature and increasing S / C ratio counteract soot formation, on the other hand, any increase in temperature, pressure and S / C increases operating costs. In addition, as the pressure increases, the conversion rate of the steam reforming reaction (2) deteriorates, and moreover, is one Temperature increase due to the capacity of the catalyst only very limited possible. For example, the carbon black may be formed when a critical steam / carbon ratio (S / C) is undershot.

Examples of operating conditions that do not cause soot formation are in TS Christensen et al., Hydrocarbon Processing, 1994, p. 39ff summarized. In this document, various value pairs for the temperature, the pressure and the S / C ratio are given by way of example, in which a soot-free operation of an ATR reformer can be ensured.

US 6,143,202 discloses a method for soot-free autothermal reforming of a hydrocarbon feed.

However, prior art pressure, temperature, and S / C ratio determination methods for soot-free operation of an autothermal reformer are not entirely satisfactory, and there is a need for improved methods and apparatus.

The invention has for its object to determine the soot limit in the operation of an autothermal reformer, i. To determine a combination matrix of pressure, temperature and S / C ratio, in which just no soot is formed.

This object is solved by the subject matter of the claims.

- bei einem Dampf/Kohlenstoff-Verhältnis S / C [mol/mol] am Eintritt des autothermen Reformers im Bereich von 0,1 bis 2,5, und
- bei einer adiabatischen Temperatur T [°C] am Austritt des autothermen Reformers von mindestens 500 °C, und
- bei einem Druck P [bar abs] im autothermen Reformer im Bereich von 10 bar abs bis 73,5 - 18· S / C bar abs,

wobei eine der folgenden Bedingungen (a), (b) oder (c) erfüllt ist:

(a) für $\frac{S}{C} < 1{,}38$ und $P\,[\text{bar abs}] \le 47 - 34 \cdot \frac{S}{C}$: $1779{,}548 \cdot Z - 231{,}076 \cdot \frac{S}{C} - 13{,}280 \cdot Q - 273{,}15 > T[°C] \ge \frac{78 - Q - 34 \cdot \frac{S}{C}}{0.04} - 273{,}15$

(b) für $\frac{S}{C} < 1{,}38$ und $P\,[\text{bar abs}] > 47 - 34 \cdot \frac{S}{C}$: $1779{,}548 \cdot Z - 231{,}076 \cdot \frac{S}{C} - 13{,}280 \cdot Q - 273{,}15 > T[°C] \ge 500$

(c) für $\frac{S}{C} \ge 1{,}38$: $1779{,}548 - 231{,}076 \cdot \frac{S}{C} - 13{,}280 \cdot Q - 273{,}15 > T[°C] \ge 500$,

wobei für Z jeweils gilt:

$Z = 0.958 + Q^3 \cdot 1.83^{-6}$ für $22.101 < \left[\frac{Q}{(S/C)}\right]^{0,1} < 26.311$, sonst Z=1,

und wobei Q jeweils der dimensionslose Zahlenwert des Drucks P [bar abs] ist. The invention relates to a process for reforming a gas mixture which comprises hydrocarbons, oxygen and water and optionally further components in an autothermal reformer

- At a steam / carbon ratio S / C [mol / mol] at the entrance of the autothermal reformer in the range of 0.1 to 2.5, and
- At an adiabatic temperature T [° C] at the outlet of the autothermal reformer of at least 500 ° C, and
- At a pressure P [bar abs] in the autothermal reformer in the range of 10 bar abs to 73.5 - 18 · S / C bar abs,

wherein one of the following conditions (a), (b) or (c) is satisfied:

(a) for $\frac{S}{C} < 1{,}38$ and $P\,[\text{bar abs}] \le 47 - 34 \cdot \frac{S}{C}$: $1779{,}548 \cdot Z - 231{,}076 \cdot \frac{S}{C} - 13{,}280 \cdot Q - 273{,}15 > T[°C] \ge \frac{78 - Q - 34 \cdot \frac{S}{C}}{0.04} - 273{,}15$

(b) for $\frac{S}{C} < 1{,}38$ and $P\,[\text{bar abs}] > 47 - 34 \cdot \frac{S}{C}$: $1779{,}548 \cdot Z - 231{,}076 \cdot \frac{S}{C} - 13{,}280 \cdot Q - 273{,}15 > T[°C] \ge 500$

(c) for $\frac{S}{C} \ge 1{,}38$: $1779{,}548 - 231{,}076 \cdot \frac{S}{C} - 13{,}280 \cdot Q - 273{,}15 > T[°C] \ge 500$,

where for each of Z applies:

$Z = 0.958 + Q^3 \cdot 1.83^{-6}$ für $22.101 < \left[\frac{Q}{(S/C)}\right]^{0,1} < 26.311$, sonst Z=1,

and Q is the dimensionless numerical value of the pressure P [bar abs].

It has surprisingly been found that when one of the conditions (a), (b) or (c) a soot-free operation of an autothermal reformer is possible, and that with the help of these conditions, the autothermal reformer quite specifically in the soot-free area at the same time economically favorable Operating conditions can be driven, which means an improvement in the economics of autothermal reformers.

The soot limit in the operation of an autothermal reformer is preferably determined by the values for pressure, temperature and steam / carbon ratio (S / C), in which just no soot is formed during operation of the autothermal reformer, whose slight undercut, however, a soot pulls. With regard to the temperature, a slight shortfall means that the maximum is less than or equal to 50 ° C, more preferably not more than 45 ° C, not more than 40 ° C, not more than 35 ° C, not more than 30 ° C, not more than 25 ° C or not more than 20 ° C. With regard to the pressure, slight undershooting means falling short of at most 1 bar, more preferably at most 0.9 bar, at most 0.8 bar, at most 0.7 bar, at most 0.6 bar, not more than 0,5bar, not more than 0.4bar, not more than 0,3bar, not more than 0,2bar or not more than 0,1bar. With respect to the steam / carbon ratio (S / C), a slight shortfall means that it falls short of at most 0.5, more preferably at most 0.45, at most 0.4, at most 0.35, at most 0.3, at most 0.25, at most 0.2, at most 0.15 or at most 0.1, or at most 0.05.

The steam / carbon ratio (S / C) is the molar ratio of molecules of water vapor to atoms of carbon in the gas mixture, but only those carbon atoms of compounds which are pure hydrocarbons, i. are free of oxygen, Carbon atoms of alcohols, aldehydes, etc. are not included accordingly. The steam / carbon ratio (S / C) has the unit [mol / mol] and is accordingly dimensionless.

The gas mixture which is reformed in the process according to the invention (process gas) comprises hydrocarbon, oxygen and water and optionally carbon monoxide, optionally carbon dioxide, optionally nitrogen, optionally hydrogen and optionally argon. The hydrocarbon comprises hydrocarbonaceous fuels comprising natural gas, light gasoline, methanol, biogas and biomass. Preferably, the hydrocarbon comprises natural gas, which preferably comprises methane. Preferably, the gas mixture comprises an oxidizer, which is preferably the oxygen. The gas mixture may comprise further inert components. inert components within the meaning of the invention are inert with regard to the reforming and the water gas shift reaction.

The components of the gas mixture can all be conducted at the same position or as substreams at different positions in the reformer. Preferably, the introduction of all components of the gas mixture, including the oxidant stream in the upper end of the reformer. The oxidizer stream preferably comprises oxygen, but may optionally also comprise further components such as nitrogen, water, carbon dioxide and / or argon. In another preferred embodiment, the components are directed at different positions in the reformer. Preferably, all components except the oxidizer stream are directed to one position and the oxidizer stream is directed to another position in the reformer. The components of the gas mixture then flow through the reformer from top to bottom. After flowing through the reformer, the exit of the gas mixture from the reformer takes place at the lower end.

The S / C ratio is at the entrance of the autothermal reformer in the range of 0.1 to 2.5, more preferably in the range of 0.2 to 2.4, more preferably in the range of 0.3 to 2.3, in the range of 0.4 to 2.2, in the range of 0.5 to 2.1, in the range of 0.6 to 2.0, in the range of 0.7 to 1.9, in the range of 0.8 to 1, 8, in the range of 0.9 to 1.7, in the range of 1.0 to 1.6 in the range of 1.1 to 1.5 or in the range of 1.2 to 1.4.

The adiabatic temperature T [° C] at the outlet of the autothermal reformer is at least 500 ° C, more preferably at least 550 ° C, at least 600 ° C, at least 650 ° C, at least 700 ° C, at least 750 ° C, at least 800 ° C, at least 850 ° C or at least 900 ° C.

The pressure P [bar abs] in the autothermal reformer is in the range of 10 bar abs to 73.5 - 18 · (S / C) bar abs. In a preferred embodiment, the pressure P [bar abs] in the autothermal reformer is in the range of 10 bar abs to 73.5 bar abs, more preferably in the range of 10 bar abs to 71.7 bar abs, in the range of 10 bar abs to 70 in the range of 10 bar abs to 50 bar abs, in the range of 10 bar abs to 40 bar abs, in the range of 10 bar abs to 30 bar abs or in the range of 10 bar abs to 28.5 bar abs.

$$Z= 0{,}958 + Q^3 \cdot 1{,}83^{-6} \text{ für } 22{,}101 < \left[\frac{Q}{S/C}\right]^{-0{,}1} < 26{,}311, \text{ sonst } Z=1.$$

The variable Z can take on any value of a rational number, where Z holds:

$$Z= 0{,}958 + Q^3 \cdot 1{,}83^{-6} \text{ für } 22{,}101 < \left[\frac{Q}{S/C}\right]^{-0{,}1} < 26{,}311, \text{ sonst } Z=1.$$

In a preferred embodiment, Z ≦ 0.99, more preferably Z ≦ 0.985, more preferably Z ≦ 0 98, Z ≦ 0.978, Z ≦ 0.975, Z ≦ 0 972, Z ≦ 0.969, Z ≦ 0.966, Z ≦ 0 963, and most preferably Z is ≤ 0.960.

In a preferred embodiment of the method according to the invention, the autothermal reformer has at least one oxidator stream inlet, which is provided to direct the oxidizer stream in a defined direction into the autothermal reformer.

in a preferred embodiment, the oxidant flow inlet is such that within the autothermal reformer, a flow regime is formed which spirally moves downwardly from top to bottom. The components of the gas mixture, with the exception of the oxidizer stream, are preferably axially passed from the top to the reformer. Preferably, the direction of the oxidant stream inlet and the associated flow regime correspond to the construction of a swirl burner in which the supply of the oxidant stream preferably has besides an axial as well as a radial and a tangential component (twisting).

In a preferred embodiment, the oxidant flow inlet is a diffusion lance. The oxidizer stream is preferably passed into the reformer via the diffusion lance. Preferably, the oxidizer stream and the remaining components of the gas mixture are mixed in the reformer and burned at least a portion of the oxidizer and a portion of the hydrocarbons of the gas mixture with flame formation. Preferably, at least 5 vol.% Of the oxidizer is burned at the oxidant flow inlet, more preferably at least 10 vol.%, At least 20 vol.%, At least 30 vol.%, At least 40 vol.%, At least 50 vol. at least 60% by volume, at least 70% by volume, at least 80% by volume or at least 90% by volume. Preferably, at least 5% by volume of the hydrocarbons of the gas mixture are burned at the oxidant stream inlet, more preferably at least 10% by volume, at least 20% by volume, at least 30% by volume or at least 40% by volume.

In another preferred embodiment, at most 90% by volume of the oxidizer of the gas mixture is burned at the oxidant flow inlet, more preferably at most 80% by volume, at most 70% by volume, at most 60% by volume, at most 50% by volume, at most 40 vol.%, At most 30 vol.%, At most 20 vol.% Or at most 10 vol.%.

Preferably, at most 40% by volume of the hydrocarbons of the gas mixture are burned at the oxidant stream inlet, more preferably at most 30% by volume, at most 20% by volume or at most 10% by volume. The ratio O / C in the ATR is typically <0.8.

- die Messung der adiabatischen Temperatur T, des Drucks P und/oder des Dampf/Kohlenstoff-Verhältnisses (S/C) und
- die Regelung des Gehalts an Sauerstoff im Gasgemisch und/oder des Dampf/Kohlenstoff-Verhältnisses im Gasgemisch unter Einhaltung einer der Bedingungen (a), (b) oder (c) gemäß dem erfindungsgemäßen Verfahren, so dass das Verfahren praktisch ohne Rußbildung erfolgt.

In a preferred embodiment, the method according to the invention comprises

The measurement of the adiabatic temperature T, the pressure P and / or the steam / carbon ratio (S / C) and
- The control of the content of oxygen in the gas mixture and / or the vapor / carbon ratio in the gas mixture in compliance with one of the conditions (a), (b) or (c) according to the inventive method, so that the process takes place practically without soot formation.

Preferably, the control of the content of oxygen in the gas mixture and / or the control of the steam / carbon ratio (S / C) in the gas mixture in dependence of the measured adiabatic temperature T and / or in dependence of the measured pressure P and / or in dependence of Measurement of the steam / carbon ratio (S / C). In this case, the content of oxygen in the gas mixture and / or the steam / carbon ratio (S / C) is controlled so that one of the conditions (a), (b) or (c) is maintained according to the inventive method and the method practically done without soot formation. For example, if the vapor / carbon ratio (S / C) falls below the minimum limit set by a particular temperature and pressure, the steam / carbon ratio will be adjusted until one of the conditions (a), (b) or (c) of the method according to the invention is maintained. Preferably, the control of the content of oxygen in the gas mixture and the control of the steam / carbon ratio (S / C) are carried out continuously, but they can also take place only temporarily.

In a preferred embodiment, an autothermal reformer is used to reform hydrocarbons according to the process of the invention.

1 illustrates schematically and by way of example the method according to the invention for operating an autothermal reformer, but is not to be construed as limiting.

At the in 1 shown autothermal reformer takes place both the entry of the process gas (1) as well as the entry of the Oxidatorstroms (2) in the upper part of the reformer. Preferably, the oxidant stream is passed via diffusion lances in the autothermal reformer and at least a portion of the oxidizer is in the combustion chamber (3) burned with flame formation. The flame direction has in addition to an axial and a radial and a tangential component. The autothermal reformer includes a manhole (4), which ensures access to the interior of the reformer. The reforming of the process gas takes place in the catalyst bed (5). After flowing through the catalyst bed (5), the process gas exits the autothermal reformer at the lower end (8th). The autothermal reformer additionally comprises a refractory lining (6) and a water jacket (7).

LIST OF REFERENCE NUMBERS

1
: Entry process gas
2
: Entry oxidizer stream
3
: combustion chamber
4
: manhole
5
: catalyst bed
6
: Refractory lining
7
: water jacket
8th
: Exit process gas.

QUOTES INCLUDE IN THE DESCRIPTION

This list of the documents listed by the applicant has been generated automatically and is included solely for the better information of the reader. The list is not part of the German patent or utility model application. The DPMA assumes no liability for any errors or omissions.

Cited patent literature

- US 6143202 **[0010]**

Cited non-patent literature

- TS Christensen et al., Hydrocarbon Processing, 1994, p. 39ff. **[0009]**

(19) Deutsches Patent- und Markenamt

(10) **DE 10 2014 209 635 A1** 2015.11.26

(12) # Offenlegungsschrift

(21) Aktenzeichen: **10 2014 209 635.9**
(22) Anmeldetag: **21.05.2014**
(43) Offenlegungstag: **26.11.2015**

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

(71) Anmelder:
ThyssenKrupp AG, 45143 Essen, DE;
ThyssenKrupp Industrial Solutions AG, 45143 Essen, DE

(74) Vertreter:
Kutzenberger Wolff & Partner Patentanwaltspartnerschaft mbB, 50668 Köln, DE

(72) Erfinder:
Gorval, Evgeni, Dr., 44135 Dortmund, DE;
Johanning, Joachim, Dr., 46045 Oberhausen, DE;
Keil, Bernd, Dr., 44141 Dortmund, DE;
Poschlad, Katja, Dr., 45529 Hattingen, DE;
Potthoff, Christiane, Dr., 44265 Dortmund, DE

(56) Ermittelter Stand der Technik:

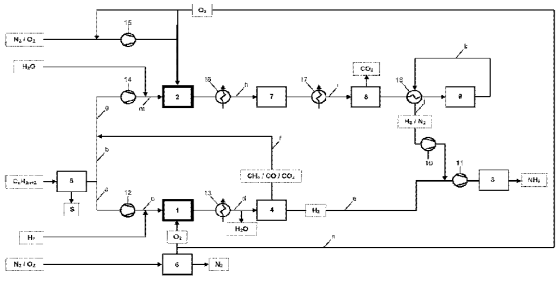
DE	**30 47 257**	**A1**
DE	**10 2008 039 014**	**A1**
US	**6 572 837**	**B1**
EP	**0 999 178**	**A1**
WO	**2012/ 173 483**	**A1**
WO	**2013/ 013 895**	**A1**

Prüfungsantrag gemäß § 44 PatG ist gestellt.

Die folgenden Angaben sind den vom Anmelder eingereichten Unterlagen entnommen

(54) Bezeichnung: **Herstellung von Synthesegas mit zwei autothermen Reformern**

(57) Zusammenfassung: Die Erfindung betrifft eine Vorrichtung und ein Verfahren zur Herstellung von Synthesegas mit Hilfe von zwei autothermen Reformern und die anschließende Synthese von Ammoniak aus dem Synthesegas.



Beschreibung

[0001] Die Erfindung betrifft eine Vorrichtung und ein Verfahren zur Herstellung von Synthesegas mit Hilfe von zwei autothermen Reformern und die anschließende Synthese von Ammoniak aus dem so hergestellten Synthesegas.

[0002] Die großtechnische Herstellung von Synthesegas aus Erdgas für die Ammoniaksynthese basiert heute weitgehend auf einer zweistufigen Reformierung mit einem extern beheizten Dampfreformer als primärem Reformer und einem mit komprimierter Luft als Oxidationsmittel betriebenen Sekundärreformer. Diese zweistufige Reformierung ist bei Kapazitäten von bis zu 3.300 tato Ammoniak technisch mit großer Zuverlässigkeit realisierbar und wirtschaftlich im Vergleich zu Alternativen für die Herstellung von Synthesegas unübertroffen.

[0003] Um die Kapazität einer Ammoniakanlage auf mehr als 3.300 tato Ammoniak zu steigern, können grundsätzlich die Abmessungen der Apparate und Rohrleitungen entsprechend vergrößert werden. Alternativ oder zusätzlich kann zur Kapazitätssteigerung auch der Betriebsdrucks bei der Herstellung von Synthesegas erhöht werden. Die Druckerhöhung im Reformer reduziert die Volumenströme im gesamten Prozessweg und ermöglicht damit größere Kapazitäten auch ohne Vergrößerung der Komponenten der Anlage. Außerdem sorgt ein höherer Betriebsdruck für eine Entlastung des Synthesegasverdichters, der für die anschließende Ammoniaksynthese bei deutlich höherem Druck benötigt wird. Dies hat besondere Bedeutung, weil die verfügbaren Synthesegasverdichter bei Anlagenkapazitäten von 3300 tato Ammoniak bereits begrenzende Komponenten darstellen. Die Gründe hierfür sind u.a. technisch bedingt und betreffen insbesondere die Antriebsturbine.

[0004] Vergrößerung der Komponenten der Anlage und Druckerhöhung sind jedoch zur Kapazitätssteigerung nicht immer wirtschaftlich sinnvoll.

[0005] Was die zweistufige Reformierung betrifft, so hat der Dampfreformer wegen seiner Komplexität und der großen Beanspruchung einen vergleichsweise großen Anteil an den Gesamterrichtungskosten. Im Prinzip kann ein Dampfreformer als eine Parallelschaltung einer großen Zahl einzelner Rohrreaktoren aufgefasst werden, deren individuelle Kapazität sich nicht mehr wesentlich steigern lässt. Die Kapazität eines Dampfreformers ist daher eng mit der Anzahl an Rohrreaktoren verbunden und eine Steigerung ist im Wesentlichen nur durch Vergrößerung der Anzahl an Rohrreaktoren möglich. Nahezu sämtliche, für die Realisierung eines Dampfreformers erforderliche Komponenten sind an die Anzahl der Rohrreaktoren gekoppelt. Die Errichtungskosten eines Dampfreformers sind deshalb weitgehend proportional zur Kapazität der Gesamtanlage. Eine Vergrößerung des Dampfreformers zur Steigerung der Kapazität ist wirtschaftlich nicht sinnvoll. Auch einer Anhebung des Betriebsdrucks sind bei der zweistufigen Reformierung relativ enge Grenzen gesetzt, weil die Rohre im Dampfreformer bereits ohnehin an der durch Druck und Temperatur definierten Belastungsgrenze arbeiten.

[0006] Eine Alternative zur zweistufigen Reformierung ist die rein autotherme Reformierung von Erdgas mit Hilfe kostengünstigerer autothermer Reformer (ATR). Um die hierfür erforderliche zusätzliche Sauerstoffmenge bereit zu stellen, ist dafür entweder Sauerstoff aus einer Luftzerlegungsanlage oder eine entsprechend größere Luftmenge erforderlich. Die Kosten für die Luftzerlegung oder die Bereitstellung der zusätzlichen Luftmenge sowie die Abtrennung des überschüssigen Stickstoffs sind allerdings erheblich und kompensieren bei Anlagenkapazitäten von bis zu 3.300 tato Ammoniak die Einsparungen, welche durch den Entfall des Dampfreformers erreicht werden. Vorrichtungen für die Luftzerlegung bzw. die Abtrennung des überschüssigen Stickstoffs zeigen jedoch bei Erhöhung ihrer Kapazität durch Vergrößerung der Komponenten eine ausgeprägte Degression der zusätzlichen Kosten. Bei wachsender Kapazität oberhalb von 3300 tato Ammoniak bringt damit die Vergrößerung der Komponenten von Anlagen auf Basis von rein autothermen Reformern im Vergleich zur zweistufigen Reformierung Kostenvorteile mit sich.

[0007] Weiterhin haben Anlagen auf Basis rein autothermer Reformierung prinzipiell ein erheblich größeres Potenzial zur Steigerung des Betriebsdrucks bei der Herstellung von Synthesegas. Eine Anhebung des Betriebsdrucks bei der Herstellung von Synthesegas ist aber auch bei rein autothermer Reformierung nicht beliebig möglich bzw. sinnvoll. Die Druckabhängigkeit der Gleichgewichtslage der Reformierungsreaktion führt dazu, dass der Methanumsatz mit wachsendem Druck zurückgeht und der Restgehalt an Methan im erzeugten Synthesegas steigt. In der Synthesegasaufbereitung muss dann ein zunehmender Anteil des Kreislaufstroms aus der Synthese abgezogen werden (Purge), wodurch die Anlagenwirtschaftlichkeit negativ beeinflusst wird. Weiterhin führt der durch die Druckanhebung zunehmende Partialdruck des in der Reformierung gebildeten Kohlenstoffmonoxids zu zusätzlicher Beanspruchung in den nachfolgenden Aufbereitungsschritten, insbesondere bei der Konvertierung von Kohlenstoffmonoxid. Dieser Partialdruck von Kohlenstoffmonoxid liegt bereits bei herkömmlichen Anlagen an der Grenze der technischen Realisierbarkeit. Die Verhältnisse werden noch dadurch verschärft, dass für die Reformierung eine möglichst geringe Wasserdampfzugabe, d.h. ein möglichst niedriges Wasserdampf-/Kohlenstoff-Verhältnis angestrebt wird, da hierdurch der Sauerstoffbedarf minimiert werden kann. Eine geringere Was-

serdampfmenge bedingt größere Partialdrücke der übrigen Gase im Gemisch und hat damit im Prinzip die gleichen Auswirkungen wie eine Anhebung des Gesamtdrucks, d.h. höherer Restgehalt an Methan und größerer Partialdruck von Kohlenstoffmonoxid im Produktgas.

[0008] WO 2004/083114 A2 offenbart ein Verfahren zur Herstellung von Wasserstoff, bei welchem ein Wärmetauscher-Reformer und ein autothermer Reformer parallel geschaltet sind.

[0009] EP 0 999 178 A1 betrifft ein Verfahren zur Herstellung von Synthesegas, u.a. für die anschließende Ammoniaksynthese, bei dem ein herkömmlicher Dampfreformer und ein autothermer Reformer parallel angeordnet sind. Die Produktströme aus beiden Reformern werden anschließend miteinander vereint und gemeinsam weiter aufbereitet.

[0010] US 6,444,712 B1 offenbart ein Verfahren zur Herstellung von Methanol aus Erdgas. Bevorzugt wird etwa die Hälfte des Erdgasstroms in einen Dampfreformer geleitet, um darin reformiertes Gas zu erzeugen. Das so reformierte Gas wird anschließend mit der anderen Hälfte des Erdgasstroms vermischt und in einen autothermen Reformer geleitet.

[0011] US 2013 312384 A1 betrifft ein Verfahren zur Herstellung von H_2 und CO aus Kohlenwasserstoffen und Biotreibstoff. Dabei werden aus Sicherheitsgründen bevorzugt mehrere kleinere parallele autotherme Reformer eingesetzt.

[0012] Diese herkömmlichen Verfahren zur Herstellung von Synthesegas sind nicht in jeder Hinsicht zufriedenstellend, insbesondere im Hinblick auf eine Kapazitätssteigerung.

[0013] Der Erfindung liegt die Aufgabe zugrunde, ein vorteilhaftes Verfahren und eine Vorrichtung zur Herstellung von Synthesegas für die anschließende Ammoniaksynthese bereitzustellen. Mit dem Verfahren und der Vorrichtung sollen signifikante Steigerungen der Kapazität über das Niveau von 3300 tato Ammoniak hinaus realisiert werden können, ohne die technischen und wirtschaftlichen Grenzen zu überschreiten.

[0014] Diese Aufgabe wird durch den Gegenstand der Patentansprüche gelöst.

[0015] Ein Aspekt der Erfindung betrifft ein Verfahren zur Herstellung von Synthesegas umfassend die Schritte

(a) Bereitstellen eines Gasgemischs umfassend Kohlenwasserstoffe, vorzugsweise Methan oder Erdgas; Wasserdampf; und ein Oxidationsmittel, vorzugsweise Sauerstoff oder mit Sauerstoff angereicherte Luft;

(b) Reformieren des in Schritt (a) bereitgestellten Gasgemischs in einem ersten autothermen Reformer, wodurch ein erstes Synthesegas umfassend Wasserstoff, Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan erhalten wird;

(c) Erhöhen des Gehalts an Wasserstoff des in Schritt (b) erhaltenen ersten Synthesegases durch Abtrennen eines Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan;

(d) Bereitstellen eines Gasgemischs umfassend das in Schritt (c) abgetrennte Gasgemisch;

(e) Reformieren des in Schritt (d) bereitgestellten Gasgemischs in einem zweiten autothermen Reformer, wodurch ein zweites Synthesegas umfassend Wasserstoff, Kohlenstoffmonoxid und Kohlenstoffdioxid erhalten wird;

wobei der erste autotherme Reformer in Schritt (b) bei einem Druck betrieben wird, der höher ist als der Druck, bei dem der zweite autotherme Reformer in Schritt (e) betrieben wird.

[0016] Das erfindungsgemäße Verfahren basiert auf der Reformierung in zwei autothermen Reformern bei verschiedenem Druck. Die erste autotherme Reformierung wird bei einem so hohen Druck betrieben, dass das gebildete wasserstoffreiche erste Synthesegas nach Abtrennung von CO, CO_2 sowie ggf. Resten an nicht umgesetztem CH_4 direkt vor die zweite Stufe des Synthesegasverdichters geleitet werden kann, welcher dem Ammoniakreaktor vorgeschaltet ist. Dieser Synthesegasverdichter ist bevorzugt mehrstufig, wobei eine erste Verdichterstufe das Gasgemisch bevorzugt auf einen ersten Druck im Bereich von 50 bis 150 bar, bevorzugter 60 bis 140 bar verdichtet, und wobei eine nachgeschaltete zweite Verdichterstufe das (vorverdichtete) Gasgemisch auf einen zweiten Druck im Bereich von bevorzugt mindestens 150 bar, bevorzugter mindestens 170 bar verdichtet, wie er für die anschließende Ammoniaksynthese benötigt wird. Die Abtrennung von CO, CO_2 und ggf. CH_4 erfolgt dabei bevorzugt durch Druckwechsel-Adsorption (PSA, Pressure Swing Absorption) oder mit Hilfe von Membranen. Das abgetrennte Gasgemisch wird ggf. (bevorzugt) verdichtet und einer zweiten autothermen Reformierung zugeführt und hier mit Luft, ggf. mäßig mit Sauerstoff angereicherter Luft, zu einem zweiten Synthesegas reformiert. Die anschließende Reinigung dieses zweiten Synthesegases aus dem zweiten autothermen Reformer erfolgt dann bevorzugt durch (i) ein- oder zweistufige Konvertierung von CO, (ii) Abtrennung von CO_2 und/oder (iii) abschließende Reinigung, beispielsweise durch Methanisierung, Druckwechsel-Adsorption oder Stickstoffwäsche. Das erste Synthesegas und das zweite Synthesegas werden anschließend ggf. nach getrennter (Vor-)Verdichtung vereint, ggf. mit der zur Erreichung der gewünschten Stöchiometrie noch erforderlichen Menge an Stick-

stoff angereichert und der Ammoniaksynthese in einem Ammoniakreaktor zugeführt. Dabei wird das erste Synthesegas bevorzugt lediglich in der zweiten Verdichterstufe des Synthesegasverdichters verdichtet, das zweite Synthesegas hingegen bevorzugt sowohl in der ersten Verdichterstufe, als auch – nach Vereinigung mit dem ersten Synthesegas – in der zweiten Verdichterstufe.

[0017] Das erfindungsgemäße Verfahren bedingt zusätzliche und/oder andere Apparate im Vergleich mit einer herkömmlichen einsträngigen Prozessführung mit nur einem einzelnen autothermen Reformer. So werden für das erfindungsgemäße Verfahren insbesondere ein zweiter autothermer Reformer (bevorzugt mitsamt Abkühlstrecke) für das Synthesegas, eine Vorrichtung zur Abtrennung der übrigen Bestandteile des Synthesegases (bevorzugt durch Druckwechsel-Adsorption) sowie ein zusätzlicher Verdichter benötigt. Dafür ermöglicht das erfindungsgemäße Verfahren jedoch, den ersten autothermen Reformer mit einem sehr kleinen Wasserdampf/Kohlenstoff-Verhältnis zu betreiben und damit den Sauerstoffbedarf, also auch die Baugröße der kostenintensiven Luftzerlegung zu minimieren. Auch die Baugrößen der Vorrichtungen zur anschließenden Reinigung des Synthesegases aus dem zweiten autothermen Reformer werden durch die im Vergleich zu der herkömmlichen einsträngigen Prozessführung kleineren Volumenströme signifikant reduziert. Insgesamt ergeben sich deshalb für das erfindungsgemäße Verfahren Kostenvorteile gegenüber einer herkömmlichen einsträngigen Anlage gleicher Kapazität, welche nach dem derzeitigen Stand der Technik einsträngig nicht realisiert werden könnten.

[0018] Autotherme Reformer haben im Vergleich zu herkömmlichen Dampfreformern einen erhöhten Sauerstoffbedarf. Es wurde überraschend gefunden, dass der Sauerstoffbedarf zur Herstellung von Synthesegas umso kleiner wird, je weniger Wasserdampf zugegeben wird, d.h. je geringer das Wasserdampf/-Kohlenstoff-Verhältnis ist. Es wurde in diesem Zusammenhang allerdings auch überraschend gefunden, dass der Restgehalt an Methan im Synthesegas nach der Reformierung im autothermen Reformer bei geringerer Wasserdampfzugabe und bei erhöhtem Druck auf für den Gesamtprozess nicht mehr akzeptable Werte zunimmt.

[0019] Bei einer rein einsträngigen Herstellung von Synthesegas auf Basis eines einzelnen autothermen Reformers müsste daher zur Steigerung der Kapazität bei Erhöhung des Drucks die Wasserdampfzugabe ebenfalls entsprechend gesteigert werden, um den Restgehalt an Methan nach der Reformierung auf dem Niveau der konventionellen Anlage zu halten und den Synthesegasverdichter zu entlasten. Mit der Steigerung der Wasserdampfzugabe wächst aber auch wieder der Bedarf an teurem Sauerstoff, so dass eine Reduzierung des Sauerstoffbedarfs und entsprechend der Betriebs- und Investitionskosten bei rein einsträngiger Herstellung von Synthesegas auf Basis eines einzelnen autothermen Reformers nicht realisierbar wäre. Wegen des hohen Anteils der Luftzerlegung an den Gesamtkosten einer Ammoniakanlage auf Basis von autothermer Reformierung hat dies signifikante Auswirkungen auf die Wirtschaftlichkeit, d.h. auf die Kostenrelationen im Vergleich zu konventionellen Anlagen. Letztlich ergibt sich damit eine größere Grenzkapazität, ab der eine Ammoniakanlage auf Basis von autothermer Reformierung Kostenvorteile gegenüber einer konventionellen Anlage aufweist.

[0020] Es wurde überraschend gefunden, dass alle Vorteile der autothermen Reformierung genutzt werden können, wenn die Reformierung in zwei Schritten auf unterschiedlichen Druckniveaus durchgeführt wird. Der erste Schritt nutzt dabei bevorzugt sowohl den Vorteil einer geringen Wasserdampfmenge im Prozessgas zur Minimierung der benötigten Sauerstoffmenge als auch den eines erhöhten Drucks zur Entlastung des Synthesegasverdichters.

[0021] Ein autothermer Reformer im Sinne der Erfindung ist ein Reformer, bei dem die bei der Reformierung durch exotherme Reaktionen hergestellte Wärme für endotherme Reaktionen genutzt wird, so dass der Reformierprozess autotherm erfolgt. Dabei weist der autotherme Reformer vorzugsweise einen Katalysator und einen Brenner auf. Reaktoren zur autothermen partiellen katalytischen Oxidation an Edelmetallkatalysatoren, welche keinen Brenner aufweisen, sind bevorzugt keine autothermen Reformer im Sinne der Erfindung.

[0022] Bei dem erfindungsgemäßen Verfahren wird bevorzugt

- der erste autotherme Reformer in Schritt (b) bei einem Druck betrieben, der mindestens um 5 bar, bevorzugter mindestens um 10 bar, noch bevorzugter mindestens um 15 bar, am bevorzugtesten mindestens um 20 bar und insbesondere mindestens um 25 bar höher ist als der Druck, bei dem der zweite autotherme Reformer in Schritt (e) betrieben wird; und/oder
- der erste autotherme Reformer in Schritt (b) bei einem Druck von mindestens 30 bar betrieben, bevorzugt mindestens 35 bar oder mindestens 40 bar, bevorzugter mindestens 45 bar oder mindestens 50 bar, noch bevorzugter mindestens 55 bar oder mindestens 60 bar, am bevorzugtesten mindestens 65 bar oder mindestens 70 bar, und insbesondere mindestens 75 bar oder mindestens 80 bar; und/oder
- der zweite autotherme Reformer in Schritt (e) bei einem Druck von höchstens 60 bar betrieben, bevorzugt höchstens 55 bar oder höchstens 50 bar, bevorzugter höchstens 45 bar oder höchstens

40 bar, noch bevorzugter höchstens 38 bar oder höchstens 36 bar, am bevorzugtesten höchstens 34 bar oder höchstens 32 bar, und insbesondere höchstens 30 bar, höchstens 28 bar, höchstens 26 bar, höchstens 24 bar, höchstens 22 bar oder höchstens 20 bar.

[0023] Bevorzugt wird der erste autotherme Reformer in Schritt (b) bei einem Druck betrieben, der um 20 bis 45 bar höher ist als der Druck, bei dem der zweite autotherme Reformer in Schritt (e) betrieben wird. Dabei wird der erste autotherme Reformer in Schritt (b) vorzugsweise bei solch einem hohen Druck betrieben, dass nach Abzug aller weiteren Druckverluste stromabwärts des ersten autothermen Reformers das erhaltene Gasgemisch sicher nach der ersten Stufe eines mehrstufigen Synthesegasverdichters der anschließenden Ammoniaksynthese zugeführt werden kann, wobei das Verdichtungsverhältnis bevorzugt beispielsweise 2,5 beträgt.

[0024] Der Druck, bei dem der erste autotherme Reformer betrieben wird, liegt bevorzugt im Bereich von 30 bis 80 bar. Ein Druck unterhalb von 30 bar ist nicht bevorzugt, da sich dies ungünstig auf die Dimensionierung des dem zweiten autothermen Reformer vorgeschalteten Verdichters auswirken würde. Ein Druck oberhalb von 80 bar ist nicht bevorzugt, da sich dies ungünstig auf die Gleichgewichtslage der im ersten autothermen Reformer stattfindenden Reaktion (Dampfreformierung) auswirken würde.

[0025] Der Druck, bei dem der zweite autotherme Reformer betrieben wird, liegt bevorzugt im Bereich von 30 bis 60 bar. Ein Druck unterhalb von 30 bar ist grundsätzlich möglich, wirkt sich allerdings ungünstig auf die Dimensionierung des zweiten autothermen Reformers aus. Ein Druck oberhalb von 60 bar ist nicht bevorzugt, da dann bei gegebenem Verdichtungsverhältnis der erste autotherme Reformer bei so hohen Drücken betrieben werden müsste, bei denen die Gleichgewichtslage der im ersten autothermen Reformer stattfindenden Reaktion (Dampfreformierung) auf der Seite der Edukte läge.

[0026] In Schritt (a) des erfindungsgemäßen Verfahrens

- wird bevorzugt das Oxidationsmittel in Form von reinem Sauerstoff oder in Form von mit Sauerstoff angereicherter Luft mit einem Gehalt an Sauerstoff von mindestens 90 Vol.-%, bevorzugter mindestens 92 Vol.-%, noch bevorzugter mindestens 94 Vol.-%, am bevorzugtesten mindestens 96 Vol.-% und insbesondere mindestens 98 Vol.-% bereitgestellt, wobei der benötigte Sauerstoff vorzugsweise aus einer Luftzerlegungsanlage stammt; und/oder
- werden bevorzugt dem Gasgemisch die Kohlenwasserstoffe in Form von Methan oder Erdgas zugesetzt, wobei das Erdgas ggf. bevorzugt zuvor entschwefelt wurde; und/oder
- weist bevorzugt das bereitgestellte Gasgemisch ein molares Wasserdampf/Kohlenstoff-Verhältnis von höchstens 3,6, höchstens 3,4 oder höchstens 3,2 auf, bevorzugt höchstens 3,0, höchstens 2,8 oder höchstens 2,6; bevorzugter höchstens 2,4, höchstens 2,2 oder höchstens 2,0; noch bevorzugter höchstens 1,8, unter Umständen ggf. auch höchstens 1,6, höchstens 1,4, höchstens 1,2, höchstens 1,0, höchstens 0,8, höchstens 0,6, höchstens 0,4 oder höchstens 0,2; und/oder
- weist bevorzugt das bereitgestellte Gasgemisch einen Gehalt an Stickstoff von höchstens 10 Vol.-% auf, bevorzugter höchstens 8 Vol.-%, noch bevorzugter höchstens 6 Vol.-%, am bevorzugtesten höchstens 4 Vol.-%, und insbesondere höchstens 2 Vol.-%.

[0027] Das molare Wasserdampf/Kohlenstoff-Verhältnis im Sinne der Erfindung ist das Stoffmengenverhältnis von Molekülen Wasserdampf zu Atomen Kohlenstoff im Gasgemisch, wobei allerdings nur diejenigen Kohlenstoffatome von Verbindungen eingerechnet werden, welche reine Kohlenwasserstoffe, d.h. frei von Sauerstoff sind. Kohlenstoffatome von Alkoholen, Aldehyden, etc. werden entsprechend nicht eingerechnet.

[0028] Ein molares Wasserdampf/Kohlenstoff-Verhältnis von größer 3,2 ist zwar technisch möglich, jedoch nicht bevorzugt, da es dazu führen würde, dass mehr Sauerstoff verbraucht werden würde als notwendig ist und die Ausbeute an Wasserstoff sinken würde. Erfindungsgemäß stellt ein molares Wasserdampf/Kohlenstoff-Verhältnis von 3,2 daher bevorzugt die ökonomische Obergrenze dar. Ein molares Wasserdampf/Kohlenstoff-Verhältnis von kleiner 0,3 ist nicht bevorzugt, da sonst Ruß entstehen würde, der den Katalysator deaktivieren würde.

[0029] Bevorzugt weist das in Schritt (b) des erfindungsgemäßen Verfahrens erhaltene erste Synthesegas

- ein molares Wasserstoff/Kohlenstoffmonoxid-Verhältnis von höchstens 4,5 auf, bevorzugt höchstens 4,2, höchstens 3,9 oder höchstens 3,6; bevorzugter höchstens 3,3, höchstens 3,0 oder höchstens 2,7; noch bevorzugter höchstens 2,4, höchstens 2,1 oder höchstens 1,8; am bevorzugtesten höchstens 1,5, höchstens 1,2 oder höchstens 1,0; und insbesondere höchstens 0,8, höchstens 0,6 oder höchstens 0,4; und/oder
- einen Gehalt an Methan von mindestens 0,3 Vol.-% auf, bevorzugt mindestens 0,6 Vol.-%, mindestens 0,9 Vol.-% oder mindestens 1,2 Vol.-%; bevorzugter mindestens 1,5 Vol.-%, mindestens 1,8 Vol.-% oder mindestens 2,1 Vol.-%; noch bevorzugter mindestens 2,4 Vol.-%, mindestens 2,7 Vol.-% oder mindestens 3,0 Vol.-%; am bevor-

zugtesten mindestens 3,3 Vol.-%, mindestens 3, 6 Vol.-% oder mindestens 3,9 Vol.-%; und insbesondere mindestens 4,2 Vol.-%, mindestens 4,5 Vol.-% oder mindestens 4,8 Vol.-%; und/oder
– einen Gehalt an Wasserstoff von mindestens 30 Vol.-% auf, bevorzugt mindestens 32 Vol.-%, mindestens 34 Vol.-% oder mindestens 36 Vol.-%; bevorzugter mindestens 38 Vol.-%, mindestens 40 Vol.-% oder mindestens 42 Vol.-%; noch bevorzugter mindestens 44 Vol.-%, mindestens 46 Vol.-% oder mindestens 48 Vol.-%; am bevorzugtesten mindestens 50 Vol.-%, mindestens 52 Vol.-% oder mindestens 54 Vol.-%; und insbesondere mindestens 56 Vol.-%, mindestens 58 Vol.-% oder mindestens 60 Vol.-%; und/oder
– einen Gehalt an Kohlenstoffmonoxid im Bereich von 20 ± 19 Vol.-% auf, bevorzugter 20 ± 16 Vol.-%, noch bevorzugter 20 ± 13 Vol.-%, am bevorzugtesten 20 ± 9 Vol.-%, und insbesondere 20 ± 5 Vol.-%; und/oder
– einen Gehalt an Kohlenstoffdioxid im Bereich von 12 ± 11 Vol.-% auf, bevorzugter 12 ± 10 Vol.-%, noch bevorzugter 12 ± 8 Vol.-%, am bevorzugtesten 12 ± 6 Vol.-%, und insbesondere 12 ± 4 Vol.-%; und/oder
– einen Gehalt an Stickstoff von höchstens 10 Vol.-% auf, bevorzugter höchstens 8 Vol.-%, noch bevorzugter höchstens 6 Vol.-%, am bevorzugtesten höchstens 4 Vol.-%, und insbesondere höchstens 2 Vol.-%; und/oder
– einen Gehalt an Wasserdampf von 30 ± 29 Vol.-% auf, bevorzugter 30 ± 25 Vol.-%, noch bevorzugter 30 ± 20 Vol.-%, am bevorzugtesten 30 ± 15 Vol.-%, und insbesondere 30 ± 10 Vol.-%;

wobei die Gehaltsangaben jeweils Feuchtkonzentrationen sind.

[0030] Sofern nicht ausdrücklich anderweitig darauf hingewiesen wird, sind alle Prozentangaben in Bezug auf Gasgemische, welche Wasserdampf enthalten, als Feuchtkonzentrationen aufzufassen.

[0031] Trocken gerechnet weist das in Schritt (b) des erfindungsgemäßen Verfahrens erhaltene erste Synthesegas bevorzugt
– einen Gehalt an Wasserstoff im Bereich von 38 bis 69 Vol.-% auf; und/oder
– einen Gehalt an Kohlenstoffmonoxid im Bereich von 7 bis 31 Vol.-% auf; und/oder
– einen Gehalt an Kohlenstoffdioxid im Bereich von 3 bis 19 Vol.-% auf.

[0032] Der Gehalt an Methan im ersten Synthesegas kann grundsätzlich auch mehr als 4,8 Vol.-% betragen, insbesondere wenn ein niedriges molares Wasserdampf/Kohlenstoff-Verhältnis eingestellt wird und dem ersten autothermen Reformer eine vergleichsweise geringe Menge an Sauerstoff zugeführt wird, so dass die Temperatur in der POX-Zone des Reaktors vergleichsweise niedrig ist. Gehalte an Methan von mehr als 4,8 Vol.-% sind jedoch nicht bevorzugt, da diese in Schritt (c) des erfindungsgemäßen Verfahrens abgetrennt werden müssen, so dass anschließend eine größere Gasmenge auf den Druck des zweiten autothermen Reformers rückverdichtet werden muss. Hierdurch steigen die Betriebskosten an.

[0033] Geeignete Maßnahmen, den relativen Gehalt der einzelnen Gaskomponenten im autotherm hergestellten ersten und zweiten Synthesegas einzustellen, sind dem Fachmann bekannt, insbesondere Sauerstoffmenge, Dampfmenge, Kohlenwasserstoffmenge, Temperatur und Druck. Der Einfluss dieser Parameter auf die Zusammensetzung des Synthesegases kann ggf. durch geeignete Routineversuche verifiziert werden.

[0034] Das im ersten autothermen Reformer hergestellte erste Synthesegas ist wegen seines vergleichsweise hohen CO-Partialdrucks und des vergleichsweise niedrigen Gehalts an Wasserdampf schlecht oder sogar ungeeignet für eine anschließende CO-Konvertierung. Mit Hilfe einer Druckwechsel-Adsorption (PSA) kann aber der Wasserstoff auf hohem Druckniveau abgetrennt und direkt dem Synthesegasverdichter zugeführt werden. Der Druck bei der ersten autothermen Reformierung wird daher bevorzugt so gewählt werden, dass der Wasserstoff direkt dem Synthesegasverdichter, vorzugsweise der zweiten Stufe eines mehrstufigen Synthesegasverdichters zugeführt werden kann.

[0035] Bevorzugt erfolgt in Schritt (c) des erfindungsgemäßen Verfahrens das Abtrennen des Gasgemischs umfassend CO, CO_2 und CH_4 vom ersten Synthesegas (i) durch Druckwechsel-Adsorption (PSA – Pressure Swing Adsorption) oder (ii) durch selektive Membran-Permeation und anschließende Druckwechsel-Adsorption.

[0036] Bei der Druckwechsel-Adsorption wird das Gasgemisch umfassend H_2, CO, CO_2 und CH_4 unter Druck mittels Adsorption physikalisch voneinander getrennt. Vorzugsweise werden poröse Materialien (z.B. Zeolithe, Aktivkohle) als Adsorbens eingesetzt. Die Trennwirkung kann erfindungsgemäß auf zwei verschiedenen Prinzipien beruhen: Gleichgewichtsadsorption oder Molekularsiebwirkung. Das Gasgemisch wird bevorzugt unter erhöhtem Druck in einen Festbettreaktor eingeleitet, welcher mit dem Adsorbens gefüllt ist, so dass dieses durchströmt wird. CO, CO_2 und CH_4 aus dem Gasgemisch werden nun adsorbiert und am Ausgang des Betts kann H_2 entnommen werden. Nach einer Weile ist das Adsorberbett gesättigt und der Prozess wird über Ventile umgeschaltet, so dass der Ausgang für H_2 geschlossen und ein Auslass für CO, CO_2 und CH_4 geöffnet wird. Dies ist begleitet von einer Druckabsenkung.

Bei dem niedrigeren Druck werden nun das adsorbierte CO, CO_2 und CH_4 wieder desorbiert und können am Auslass gewonnen werden. Zwei oder mehr wechselseitig be- und entladene Adsorber ermöglichen dabei bevorzugt einen kontinuierlichen Betrieb.

[0037] In einer bevorzugten Variante des erfindungsgemäßen Verfahrens wird in Schritt (c) das erste Synthesegas zunächst einer Membran-Trennanlage zum Abtrennen von Kohlenstoffmonoxid und Kohlenstoffdioxid durch selektive Membran-Permeation zugeführt. Die Membran hat die Eigenschaft, dass sie Kohlenstoffmonoxid und Kohlenstoffdioxid wesentlich schneller durchlässt als Wasserstoff. Die Triebkraft für diesen Trennprozess ist der Unterschied der Partialdrücke der abzutrennenden Komponente auf der Hoch- und Niederdruckseite der Membran. Hierbei wird der Druck auf der Niederdruckseite der Membran so eingestellt, dass er nur wenig höher als der Druck der Kohlenwasserstoffe (Erdgas) an der Anlagengrenze ist. In der Membran-Trennanlage wird das erste Synthesegas in einen an Wasserstoff und Methan angereicherten Retentatstrom und einen an Kohlenstoffmonoxid und Kohlenstoffdioxid angereicherten Permeatstrom getrennt. Der Retentatstrom wird erst dann dem Abtrennen von Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan gemäß Schritt (c) zugeführt, wobei das Abtrennen von Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan dann vorzugsweise ebenfalls durch Druckwechsel-Adsorption erfolgt. Das anfallende Abgas enthält überwiegend Methan, vorher nicht abgeschiedenes Kohlenstoffmonoxid und Kohlenstoffdioxid sowie in geringen Mengen auch Wasserstoff. Es kann als Brenngas weiter verwendet werden, z.B. in einem Hilfskessel zur Dampferzeugung.

[0038] Nach dem Abtrennen des Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan in Schritt (c) hat das erste Synthesegas bevorzugt

- einen Gehalt an Wasserstoff von mindestens 90 Vol.-%, bevorzugter mindestens 92 Vol.-%, noch bevorzugter mindestens 94 Vol.-%, am bevorzugtesten mindestens 96 Vol.-%, und insbesondere mindestens 98 Vol.-%; und/oder
- einen Gehalt an Stickstoff von höchstens 10 Vol.-% auf, bevorzugter höchstens 8 Vol.-%, noch bevorzugter höchstens 6 Vol.-%, am bevorzugtesten höchstens 4 Vol.-%, und insbesondere höchstens 2 Vol.-%.

[0039] Der Hauptteil des Wasserstoffs ist nach der Abtrennung des Gasgemisches im ersten Synthesegas enthalten. Das abgetrennte Gasgemisch umfasst seinerseits zum größten Teil in der Reformierung gebildetes CO, nicht umgesetztes CH_4 und weitere, vergleichsweise kleine Anteile an CO_2 sowie H_2. Es wurde überraschend gefunden, dass die weitere Umsetzung dieses Stroms am vorteilhaftesten in einem zweiten autothermen Reformierungsschritt erfolgt, um sowohl das restliche Methan umzusetzen als auch Probleme mit der CO-Konvertierung durch den großen Partialdruck des Kohlenstoffmonoxids zu vermeiden. Ggf. nach Zugabe von weiteren Kohlenwasserstoffen, vorzugsweise von Methan oder Erdgas, wird das abgetrennte Gasgemisch, welches vorzugsweise der Druckwechsel-Adsorption entstammt, einem zweiten autothermen Reformer zugeführt und hier mit komprimierter Luft, ggf. auch mäßig mit Sauerstoff angereicherter Luft als Oxidationsmedium ebenfalls autotherm reformiert. Auf Grund des niedrigeren Drucks in dieser Reformierung und einer spezifisch größeren Wasserdampfzugabe zum Prozessgas ergibt sich in diesem zweiten autothermen Reformer ein Restgehalt an Methan, welcher mit dem einer konventionellen Anlage vergleichbar ist.

[0040] Das erfindungsgemäße Verfahren nutzt so die Vorteile eines höheren Druckniveaus in der ersten autothermen Reformierung, vermeidet aber einen größeren Methaneintrag in die bevorzugt im Anschluss erfolgende Ammoniaksynthese sowie eine größere Beanspruchung der nachfolgenden Prozessstufen für die Reinigung des Synthesegases und ermöglicht auch eine signifikante Entlastung des Synthesegasverdichters.

[0041] In Schritt (d) des erfindungsgemäßen Verfahrens

- wird bevorzugt dem Gasgemisch Luft oder mit durch Sauerstoff angereicherte Luft mit einem Gehalt an Sauerstoff von höchstens 90 Vol.-%, bevorzugter höchstens 80 Vol.-%, noch bevorzugter 70 Vol.-%, am bevorzugtesten höchstens 60 Vol.-% und insbesondere höchstens 50 Vol.-% zugesetzt; und/oder
- werden bevorzugt dem Gasgemisch Kohlenwasserstoffe in Form von Methan oder Erdgas zugesetzt, wobei das Erdgas ggf. bevorzugt zuvor entschwefelt wurde; und/oder
- weist bevorzugt das bereitgestellte Gasgemisch ein molares Wasserdampf/Kohlenstoff-Verhältnis von mindestens 3,2 auf, bevorzugt mindestens 3,4, mindestens 3,6 oder mindestens 3,8; bevorzugter mindestens 4,0, mindestens 4,2 oder mindestens 4,4; noch bevorzugter mindestens 4,6, mindestens 4,8 oder mindestens 5,0; am bevorzugtesten mindestens 5,2, mindestens 5,4 oder mindestens 5,6; und insbesondere mindestens 5,8, mindestens 6,0 oder mindestens 6,2; und/oder
- weist bevorzugt das bereitgestellte Gasgemisch einen Gehalt an Stickstoff von höchstens 70 Vol.-% auf, bevorzugter höchstens 60 Vol.-%, noch bevorzugter höchstens 50 Vol.-%, am bevorzugtesten höchstens 40 Vol.-%, und insbesondere höchstens 30 Vol.-%; und/oder
- weist bevorzugt das bereitgestellte Gasgemisch einen Gehalt an Stickstoff von mindestens 10 Vol.-

% auf, bevorzugter mindestens 20 Vol.-%, noch bevorzugter mindestens 30 Vol.-%, am bevorzugtesten mindestens 40 Vol.-%, und insbesondere mindestens 50 Vol.-%.

[0042] Nach der Umsetzung im zweiten autothermen Reformer erfolgt erfindungsgemäß bevorzugt eine Hochtemperaturkonvertierung von Kohlenstoffmonoxid mit Wasserdampf zu Kohlenstoffdioxid und Wasserstoff. Daher wird der zweite autotherme Reformer vorzugsweise so betrieben, dass nach der Dampfreformierung immer noch genügend Wasserdampf im zweiten Synthesegas enthalten ist, damit die Hochtemperaturkonvertierung von Kohlenstoffmonoxid effizient erfolgen werden kann.

[0043] Das molare Wasserdampf/Kohlenstoff-Verhältnis bei der autothermen Reformierung im zweiten autothermen Reformer in Schritt (e) des erfindungsgemäßen Verfahrens ist bevorzugt größer als das molare Wasserdampf/Kohlenstoff-Verhältnis bei der autothermen Reformierung im ersten autothermen Reformer in Schritt (b). Vorzugsweise beträgt die relative Differenz des molaren Wasserdampf/-Kohlenstoff-Verhältnis in Schritt (e) zum molaren Wasserdampf/Kohlenstoff-Verhältnis in Schritt (b) mindestens 0,1 oder mindestens 0,2, bevorzugter mindestens 0,3 oder mindestens 0,4, noch bevorzugter mindestens 0,5 oder mindestens 0,6, am bevorzugtesten mindestens 0,7 oder mindestens 0,8 und insbesondere mindestens 0,9 oder mindestens 1,0.

[0044] Bevorzugt weist das in Schritt (e) des erfindungsgemäßen Verfahrens erhaltene zweite Synthesegas

- ein molares Wasserstoff/Kohlenstoffmonoxid-Verhältnis von höchstens 4,5 auf, bevorzugt höchstens 4,2, höchstens 3,9 oder höchstens 3,6; bevorzugter höchstens 3,3, höchstens 3,0 oder höchstens 2,7; noch bevorzugter höchstens 2,4, höchstens 2,1 oder höchstens 1,8; unter Umständen ggf. auch höchstens 1,5, höchstens 1,2, höchstens 1,0, höchstens 0,8, höchstens 0,6 oder höchstens 0,4; und/oder
- einen Gehalt an Methan von höchstens 10 Vol.-%, höchstens 7,5 Vol.-%, höchstens 5,0 Vol.-% oder höchstens 4,8 Vol.-% auf, bevorzugt höchstens 4,5 Vol.-%, höchstens 4,2 Vol.-% oder höchstens 3,9 Vol.-%; bevorzugter höchstens 3,6 Vol.-%, höchstens 3,3 Vol.-% oder höchstens 3,0 Vol.-%; noch bevorzugter höchstens 2,7 Vol.-%, höchstens 2,4 Vol.-% oder höchstens 2,1 Vol.-%; am bevorzugtesten höchstens 1,8 Vol.-%, höchstens 1,5 Vol.-% oder höchstens 1,2 Vol.-%; und insbesondere höchstens 0,9 Vol.-%, höchstens 0,6 Vol.-% oder höchstens 0,3 Vol.-%; und/oder
- einen Gehalt an Wasserstoff von mindestens 50 Vol.-% auf, bevorzugt mindestens 52 Vol.-%, mindestens 54 Vol.-% oder mindestens 56 Vol.-%; bevorzugter mindestens 58 Vol.-%, mindestens 60 Vol.-% oder mindestens 62 Vol.-%; noch bevorzugter mindestens 64 Vol.-%, mindestens 66 Vol.-% oder mindestens 68 Vol.-%; am bevorzugtesten mindestens 70 Vol.-%, mindestens 72 Vol.-% oder mindestens 74 Vol.-%; und insbesondere mindestens 76 Vol.-%, mindestens 78 Vol.-% oder mindestens 80 Vol.-%; und/oder
- einen Gehalt an Kohlenstoffmonoxid im Bereich von 20 ± 19 Vol.-% auf, bevorzugter 20 ± 16 Vol.-%, noch bevorzugter 20 ± 13 Vol.-%, am bevorzugtesten 20 ± 9 Vol.-%, und insbesondere 20 ± 5 Vol.-%; und/oder
- einen Gehalt an Kohlenstoffdioxid im Bereich von 12 ± 11 Vol.-% auf, bevorzugter 12 ± 10 Vol.-%, noch bevorzugter 12 ± 8 Vol.-%, am bevorzugtesten 12 ± 6 Vol.-%, und insbesondere 12 ± 4 Vol.-%; und/oder
- einen Gehalt an Stickstoff von höchstens 10 Vol.-% auf, bevorzugter höchstens 8 Vol.-%, noch bevorzugter höchstens 6 Vol.-%, am bevorzugtesten höchstens 4 Vol.-%, und insbesondere höchstens 2 Vol.-%; und/oder
- einen Gehalt an Wasserdampf von 40 ± 30 Vol.-% auf, bevorzugter 40 ± 25 Vol.-%, noch bevorzugter 40 ± 20 Vol.-%, am bevorzugtesten 40 ± 15 Vol.-%, und insbesondere 40 ± 10 Vol.-%;

wobei die Gehaltsangaben jeweils Feuchtkonzentrationen sind.

[0045] Trocken gerechnet weist das in Schritt (e) des erfindungsgemäßen Verfahrens erhaltene zweite Synthesegas bevorzugt

- einen Gehalt an Wasserstoff im Bereich von 38 bis 69 Vol.-% auf; und/oder
- einen Gehalt an Kohlenstoffmonoxid im Bereich von 7 bis 31 Vol.-% auf; und/oder
- einen Gehalt an Kohlenstoffdioxid im Bereich von 3 bis 19 Vol.-% auf.

[0046] Insbesondere wenn die nachfolgende Aufreinigung des zweiten Synthesegases nicht durch CO_2-Wäsche und Methanisierung, sondern durch Druckwechsel-Adsorption oder N_2-Wäsche erfolgt, kann dadurch das restliche Methan von dem zweiten Synthesegas mit abgetrennt werden. Das abgetrennte Methan kann dann zusammen mit dem ebenfalls abgetrennten Kohlenstoffmonoxid, Kohlenstoffdioxid und überschüssigem Stickstoff als Fuel Gas verwendet werden. Bei dieser Variante des erfindungsgemäßen Verfahrens ist es durchaus tolerabel, wenn der Gehalt an Methan im zweiten Synthesegas mehr als 5 Vol.-% beträgt. Erfolgt die nachfolgende Aufreinigung des zweiten Synthesegases hingegen durch CO_2-Wäsche und Methanisierung, so liegt der Gehalt an Methan im zweiten Synthesegas bevorzugt unterhalb von 5 Vol.-%.

[0047] Ein vergleichsweise hoher Gehalt an Wasserdampf im zweiten Synthesegas ist bevorzugt, damit

für die bevorzugt im Anschluss erfolgende Hochtemperaturkonvertierung von Kohlenstoffmonoxid genügend Wasserdampf zur Verfügung steht. Ein Gehalt an Wasserdampf vor der Hochtemperaturkonvertierung von z.B. 35 bis 40 Vol.-% ist bevorzugt. Ein Gehalt an Wasserdampf von mehr als 40 Vol.-% ebenfalls kann durchaus relevant sein, ist allerdings nicht bevorzugt. Für ein entsprechend hohes relatives molares Wasserdampf-/Kohlenstoff-Verhältnis am Eintritt des zweiten autothermen Reformers und damit einen hohen Gehalt an Wasserdampf im zweiten Synthesegas am Austritt des zweiten autothermen Reformers wäre nämlich mehr Sauerstoff erforderlich, was sich ungünstig auf die Ausbeute an Wasserstoff auswirken würde.

[0048] Der Restgehalt an Methan im ersten Synthesegas, welches bei der autothermen Reformierung im ersten autothermen Reformer in Schritt (b) erhalten wird, ist bevorzugt größer als der Restgehalt an Methan im zweiten Synthesegas, welches bei der autothermen Reformierung im zweiten autothermen Reformer in Schritt (e) erhalten wird. Vorzugsweise beträgt die relative Differenz des Restgehalts an Methan des in Schritt (b) erhaltenen ersten Synthesegases und des Restgehalts an Methan des in Schritt (e) erhaltenen zweiten Synthesegases mindestens 0,4 Vol.-% oder mindestens 0,8 Vol.-%, bevorzugter mindestens 1,2 Vol.-% oder mindestens 1,6 Vol.-%, noch bevorzugter mindestens 2,0 Vol.-% oder mindestens 2,4 Vol.-%, am bevorzugtesten mindestens 2,8 Vol.-% oder mindestens 3,2 Vol.-% und insbesondere mindestens 3,6 Vol.-% oder mindestens 4,0 Vol.-%.

[0049] Der Gehalt an Kohlenstoffmonoxid im ersten Synthesegas, welches bei der autothermen Reformierung im ersten autothermen Reformer in Schritt (b) erhalten wird, ist bevorzugt größer als der Gehalt an Kohlenstoffmonoxid im zweiten Synthesegas, welches bei der autothermen Reformierung im zweiten autothermen Reformer in Schritt (e) erhalten wird. Vorzugsweise beträgt die relative Differenz des Gehalts an Kohlenstoffmonoxid des in Schritt (b) erhaltenen ersten Synthesegases und des Gehalts an Kohlenstoffmonoxid des in Schritt (e) erhaltenen zweiten Synthesegases mindestens 0,4 Vol.-% oder mindestens 0,8 Vol.-%, bevorzugter mindestens 1,2 Vol.-% oder mindestens 1,6 Vol.-%, noch bevorzugter mindestens 2,0 Vol.-% oder mindestens 2,4 Vol.-%, am bevorzugtesten mindestens 2,8 Vol.-% oder mindestens 3,2 Vol.-% und insbesondere mindestens 3,6 Vol.-% oder mindestens 4,0 Vol.-%.

[0050] Der Gehalt an Wasserdampf im ersten Synthesegas, welches bei der autothermen Reformierung im ersten autothermen Reformer in Schritt (b) erhalten wird, ist bevorzugt kleiner als der Gehalt an Wasserdampf im zweiten Synthesegas, welches bei der autothermen Reformierung im zweiten autothermen Reformer in Schritt (e) erhalten wird. Vorzugsweise beträgt die relative Differenz des Gehalts an Wasserdampf des in Schritt (e) erhaltenen zweiten Synthesegases und des Gehalts an Wasserdampf des in Schritt (b) erhaltenen ersten Synthesegases mindestens 5 Vol.-% oder mindestens 6 Vol.-%, bevorzugter mindestens 7 Vol.-% oder mindestens 8 Vol.-%, noch bevorzugter mindestens 9 Vol.-% oder mindestens 10 Vol.-%, am bevorzugtesten mindestens 11 Vol.-% oder mindestens 12 Vol.-% und insbesondere mindestens 13 Vol.-% oder mindestens 14 Vol.-%.

[0051] Bevorzugt umfasst das erfindungsgemäße Verfahren die zusätzlichen Schritte

(f) ein- oder zweistufiges Konvertieren von Kohlenstoffmonoxid, welches in dem in Schritt (e) erhaltenen zweiten Synthesegas enthalten ist, zu Kohlenstoffdioxid;

(g) Abtrennen von Kohlenstoffdioxid, welches in dem in Schritt (f) erhaltenen zweiten Synthesegas enthalten ist; und

(h) abschließendes Reinigen des in Schritt (g) erhaltenen zweiten Synthesegases vorzugsweise durch Methanisierung oder Stickstoffwäsche.

[0052] Alternativ umfasst das erfindungsgemäße Verfahren die zusätzlichen Schritte

(f) ein- oder zweistufiges Konvertieren von Kohlenstoffmonoxid, welches in dem in Schritt (e) erhaltenen zweiten Synthesegas enthalten ist, zu Kohlenstoffdioxid; und

(g') Abtrennen eines Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan vom zweiten Synthesegas durch Druckwechsel-Adsorption.

[0053] Umfasst das erfindungsgemäße Verfahren die Druckwechsel-Adsorption gemäß Schritt (g'), so werden Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan durch die Druckwechsel-Adsorption vollständig aus dem zweiten Synthesegas abgetrennt. Stickstoff wird lediglich zum Teil abgetrennt, so dass genügend Stickstoff im zweiten Synthesegas verbleibt, um das benötigte H_2/N_2-Verhältnis für die Ammoniaksynthese einstellen zu können. Wasserstoff wird durch die Druckwechsel-Adsorption praktisch nicht abgetrennt. Der Abgasstrom der Druckwechsel-Adsorption kann beispielsweise als Fuel Gas in einem Hilfskessel verfeuert werden. Umfasst das erfindungsgemäße Verfahren auch in Schritt (c) eine Abtrennung durch Druckwechsel-Adsorption, so umfasst das erfindungsgemäße Verfahren insgesamt zwei Druckwechsel-Adsorptionen.

[0054] Die für die Durchführung dieser Schritte erforderlichen Maßnahmen sind dem Fachmann bekannt. Diesbezüglich kann beispielsweise verweisen werden auf A. Nielsen, I. Dybkjaer, Ammonia-Catalys-

sis and Manufacture, Springer Berlin 1995, Kapitel 6, Seiten 202–326.

[0055] Die Schritte (a) bis (h) des erfindungsgemäßen Verfahrens werden vorzugsweise zeitlich nacheinander durchgeführt, wobei allerdings die Bereitstellung in Schritt (a) zumindest teilweise zeitgleich mit der ersten autothermen Reformierung in Schritt (b) und/oder wobei entsprechend die Bereitstellung in Schritt (d) zumindest teilweise zeitgleich mit der ersten autothermen Reformierung in Schritt (e) durchgeführt werden kann.

[0056] Nach dem Konvertieren von Kohlenstoffmonoxid in Schritt (f), dem Abtrennen von Kohlenstoffdioxid in Schritt (g) und dem abschließenden Reinigen in Schritt (h) bzw. nach dem Abtrennen von Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan in Schritt (g') hat das zweite Synthesegas bevorzugt

- einen Gehalt an Wasserstoff im Bereich von 40 ± 35 Vol.-% auf, bevorzugter 40 ± 30 Vol.-%, noch bevorzugter 40 ± 25 Vol.-%, am bevorzugtesten 40 ± 20 Vol.-%, und insbesondere 40 ± 15 Vol.-%; und/oder
- einen Gehalt an Stickstoff im Bereich von 60 ± 55 Vol.-% auf, bevorzugter 60 ± 50 Vol.-%, noch bevorzugter 60 ± 45 Vol.-%, am bevorzugtesten 60 ± 40 Vol.-%, und insbesondere 60 ± 35 Vol.-%.

[0057] Das erfindungsgemäße Verfahren wird bevorzugt kontinuierlich betrieben. Das erfindungsgemäße Verfahren liefert bevorzugt eine Gesamtproduktion von mehr als 3300 tato an Synthesegas (Summe über das erste Synthesegas und das zweite Synthesegas, vorzugsweise nach Abtrennung in Schritt (c) und abschließender Reinigung in Schritt (h)), bevorzugter mindestens 3500 tato Synthesegas, noch bevorzugter mindestens 3800 tato Synthesegas und insbesondere mindestens 4000 tato Synthesegas.

[0058] Der erste autotherme Reformer hat bevorzugt eine Kapazität von mindestens 1000 tato an Synthesegas, bezogen auf das unmittelbare, ungereinigte Reaktionsprodukt der ersten autothermen Reformierung aus Schritt (b), bevorzugter mindestens 1500 tato, noch bevorzugter mindestens 2000 tato, am bevorzugtesten mindestens 2500 tato und insbesondere mindestens 3000 tato an Synthesegas.

[0059] Der zweite autotherme Reformer hat bevorzugt eine Kapazität von mindestens 1000 tato an Synthesegas, bezogen auf das unmittelbare, ungereinigte Reaktionsprodukt der zweiten autothermen Reformierung in Schritt (e), bevorzugter mindestens 1500 tato, noch bevorzugter mindestens 2000 tato, am bevorzugtesten mindestens 2500 tato und insbesondere mindestens 3000 tato an Synthesegas.

[0060] Bevorzugt entspricht die Kapazität des ersten autothermen Reformers im Wesentlichen der Kapazität des zweiten autothermen Reformers.

[0061] Als Kohlenwasserstoff wird in Schritt (a) und ggf. zusätzlich in Schritt (d) des erfindungsgemäßen Verfahrens bevorzugt Erdgas eingesetzt, welches ggf. zunächst entschwefelt wird. Der Gesamtverbrauch an Erdgas wird bevorzugt als Erdgasstrom bereitgestellt, welcher bevorzugt in zwei Teilströme aufgeteilt wird: Der erste Erdgasteilstrom wird in Schritt (a) dem Gasgemisch zugesetzt, welches anschließend in Schritt (b) im ersten autothermen Reformer reformiert wird; und der zweite Erdgasteilstrom wird in Schritt (d) dem Gasgemisch zugesetzt, welches anschließend in Schritt (e) im zweiten autothermen Reformer reformiert wird. In einer bevorzugten Ausführungsform beträgt das relative Gewichtsverhältnis des ersten Erdgasteilstroms zum zweiten Erdgasteilstrom weniger als 1:1, bevorzugter weniger als 1:1,5. In einer anderen bevorzugten Ausführungsform beträgt das relative Gewichtsverhältnis des ersten Erdgasteilstroms zum zweiten Erdgasteilstrom mehr als 1:1, bevorzugter mehr als 1,5:1. In einer weiteren bevorzugten Ausführungsform liegt das relative Gewichtsverhältnis des ersten Erdgasteilstroms zum zweiten Erdgasteilstrom im Bereich von 70:30 bis 30:70, bevorzugter 60:40 bis 40:60 und insbesondere 55:45 bis 45:55.

[0062] Ein weiterer Aspekt der Erfindung betrifft ein Verfahren zur Herstellung von Ammoniak umfassend das vorstehend beschriebene erfindungsgemäße Verfahren zur Herstellung von Synthesegas, wobei das erste Synthesegas und das zweite Synthesegas gemeinsam einem Ammoniakreaktor zugeführt werden.

[0063] Bevorzugt wird dabei das in Schritt (c) erhaltene erste Synthesegas ohne weitere Reinigung mit Hilfe eines Synthesegasverdichters auf einen Druck verdichtet, bei welchem der Ammoniakreaktor betrieben wird. Vorzugsweise wird der Ammoniakreaktor bei einem Druck von mindestens 150 bar betrieben, bevorzugter mindestens 170 bar, noch bevorzugter mindestens 190 bar, am bevorzugtesten mindestens 210 bar und insbesondere mindestens 230 bar.

[0064] Bevorzugt wird dabei das in Schritt (e) erhaltene zweite Synthesegas gemäß den zusätzlichen Schritten (f), (g) und (h) oder gemäß den zusätzlichen Schritten (f) und (g') gereinigt; danach mit Hilfe eines Synthesegasverdichters zunächst auf einen Druck vorverdichtet, welcher geringer ist als der Druck, bei welchem der Ammoniakreaktor betrieben wird; und anschließend mit Hilfe eines weiteren Synthesegasverdichters auf einen Druck verdichtet, bei welchem der Ammoniakreaktor betrieben wird. Vorzugsweise wird das zweite Synthesegas zunächst mit Hilfe eines Synthesegasverdichters auf einem Druck im Bereich

von 100 ± 50 bar vorverdichtet, bevorzugter 100 ± 40 bar, noch bevorzugter 100 ± 30 bar, am bevorzugtesten 100 ± 20 bar und insbesondere 100 ± 10 bar; und anschließend mit Hilfe eines weiteren Synthesegasverdichters auf einen Druck verdichtet, bei welchem der Ammoniakreaktor betrieben wird, welcher bevorzugt mindestens 150 bar beträgt, bevorzugter mindestens 170 bar, noch bevorzugter mindestens 190 bar, am bevorzugtesten mindestens 210 bar und insbesondere mindestens 230 bar.

[0065] Das erfindungsgemäße Verfahren liefert bevorzugt eine Gesamtproduktion von mehr als 3300 tato an Ammoniak, bevorzugter mindestens 3500 tato, noch bevorzugter mindestens 3700 tato, am bevorzugtesten mindestens 3900 tato und insbesondere mindestens 4000 tato an Ammoniak.

[0066] Ein weiterer Aspekt der Erfindung betrifft eine Vorrichtung zur Herstellung von Synthesegas umfassend

- einen ersten autothermen Reformer zum Herstellen eines ersten Synthesegases umfassend Wasserstoff, Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan aus einem Gasgemisch umfassend Kohlenwasserstoffe, Wasserdampf und ein Oxidationsmittel, vorzugsweise Sauerstoff oder mit Sauerstoff angereicherte Luft;
- eine Anlage zum Abtrennen eines Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan von dem ersten Synthesegas;
- einen zweiten autothermen Reformer zum Herstellen eines zweiten Synthesegases umfassend Wasserstoff, Kohlenstoffmonoxid und Kohlenstoffdioxid aus einem Gasgemisch umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan;
- Mittel zum Überführen des von dem ersten Synthesegas abtrennten Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan zu dem zweiten autothermen Reformer;

wobei der erste autotherme Reformer für einen Druck ausgelegt ist, der höher ist als der Druck, für den der zweite autotherme Reformer ausgelegt ist.

[0067] Die erfindungsgemäße Vorrichtung eignet sich zur Durchführung des erfindungsgemäßen Verfahrens zur Herstellung von Synthesegas. Ein weiterer Aspekt der Erfindung betrifft daher die Verwendung der erfindungsgemäßen Vorrichtung zur Herstellung von Synthesegas in dem erfindungsgemäßen Verfahren zur Herstellung von Synthesegas.

[0068] Alle bevorzugten Ausführungsformen, welche vorstehend im Zusammenhang mit dem erfindungsgemäßen Verfahren beschrieben wurden, gelten analog auch im Hinblick auf die Auslegung und Gestaltung der erfindungsgemäßen Vorrichtung und werden daher diesbezüglich nicht wiederholt.

[0069] Bevorzugt umfasst die Anlage zum Abtrennen des Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan von dem ersten Synthesegas eine Druckwechsel-Adsorptions-Anlage. In einer bevorzugten Ausführungsform ist der Druckwechsel-Adsorptions-Anlage eine Membran-Trennanlage vorgeschaltet, in welcher zunächst ein Großteil des im ersten Synthesegas enthaltenen Kohlenstoffmonoxid und Kohlenstoffdioxid als Permeatstrom abgetrennt wird. Der Retentatstrom, welcher Wasserstoff sowie Methan und nicht abgetrenntes Kohlenstoffmonoxid und Kohlenstoffdioxid enthält, wird dann der Druckwechsel-Adsorptions-Anlage zugeführt.

[0070] Bevorzugt umfasst die erfindungsgemäße Vorrichtung

- eine Entschwefelungsanlage zum Entfernen von Schwefelverbindungen aus Kohlenwasserstoffen und Mittel zum Überführen der entschwefelten Kohlenwasserstoffe zum ersten autothermen Reformer oder einer dem autothermen Reformer vorgeschalteten Mischanlage; und/oder
- eine Luftzerlegungsanlage und Mittel zum Überführen von reinem Sauerstoff oder von mit Sauerstoff angereicherter Luft mit einem Gehalt an Sauerstoff von mindestens 90 Vol.-% zum ersten autothermen Reformer oder einer dem autothermen Reformer vorgeschalteten Mischanlage; und/oder
- eine ein- oder zweistufige Konvertierungsanlage zur Konvertierung von Kohlenstoffmonoxid, welches in dem zweiten Synthesegas enthalten ist, zu Kohlenstoffdioxid; und/oder
- eine Anlage zur Abtrennung von Kohlenstoffdioxid, welches in dem zweiten Synthesegas enthalten ist; und/oder
- eine Anlage zum Abtrennen eines Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan von dem zweiten Synthesegas, vorzugsweise durch Druckwechsel-Adsorption; und/oder
- eine Anlage zur abschließenden Reinigung des zweiten Synthesegases, vorzugsweise durch Methanisierung oder Stickstoffwäsche.

[0071] Die Luftzerlegungsanlage ist vorzugsweise so dimensioniert, dass sie genügend reinen Sauerstoff produziert, wie in dem erfindungsgemäßen Verfahren benötigt wird. Für die Erzeugung von Synthesegas für eine Ammoniakanlage mit einer Kapazität von 3600 tato können beispielsweise 73 t/h reiner Sauerstoff benötigt werden.

[0072] Die Schwefelverbindungen können dabei durch herkömmliche, dem Fachmann bekannte Verfahren abgetrennt werden. Beispielsweise können die Schwefelverbindungen durch Adsorption an Ak-

tivkohle oder an Molekularsiebe abgetrennt werden oder durch katalytische Hydrierung der organischen Schwefelverbindungen und anschließende Adsorption des gebildeten Schwefelwasserstoffs an Zinkoxid.

[0073] Bevorzugt umfasst die erfindungsgemäße Vorrichtung

- einen mehrstufigen Verdichter umfassend eine erste Verdichtungsstufe und eine nachgeschaltete zweite Verdichtungsstufe;
- Mittel zum Überführen des ersten Synthesegases aus der Anlage zum Abtrennen des Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan von dem ersten Synthesegas zur zweiten Verdichtungsstufe; und
- eine Anlage zur abschließenden Reinigung des zweiten Synthesegases, vorzugsweise durch Methanisierung, Druckwechsel-Adsorption oder Stickstoffwäsche, und Mittel zum Überführen des abschließend gereinigten zweiten Synthesegases zur ersten Verdichtungsstufe.

[0074] Ein weiterer Aspekt der Erfindung betrifft eine Vorrichtung zur Herstellung von Ammoniak aus Synthesegas umfassend die erfindungsgemäße, vorstehend beschriebene Vorrichtung zur Herstellung von Synthesegas und einen Ammoniakreaktor.

[0075] Die erfindungsgemäße Vorrichtung eignet sich zur Durchführung des erfindungsgemäßen Verfahrens zur Herstellung von Ammoniak. Ein weiterer Aspekt der Erfindung betrifft daher die Verwendung der erfindungsgemäßen Vorrichtung zur Herstellung von Ammoniak in dem erfindungsgemäßen Verfahren zur Herstellung von Ammoniak.

[0076] Der Erfindung wird anhand der **Fig.** 1 beispielhaft illustriert. Ein Fachmann erkennt, dass bei einer erfindungsgemäßen Vorrichtung nicht zwingend alle abgebildeten Merkmale gleichzeitig verwirklicht sein müssen.

[0077] **Fig.** 1 illustriert schematisch eine erfindungsgemäße Vorrichtung bzw. das erfindungsgemäße Verfahren zur Herstellung von Ammoniak aus Erdgas (C_nH_{2n+2}). Das Erdgas wird bevorzugt zunächst von der C_{2+}-Fraktion befreit und ggf. in einer Entschwefelungsanlage (**5**) entschwefelt. Anschließend wird ein erster Erdgasstrom über Leitung (a) einem Verdichter (**12**) zugeführt, worin das Erdgas auf den Betriebsdruck des ersten autothermen Reformers (**1**) verdichtet wird. Hinter dem Verdichter (**12**) wird der Erdgasstrom bevorzugt mit Wasserdampf vermischt und das Gemisch umfassend Erdgas und Wasserdampf dem ersten autothermen Reformer (**1**) zugeführt. Eine Luftzerlegungsanlage (**6**) stellt vorzugsweise reinen Sauerstoff oder mit Sauerstoff angereicherte Luft bereit, welche ebenfalls dem ersten autothermen Reformer (**1**) zugeführt wird. Die Vermischung von Erdgas und Wasserdampf kann alternativ im ersten autothermen Reformer (**1**) oder auch außerhalb des ersten autothermen Reformers (**1**) in Leitung (c) oder in einer dem ersten autothermen Reformer (**1**) vorgeschalteten Mischanlage erfolgen. Gemäß **Fig.** 1 erfolgt zunächst die Vermischung vom ersten Erdgasstrom mit Wasserdampf in Leitung (c) und anschließend die Zugabe von Sauerstoff in den ersten autothermen Reformer (**1**).

[0078] Die autotherme Reformierung im ersten autothermen Reformer (**1**) liefert ein erstes Synthesegas, welches vorzugsweise im Wärmetauscher (**13**) abgekühlt und anschließend über Leitung (d) einer Anlage (**4**) zum Abtrennen von CO, CO_2 und CH_4 zugeführt wird, wobei das Abtrennen von CO, CO_2 und CH_4 vorzugsweise durch Druckwechsel-Adsorption erfolgt. Das so gereinigte erste Synthesegas, welches einen erhöhten Gehalt an Wasserstoff aufweist, wird über Leitung (e), vorzugsweise ohne weitere Aufbereitung, ggf. nach Vermischung mit der für die Ammoniaksynthese erforderlichen Menge an verdichtetem Stickstoff, unmittelbar Verdichtungsstufe (**11**) zugeführt, welche bevorzugt die zweite Stufe eines mehrstufigen Verdichters bildet, der die vorgeschaltete erste Verdichtungsstufe (**10**) sowie die nachgeschaltete zweite Verdichtungsstufe (**11**) umfasst. Von der zweiten Verdichtungsstufe (**11**) wird das erste Synthesegas dem Ammoniakreaktor (**3**) zugeführt.

[0079] Das in Anlage (**4**) abgetrennte Gasgemisch umfassend CO, CO_2 und CH_4 wird über Leitungen (f) und (g) dem Verdichter (**14**) zugeführt, welcher dem zweiten autothermen Reformer (**2**) vorgeschaltet ist. Dabei wird es bevorzugt zunächst mit einem zweiten Erdgasstrom vermischt, welcher über Leitung (b) herangeführt wird. Das Gemisch aus dem zweiten Erdgasstrom und dem Gasgemisch umfassend CO, CO_2 und CH_4 wird dann im Verdichter (**14**) auf den Betriebsdruck des zweiten autothermen Reformers (**2**) verdichtet. Anschließend wird dem Gemisch Wasserdampf zugesetzt. Vom Verdichter (**14**) wird das Gasgemisch, ggf. nach Vorwärmung, dem zweiten autothermen Reformer (**2**) zugeführt. Luft oder mit Sauerstoff angereicherte Luft wird in Verdichter (**15**) auf den Betriebsdruck des zweiten autothermen Reformers (**2**) verdichtet und ebenfalls dem zweiten autothermen Reformer (**2**) zugeführt. Dazu kann ggf. reiner Sauerstoff aus der Luftzerlegungsanlage (**6**) über Leitung (n) direkt dem zweiten autothermen Reformer (**2**) und/oder der Luft vor Verdichter (**15**) zugeführt werden. Die Vermischung von Erdgas, Gasgemisch umfassend CO, CO_2 und CH_4, und Wasserdampf kann alternativ im zweiten autothermen Reformer (**2**) oder auch außerhalb des zweiten autothermen Reformers (**2**) in Leitung (m) oder in einer dem zweiten autothermen Reformer (**2**) vorgeschalteten Mischanlage erfolgen. Gemäß **Fig.** 1 erfolgt zunächst die Vermischung vom zweiten Erdgasstrom, Gasgemisch umfassend CO, CO_2 und CH_4, und Wasser-

dampf in Leitung (g) und anschließend die Zugabe von Luft in den zweiten autothermen Reformer (**2**). Erfolgt die Abtrennung in Anlage (**4**) durch Druckwechsel-Adsorption, so fällt das in Anlage (**4**) abgetrennte Gasgemisch umfassend CO, CO_2 und CH_4 bei einem Druck an, welcher üblicherweise nicht ausreicht, um es zur Saugseite des Verdichters (**14**) zurückzuführen. In diesem Fall wird bevorzugt ein zusätzlicher Kreislaufverdichter installiert (in **Fig.** 1 nicht dargestellt), der das abgetrennte Gasgemisch wieder auf den Druck des Erdgases an der Anlagengrenze verdichtet.

[0080] Die autotherme Reformierung im zweiten autothermen Reformer (**2**) liefert ein zweites Synthesegas, welches vorzugsweise im Wärmetauscher (**16**) abgekühlt und anschließend über Leitung (h) einer ein- oder zweistufigen Konvertierungsanlage (**7**) zur Konvertierung von CO zugeführt wird. Dabei wird das CO unter Zusatz von H_2O zu CO_2 und H_2 konvertiert und auf diese Weise der Gehalt an H_2 und CO_2 im zweiten Synthesegas weiter erhöht sowie der Gehalt an CO verringert. Nach bevorzugter Abkühlung im Wärmetauscher (**17**) wird das konvertierte zweite Synthesegas über Leitung (i) einer Anlage (**8**) zur Abtrennung von CO_2 zugeführt, vorzugsweise unter Einsatz geeigneter chemischer oder physikalischer Lösungsmittel (Kohlenstoffdioxidwäsche). Das zweite Synthesegas, welches nun neben H_2 und N_2 nur noch Restmengen an CO und anderen Verunreinigungen enthält, wird in einer über Leitung (k) Anlage (**9**) einer abschließenden Reinigung unterzogen, vorzugsweise durch Methanisierung, Druckwechsel-Adsorption oder N_2-Wäsche. Anschließend wird das abschließend gereinigte zweite Synthesegas der ersten Verdichtungsstufe (**10**) zugeführt, in der es vorverdichtet wird, ehe es mit dem ersten Synthesegasstrom vereint und der zweiten Verdichtungsstufe (**11**) zugeführt wird, von der es nach Verdichtung dem Ammoniakreaktor (**3**) zugeführt wird.

[0081] **Fig.** 2 illustriert schematisch eine weitere bevorzugte erfindungsgemäße Variante der Vorrichtung bzw. des erfindungsgemäßen Verfahrens zur Herstellung von Ammoniak aus Erdgas. Im Unterschied zu der in **Fig.** 1 illustrierten Ausführungsform wird das konvertierte zweite Synthesegas nach bevorzugter Abkühlung im Wärmetauscher (**17**) über Leitung (i) einer Anlage (**10**) zum Abtrennen von CO, CO_2 und CH_4 zugeführt wird, wobei das Abtrennen von CO, CO_2 und CH_4 vorzugsweise durch Druckwechsel-Adsorption erfolgt. Das so gereinigte zweite Synthesegas wird über Leitung (j), vorzugsweise ohne weitere Aufbereitung, ggf. nach Vermischung mit der für die Ammoniaksynthese erforderlichen Menge an verdichtetem Stickstoff, unmittelbar der ersten Verdichtungsstufe (**10**) zugeführt.

[0082] **Fig.** 3 illustriert schematisch eine weitere bevorzugte erfindungsgemäße Variante der Vorrichtung bzw. des erfindungsgemäßen Verfahrens zur Herstellung von Ammoniak aus Erdgas. Im Unterschied zu den in **Fig.** 1 und **Fig.** 2 illustrierten Ausführungsformen wird das erste Synthesegas vorzugsweise im Wärmetauscher (**13**) abgekühlt und anschließend über Leitung (d) einer Membran-Trennanlage (**11**) zum Abtrennen von CO und CO_2 zugeführt. In der Membran-Trennanlage (**11**) wird das abgekühlte erste Synthesegas in einen an Wasserstoff und Methan angereicherten Retentatstrom und einen an CO und CO_2 angereicherten Permeatstrom getrennt. Der Permeatstrom wird über Leitung (f) zur Saugseite des Verdichters (**14**) geleitet. Der Retentatstrom wird weiter über Leitung (o) der Anlage (**4**) zum Abtrennen von CO, CO_2 und CH_4 zugeführt, wobei das Abtrennen von CO, CO_2 und CH_4 vorzugsweise durch Druckwechsel-Adsorption erfolgt. Das Abgas, welches in Anage (**4**) abgetrennt wird, enthält überwiegend Methan, vorher nicht abgeschiedenes CO und CO_2 sowie in geringen Mengen auch H_2.

ZITATE ENTHALTEN IN DER BESCHREIBUNG

Diese Liste der vom Anmelder aufgeführten Dokumente wurde automatisiert erzeugt und ist ausschließlich zur besseren Information des Lesers aufgenommen. Die Liste ist nicht Bestandteil der deutschen Patent- bzw. Gebrauchsmusteranmeldung. Das DPMA übernimmt keinerlei Haftung für etwaige Fehler oder Auslassungen.

Zitierte Patentliteratur

- WO 2004/083114 [0008]
- EP 0999178 A1 [0009]
- US 6444712 B1 [0010]
- US 2013312384 A1 [0011]

Zitierte Nicht-Patentliteratur

- A. Nielsen, I. Dybkjaer, Ammonia-Catalysis and Manufacture, Springer Berlin 1995, Kapitel 6, Seiten 202–326 [0054]

Patentansprüche

1. Verfahren zur Herstellung von Synthesegas umfassend die Schritte
(a) Bereitstellen eines Gasgemischs umfassend Kohlenwasserstoffe, Wasserdampf und ein Oxidationsmittel;
(b) Reformieren des in Schritt (a) bereitgestellten Gasgemischs in einem ersten autothermen Reformer (**1**), wodurch ein erstes Synthesegas umfassend Wasserstoff, Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan erhalten wird;
(c) Erhöhen des Gehalts an Wasserstoff des in Schritt (b) erhaltenen ersten Synthesegases durch Abtrennen eines Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan;
(d) Bereitstellen eines Gasgemischs umfassend das in Schritt (c) abgetrennte Gasgemisch;
(e) Reformieren des in Schritt (d) bereitgestellten Gasgemischs in einem zweiten autothermen Reformer (**2**), wodurch ein zweites Synthesegas umfassend Wasserstoff, Kohlenstoffmonoxid und Kohlenstoffdioxid erhalten wird;
wobei der erste autotherme Reformer (**1**) in Schritt (b) bei einem Druck betrieben wird, der höher ist als der Druck, bei dem der zweite autotherme Reformer (**2**) in Schritt (e) betrieben wird.

2. Das Verfahren nach Anspruch 1, wobei
– der erste autotherme Reformer (**1**) in Schritt (b) bei einem Druck betrieben wird, der mindestens um 10 bar höher ist als der Druck, bei dem der zweite autotherme Reformer (**2**) in Schritt (e) betrieben wird; und/oder
– der erste autotherme Reformer (**1**) in Schritt (b) bei einem Druck von mindestens 30 bar betrieben wird; und/oder
– der zweite autotherme Reformer (**2**) in Schritt (e) bei einem Druck von höchstens 60 bar betrieben wird.

3. Das Verfahren nach Anspruch 1 oder 2, wobei in Schritt (a)
– dem Gasgemisch das Oxidationsmittel in Form von reinem Sauerstoff oder in Form von mit Sauerstoff angereicherter Luft mit einem Gehalt an Sauerstoff von mindestens 90 Vol.-% zugesetzt wird; und/oder
– dem Gasgemisch die Kohlenwasserstoffe in Form von Methan oder Erdgas zugesetzt werden; und/oder
– das Gasgemisch ein molares Wasserdampf/Kohlenstoff-Verhältnis von höchstens 3,2 aufweist; und/oder
– das Gasgemisch einen Gehalt an Stickstoff von höchstens 10 Vol.-% aufweist.

4. Das Verfahren nach einem der vorstehenden Ansprüche, wobei das in Schritt (b) erhaltene erste Synthesegas
– ein molares Wasserstoff/Kohlenstoffmonoxid-Verhältnis von höchstens 4,5 aufweist; und/oder
– einen Gehalt an Methan von mindestens 0,3 Vol.-% aufweist; und/oder
– einen Gehalt an Wasserstoff von mindestens 30 Vol.-% aufweist; und/oder
– einen Gehalt an Kohlenstoffmonoxid im Bereich von 20 ± 19 Vol.-% aufweist; und/oder
– einen Gehalt an Kohlenstoffdioxid im Bereich von 12 ± 11 Vol.-% aufweist; und/oder
– einen Gehalt an Stickstoff von höchstens 10 Vol.-% aufweist; und/oder
– einen Gehalt an Wasserdampf von 30 ± 29 Vol.-% aufweist; wobei die Gehaltsangaben jeweils Feuchtkonzentrationen sind.

5. Das Verfahren nach einem der vorstehenden Ansprüche, wobei in Schritt (c) das Abtrennen des Gasgemischs
(i) durch Druckwechsel-Adsorption oder
(ii) durch selektive Membran-Permeation und anschließende Druckwechsel-Adsorption erfolgt.

6. Das Verfahren nach einem der vorstehenden Ansprüche, wobei in Schritt (d)
– dem Gasgemisch Luft oder mit durch Sauerstoff angereicherte Luft mit einem Gehalt an Sauerstoff von höchstens 90 Vol.-% zugesetzt wird; und/oder
– dem Gasgemisch Kohlenwasserstoffe zugesetzt werden; und/oder
– das Gasgemisch ein molares Wasserdampf/Kohlenstoff-Verhältnis von mindestens 0,2 aufweist; und/oder
– das Gasgemisch einen Gehalt an Stickstoff von höchstens 70 Vol.-% aufweist.

7. Das Verfahren nach einem der vorstehenden Ansprüche, umfassend die zusätzlichen Schritte
(f) ein- oder zweistufiges Konvertieren von Kohlenstoffmonoxid, welches in dem in Schritt (e) erhaltenen zweiten Synthesegas enthalten ist, zu Kohlenstoffdioxid;
(g) Abtrennen von Kohlenstoffdioxid, welches in dem in Schritt (f) erhaltenen zweiten Synthesegas enthalten ist; und
(h) abschließendes Reinigen des in Schritt (g) erhaltenen zweiten Synthesegases.

8. Das Verfahren nach einem der Ansprüche 1 bis 6, umfassend die zusätzlichen Schritte
(f) ein- oder zweistufiges Konvertieren von Kohlenstoffmonoxid, welches in dem in Schritt (e) erhaltenen zweiten Synthesegas enthalten ist, zu Kohlenstoffdioxid; und
(g') Abtrennen eines Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan vom zweiten Synthesegas durch Druckwechsel-Adsorption.

9. Verfahren zur Herstellung von Ammoniak umfassend das Verfahren nach einem der Ansprüche 1 bis 8, wobei das erste Synthesegas und das zwei-

te Synthesegas gemeinsam einem Ammoniakreaktor (**3**) zugeführt werden.

10. Das Verfahren nach Anspruch 9, wobei das in Schritt (c) erhaltene erste Synthesegas ohne weitere Reinigung auf einen Druck verdichtet wird, bei welchem der Ammoniakreaktor (**3**) betrieben wird.

11. Das Verfahren nach Anspruch 9 oder 10, wobei das in Schritt (e) erhaltene zweite Synthesegas gemäß den zusätzlichen Schritten (f), (g) und (h) nach Anspruch 7 oder gemäß den zusätzlichen Schritten (f) und (g') gemäß Anspruch 8 gereinigt wird; danach zunächst auf einen Druck vorverdichtet wird, welcher geringer ist als der Druck, bei welchem der Ammoniakreaktor (**3**) betrieben wird; und anschließend auf einen Druck verdichtet wird, bei welchem der Ammoniakreaktor (**3**) betrieben wird.

12. Vorrichtung zur Herstellung von Synthesegas umfassend
– einen ersten autothermen Reformer (**1**) zum Herstellen eines ersten Synthesegases umfassend Wasserstoff, Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan aus einem Gasgemisch umfassend Kohlenwasserstoffe, Sauerstoff und Wasserdampf;
– eine Anlage (**4**) zum Abtrennen eines Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan von dem ersten Synthesegas;
– einen zweiten autothermen Reformer (**2**) zum Herstellen eines zweiten Synthesegases umfassend Wasserstoff, Kohlenstoffmonoxid und Kohlenstoffdioxid aus einem Gasgemisch umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan;
– Mittel zum Überführen des von dem ersten Synthesegas abtrennten Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan zu dem zweiten autothermen Reformer (**2**);
wobei der erste autotherme Reformer (**1**) für einen Druck ausgelegt ist, der höher ist als der Druck, für den der zweite autotherme Reformer (**2**) ausgelegt ist.

13. Die Vorrichtung nach Anspruch 12, wobei die Anlage (**4**) zum Abtrennen des Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan von dem ersten Synthesegas eine Druckwechsel-Adsorptions-Anlage umfasst.

14. Die Vorrichtung nach Anspruch 12 oder 13, umfassend
– eine Entschwefelungsanlage (**5**) zum Entfernen von Schwefelverbindungen aus Kohlenwasserstoffen und Mittel zum Überführen der entschwefelten Kohlenwasserstoffe zum ersten autothermen Reformer (**1**) oder einer dem autothermen Reformer vorgeschalteten Mischanlage; und/oder
– eine Luftzerlegungsanlage (**6**) und Mittel zum Überführen von reinem Sauerstoff oder von mit Sauerstoff angereicherter Luft mit einem Gehalt an Sauerstoff von mindestens 90 Vol.-% zum ersten autothermen Reformer (**1**) oder einer dem autothermen Reformer vorgeschalteten Mischanlage; und/oder
– eine ein- oder zweistufiges Konvertierungsanlage (**7**) zur Konvertierung von Kohlenstoffmonoxid, welches in dem zweiten Synthesegas enthalten ist; und/oder
– eine Anlage (**8**) zur Abtrennung von Kohlenstoffdioxid, welches in dem zweiten Synthesegas enthalten ist; und/oder
– eine Anlage (**10**) zum Abtrennen eines Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan von dem zweiten Synthesegas; und/oder
– eine Anlage (**9**) zur abschließenden Reinigung des zweiten Synthesegases.

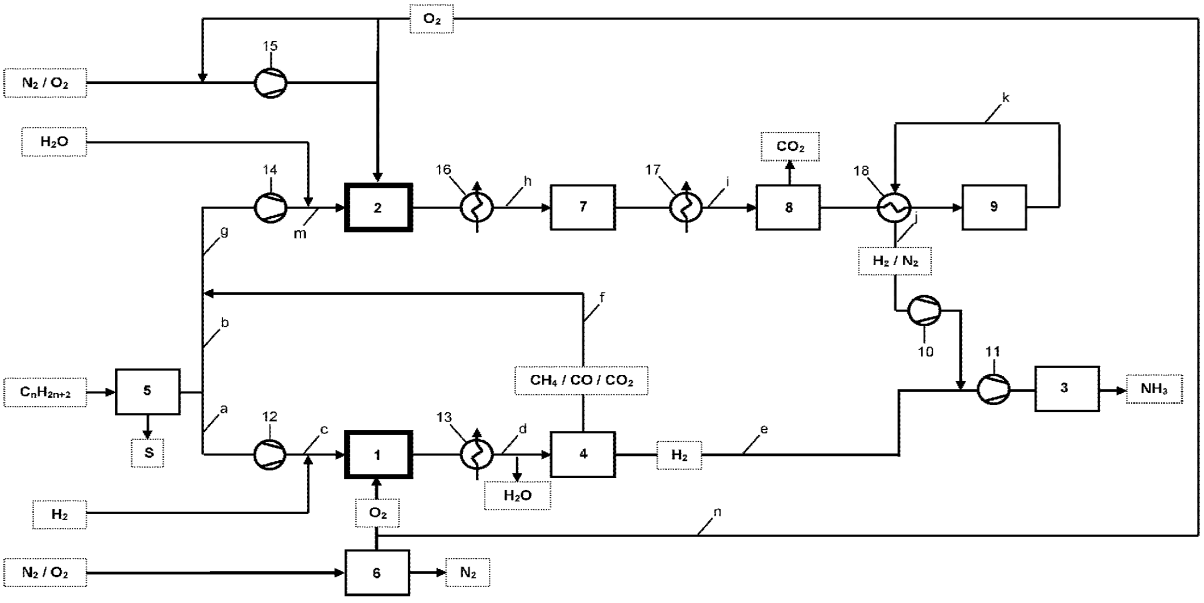
15. Die Vorrichtung nach einem der Ansprüche 12 bis 14, umfassend
– einen mehrstufigen Verdichter umfassend eine erste Verdichtungsstufe (**10**) und eine nachgeschaltete zweite Verdichtungsstufe (**11**);
– Mittel zum Überführen des ersten Synthesegases aus der Anlage (**4**) zur zweiten Verdichtungsstufe (**11**); und
– eine Anlage (**9**) zur abschließenden Reinigung des zweiten Synthesegases und Mittel zum Überführen des zweiten Synthesegases aus der Anlage (**9**) zur ersten Verdichtungsstufe (**10**).

16. Vorrichtung zur Herstellung von Ammoniak aus Synthesegas umfassend die Vorrichtung nach einem der Ansprüche 12 bis 15 und einen Ammoniakreaktor (**3**).

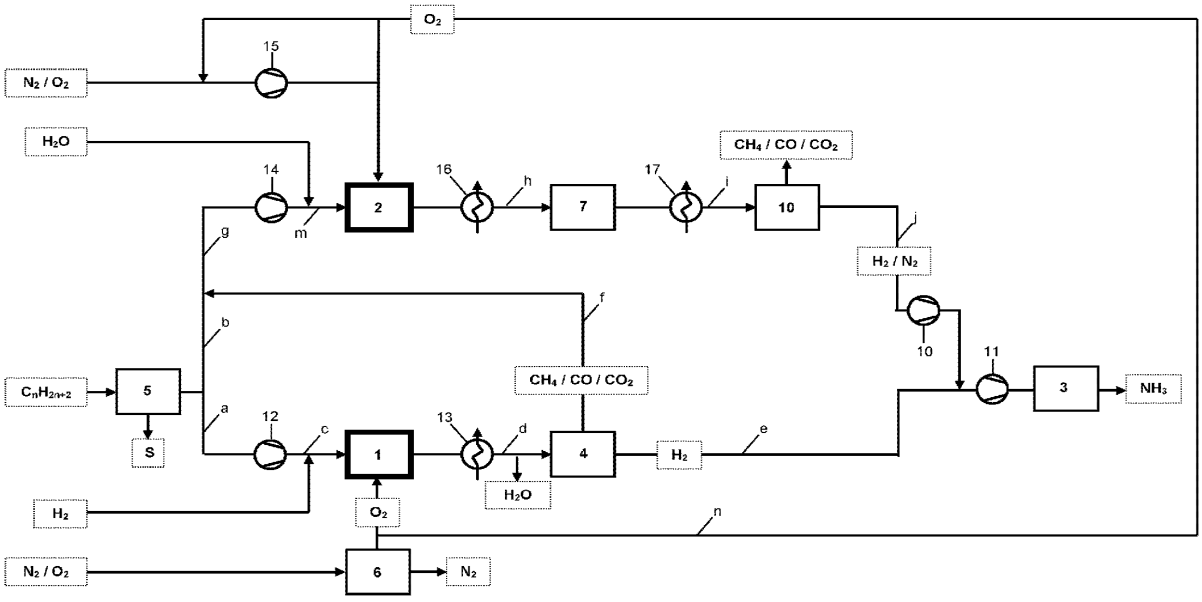
Es folgen 3 Seiten Zeichnungen

Anhängende Zeichnungen

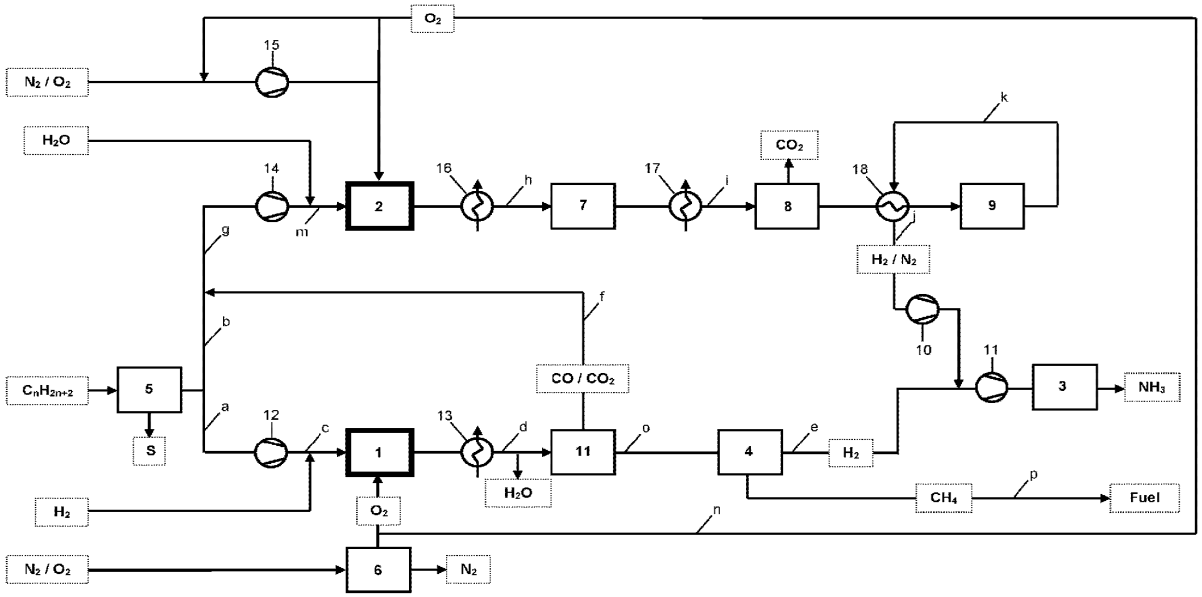
Figur 1



Figur 2


O2
15
N2 / O2
H2O
14
16
h
17
i
CH4 / CO / CO2
2
7
10
m
g
j
H2 / N2
f
b
10
11
CnH2n+2
5
CH4 / CO / CO2
3
NH3
a
12
c
13
d
e
S
1
4
H2
H2O
H2
O2
n
N2 / O2
6
N2

Figur 3


O2
N2 / O2
15
H2O
14
m
2
16
h
7
17
i
CO2
8
18
k
9
j
H2 / N2
10
11
3
NH3
g
b
f
CO / CO2
CnH2n+2
5
S
a
12
c
1
13
d
H2O
11
o
4
e
H2
CH4
p
Fuel
H2
O2
n
N2 / O2
6
N2

Synthesis of synthesis gas with two autothermal reformers

Abstract

translated from German

The invention relates to an apparatus and a process for the production of synthesis gas with the aid of two autothermal reformers and the subsequent synthesis of ammonia from the synthesis gas.

Images (3)



Classifications

- C01B3/382 Multi-step processes

View 16 more classifications

DE102014209635A1

Germany

Download PDF Find Prior Art Similar

Other languages: German

Inventor: Evgeni Gerval, Joachim Johanning, Bernd Keil, Katja Peschlad, Dr. Potthoff Christiane

Current Assignee : ThyssenKrupp AG , ThyssenKrupp Industrial Solutions AG

Worldwide applications

2014 DE 2015 WO

Application DE102014209635.9A events

2014-05-21 Application filed by ThyssenKrupp AG, ThyssenKrupp Industrial Solutions AG

2014-05-21 Priority to DE102014209635.9A

2015-11-26 Publication of DE102014209635A1

Status Ceased

Info: Patent citations (11), Non-patent citations (1), Cited by (2), Legal events, Similar documents, Priority and Related Applications

External links: Espacenet, Global Dossier, DPMA, Discuss

Claims (16)

Hide Dependent

translated from German

A process for producing synthesis gas comprising the steps of (a) providing a gas mixture comprising hydrocarbons, water vapor and an oxidizing agent; (b) reforming the gas mixture provided in step (a) in a first autothermal reformer (1), whereby a first synthesis gas comprising hydrogen, carbon monoxide, carbon dioxide and methane is obtained; (c) increasing the content of hydrogen of the first synthesis gas obtained in step (b) by separating a mixed gas comprising carbon monoxide, carbon dioxide and methane; (d) providing a gas mixture comprising the gas mixture separated in step (c); (e) reforming the gas mixture provided in step (d) in a second autothermal reformer (2), whereby a second synthesis gas comprising hydrogen, carbon monoxide and carbon dioxide is obtained; the first autothermal reformer (1) is operated in step (b) at a pressure which is higher than the pressure at which the second autothermal reformer (2) is operated in step (e). The method of claim 1, wherein - the first autothermal reformer (1) is operated in step (b) at a pressure which is at least 10 bar higher than the pressure at which the second autothermal reformer (2) is operated in step (e); and / or - the first autothermal reformer (1) is operated in step (b) at a pressure of at least 30 bar; and / or - the second autothermal reformer (2) is operated in step (e) at a pressure of at most 60 bar. The method of claim 1 or 2, wherein in step (a) - the oxidizing agent is added to the gas mixture in the form of pure oxygen or in the form of oxygen-enriched air containing at least 90% by volume of oxygen; and or - added to the gas mixture, the hydrocarbons in the form of methane or natural gas, and or - The gas mixture has a molar water vapor / carbon ratio of at most 3.2; and or - The gas mixture has a content of nitrogen of at most 10 vol .-%. The process according to any one of the preceding claims, wherein the first synthesis gas obtained in step (b) - Has a molar hydrogen / carbon monoxide ratio of at most 4.5, and or - Has a content of methane of at least 0.3 vol .-%; and or - Has a content of hydrogen of at least 30 vol .-%; and or - Has a content of carbon monoxide in the range of 20 ± 19 vol .-%; and or - Has a content of carbon dioxide in the range of 12 ± 11 vol .-%; and or - has a content of nitrogen of at most 10% by volume; and or - Has a content of water vapor of 30 ± 29 vol .-%, wherein the contents are each moist concentrations. The process according to any one of the preceding claims, wherein in step (c) the separation of the gas mixture (i) by pressure swing adsorption or (ii) by selective membrane permeation followed by pressure swing adsorption. The method according to any one of the preceding claims, wherein in step (d) - air is added to the gas mixture or oxygen-enriched air containing not more than 90% by volume of oxygen; and or - hydrocarbons are added to the gas mixture, and or - The gas mixture has a molar water vapor / carbon ratio of at least 0.2; and or - The gas mixture has a content of nitrogen of at most 70 vol .-%. The method of any one of the preceding claims comprising the additional steps (f) converting one or two stages of carbon monoxide contained in the second synthesis gas obtained in step (e) into carbon dioxide; (g) separating carbon dioxide contained in the second synthesis gas obtained in step (f); and (h) finally purifying the second synthesis gas obtained in step (g). The method of any of claims 1 to 6, comprising the additional steps (f) converting one or two stages of carbon monoxide contained in the second synthesis gas obtained in step (e) into carbon dioxide; and (g ') separating a gas mixture comprising carbon monoxide, carbon dioxide and methane from the second synthesis gas by pressure swing adsorption. A process for producing ammonia comprising the process according to any one of claims 1 to 8, wherein the first synthesis gas and the second synthesis gas together an ammonia reactor (3). The process according to claim 9, wherein the first synthesis gas obtained in step (c) is compressed without further purification to a pressure at which the ammonia reactor (3) is operated. The process according to claim 9 or 10, wherein the second synthesis gas obtained in step (e) according to additional steps (f), (g) and (h) according to claim 7 or according to the additional steps (f) and (g ') according to Claim 8 is cleaned; is then first precompressed to a pressure which is lower than the pressure at which the ammonia reactor (3) is operated; and then compressed to a pressure at which the ammonia reactor (3) is operated. Apparatus for producing synthesis gas comprising - a first autothermal reformer (1) for producing a first synthesis gas comprising hydrogen, carbon monoxide, carbon dioxide and methane from a gas mixture comprising hydrocarbons, oxygen and water vapor; - an annex (4) for separating a gas mixture comprising carbon monoxide, carbon dioxide and methane from the first synthesis gas; - a second autothermal reformer (2) for producing a second synthesis gas comprising hydrogen, carbon monoxide and

carbon dioxide from a gas mixture comprising carbon monoxide, carbon dioxide and methane; Means for transferring the gas mixture separated from the first synthesis gas comprising carbon monoxide, carbon dioxide and methane to the second autothermal reformer (2); the first autothermal reformer (1) is designed for a pressure which is higher than the pressure for which the second autothermal reformer (2) is designed. The device according to claim 12, wherein the system (4) for separating the gas mixture comprising carbon monoxide, carbon dioxide and methane from the first synthesis gas comprises a pressure swing adsorption plant. The apparatus according to claim 12 or 13, comprising - a desulphurisation plant (5) for removing sulfur compounds from hydrocarbons and means for transferring the desulfurized hydrocarbons to the first autothermal reformer (1) or an upstream of the autothermal reformer mixing plant; and / or - an air separation plant (6) and means for transferring pure oxygen or oxygen-enriched air containing at least 90% by volume of oxygen to the first autothermal reformer (1) or an upstream of the autothermal reformer mixing plant; and / or a one or two-stage conversion system (7 to convert carbon monoxide contained in the second synthesis gas; and / or - an attachment (8th) for separating carbon dioxide contained in the second synthesis gas; and / or - an attachment (10) for separating a gas mixture comprising carbon monoxide, carbon dioxide and methane from the second synthesis gas; and / or - an attachment (9) for final purification of the second synthesis gas. The apparatus according to any one of claims 12 to 14, comprising - a multi-stage compressor comprising a first compression stage (10) and a downstream second compression stage (11); - means for transferring the first synthesis gas from the plant (4) to the second compression stage (11); and - a facility (9) for the final purification of the second synthesis gas and means for transferring the second synthesis gas from the plant (9) to the first consolidation stage (10). Apparatus for the production of ammonia from synthesis gas comprising the apparatus according to any one of claims 12 to 15 and an ammonia reactor (3).

Description

translated from German

The invention relates to an apparatus and a process for the production of synthesis gas with the aid of two autothermal reformers and the subsequent synthesis of ammonia from the synthesis gas thus produced.

The large-scale production of synthesis gas from natural gas for ammonia synthesis is based today largely on a two-stage reforming with an externally heated steam reformer as a primary reformer and operated with compressed air as the oxidant secondary reformer. With capacities of up to 3,300 tpd of ammonia, this two-stage reforming is technically feasible with great reliability and economically unsurpassed compared to alternatives for the production of syngas.

In order to increase the capacity of an ammonia plant to more than 3,300 tpd ammonia, the dimensions of the apparatuses and pipelines can generally be increased accordingly. Alternatively or additionally, to increase the capacity and the operating pressure in the production of synthesis gas can be increased. The increase in pressure in the reformer reduces the volume flow in the entire process path and thus allows larger capacities even without increasing the components of the system. In addition, a higher operating pressure for a discharge of the syngas compressor, which is required for the subsequent ammonia synthesis at significantly higher pressure. This is of particular importance because the available syngas compressors are already limiting components for plant capacities of 3300 tpd of ammonia. The reasons are u.a. For technical reasons and in particular concern the drive turbine.

However, increasing the components of the system and increasing the pressure are not always economically viable to increase capacity.

As far as the two-stage reforming process is concerned, the steam reformer has a comparatively large share of the total construction costs due to its complexity and the great demands placed on it. In principle, a steam reformer can be considered as a parallel connection of a large number of individual tubular reactors whose individual capacity can not be significantly increased. The capacity of a steam reformer is therefore closely related to the number of tubular reactors and an increase is essentially only possible by increasing the number of tubular reactors. Almost all components required for the realization of a steam reformer are coupled to the number of tube reactors. The construction costs of a steam reformer are therefore largely proportional to the capacity of the entire system. Increasing the steam reformer to increase capacity is not economically viable. Also, an increase in the operating pressure are set relatively narrow limits in the two-stage reforming, because the pipes already work in the steam reformer anyway at the load limit defined by pressure and temperature.

An alternative to two-stage reforming is the purely autothermal reforming of natural gas with the help of cheaper autothermal reformers (ATR). In order to provide the additional amount of oxygen required for this purpose, either oxygen from an air separation plant or a correspondingly larger amount of air is required. However, the cost of air separation or the provision of additional air and the removal of excess nitrogen are significant and, with plant capacities of up to 3,300 tpd of ammonia, compensate for the savings achieved by eliminating the steam reformer. However, devices for the separation of air and the separation of the excess nitrogen show a significant degression of the additional costs when increasing their capacity by increasing the components. With increasing capacity above 3300 tpd of ammonia, the increase in the components of plants based on purely autothermal reformers brings cost advantages compared to the two-stage reforming.

Furthermore, systems based on purely autothermal reforming have, in principle, a considerably greater potential for increasing the operating pressure in the production of synthesis gas. An increase in the operating pressure in the production of synthesis gas is not arbitrarily possible or useful even with purely autothermal reforming. The pressure dependence of the equilibrium position of the reforming reaction means that the methane conversion decreases with increasing pressure and the residual content of methane in the synthesis gas produced increases. In the synthesis gas treatment then an increasing proportion of the cycle stream must be removed from the synthesis (purge), whereby the plant economy is adversely affected. Furthermore, increasing the partial pressure of the carbon monoxide formed in the reforming by the pressure increase leads to additional stress in the subsequent treatment steps, in particular in the conversion of carbon monoxide. This partial pressure of carbon monoxide is already in conventional systems at the limit of technical feasibility. The conditions are exacerbated by the fact that the lowest possible addition of water vapor, ie the lowest possible water vapor / carbon ratio is sought for the reforming, as this allows the oxygen demand can be minimized. A smaller one Water vapor quantity causes larger partial pressures of the other gases in the mixture and thus has in principle the same effects as an increase in the total pressure, ie higher residual content of methane and greater partial pressure of carbon monoxide in the product gas.

WO 2004/063114 A2 discloses a method of producing hydrogen in which a heat exchanger reformer and an autothermal reformer are connected in parallel.

EP 0 999 178 A1 relates to a process for the production of synthesis gas, inter alia for the subsequent ammonia synthesis, in which a conventional steam reformer and an autothermal reformer are arranged in parallel. The product streams from both reformers are then combined with each other and further processed together.

US Pat. No. 6,444,712 B1 discloses a process for producing methanol from natural gas. Preferably, about half of the natural gas flow is directed to a steam reformer to produce reformed gas therein. The thus reformed gas is then mixed with the other half of the natural gas stream and sent to an autothermal reformer.

US 2013 312354 A1 relates to a process for the production of H_2 and CO from hydrocarbons and biofuel. For safety reasons, several smaller parallel autothermal reformers are preferably used.

These conventional processes for the production of synthesis gas are not satisfactory in every respect, especially with regard to an increase in capacity.

The invention has for its object to provide an advantageous method and apparatus for the production of synthesis gas for the subsequent ammonia synthesis. The process and apparatus should enable significant increases in capacity above the level of 3300 tpd of ammonia to be achieved without exceeding the technical and economical limits.

This object is solved by the subject matter of the claims.

(a) Bereitstellen eines Gasgemischs umfassend Kohlenwasserstoffe, vorzugsweise Methan oder Erdgas; Wasserdampf; und ein Oxidationsmittel, vorzugsweise Sauerstoff oder mit Sauerstoff angereicherte Luft;
(b) Reformieren des in Schritt (a) bereitgestellten Gasgemischs in einem ersten autothermen Reformer, wodurch ein erstes Synthesegas umfassend Wasserstoff, Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan erhalten wird;
(c) Erhöhen des Gehalts an Wasserstoff des in Schritt (b) erhaltenen ersten Synthesegases durch Abtrennen eines Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan;
(d) Bereitstellen eines Gasgemischs umfassend das in Schritt (c) abgetrennte Gasgemisch,
(e) Reformieren des in Schritt (d) bereitgestellten Gasgemischs in einem zweiten autothermen Reformer, wodurch ein zweites Synthesegas umfassend Wasserstoff, Kohlenstoffmonoxid und Kohlenstoffdioxid erhalten wird;

wobei der erste autotherme Reformer in Schritt (b) bei einem Druck betrieben wird, der höher ist als der Druck, bei dem der zweite autotherme Reformer in Schritt (e) betrieben wird.One aspect of the invention relates to a process for the production of synthesis gas comprising the steps

(A) providing a gas mixture comprising hydrocarbons, preferably methane or natural gas; Steam; and an oxidizing agent, preferably oxygen or oxygen-enriched air;
(b) reforming the gas mixture provided in step (a) in a first autothermal reformer, thereby obtaining a first synthesis gas comprising hydrogen, carbon monoxide, carbon dioxide and methane,
(c) increasing the content of hydrogen of the first synthesis gas obtained in step (b) by separating a mixed gas comprising carbon monoxide, carbon dioxide and methane;
(d) providing a gas mixture comprising the gas mixture separated in step (c);
(e) reforming the gas mixture provided in step (d) in a second autothermal reformer, thereby obtaining a second synthesis gas comprising hydrogen, carbon monoxide and carbon dioxide;

wherein the first autothermal reformer in step (b) is operated at a pressure higher than the pressure at which the second autothermal reformer is operated in step (e).

The inventive method is based on the reforming in two autothermal reformers at different pressures. The first autothermal reforming is operated at such a high pressure that the hydrogen-rich first synthesis gas formed after separation of CO, CO_2 and possibly residues of unreacted CH_4 can be passed directly before the second stage of the synthesis gas compressor, which is upstream of the ammonia reactor . This synthesis gas compressor is preferably multi-stage, wherein a first compressor stage preferably compresses the gas mixture to a first pressure in the range of 50 to 150 bar, more preferably 60 to 140 bar, and wherein a downstream second compressor stage the (pre-compressed) gas mixture to a second pressure in the range of preferably at least 150 bar, more preferably compressed at least 170, as required for the subsequent ammonia synthesis. The separation of CO, CO_2 and optionally CH_4 is preferably carried out by pressure swing adsorption (PSA, Pressure Swing Absorption) or with the aid of membranes. The separated gas mixture is optionally (preferably) compressed and fed to a second autothermal reforming and reformed here with air, possibly moderately oxygen-enriched air to a second synthesis gas. The subsequent purification of this second synthesis gas from the second autothermal reformer is then preferably carried out by (i) one or two-stage conversion of CO, (ii) separation of CO_2 and / or (iii) final purification, for example by methanation, pressure swing adsorption or nitrogen wash. The first synthesis gas and the second synthesis gas are then optionally combined after separate (pre-) compression, if necessary with the amount still required to achieve the desired stoichiometry Nitrogen enriched and fed to the ammonia synthesis in an ammonia reactor. In this case, the first synthesis gas is preferably compressed only in the second compressor stage of the synthesis gas compressor, while the second synthesis gas is preferred both in the first compressor stage and - after being combined with the first synthesis gas - in the second compressor stage.

The inventive method requires additional and / or other apparatus in comparison with a conventional single-stranded process management with only a single autothermal reformer. For example, a second autothermal reformer (preferably together with cooling section) for the synthesis gas, a device for separating off the remaining constituents of the synthesis gas (preferably by pressure swing adsorption) and an additional compressor are required for the process according to the invention. However, the method according to the invention makes it possible to operate the first autothermal reformer with a very low steam / carbon ratio and thus to minimize the oxygen requirement, ie also the size of the expensive air separation. The sizes of the devices for the subsequent purification of the synthesis gas from the second autothermal reformer are significantly reduced by the compared to the conventional single-strand process control smaller volume flows. Overall, therefore, there are cost advantages for the inventive method over a conventional single-strand system of the same capacity, which could not be realized single-stranded according to the current state of the art.

Autothermal reformers have an increased oxygen demand compared to conventional steam reformers. It has surprisingly been found that the less water vapor is added, the smaller the oxygen requirement for synthesis gas production becomes, the lower the water vapor / carbon ratio is. However, it was surprisingly found in this connection that the residual content of methane in the synthesis gas after reforming in the autothermal reformer increases with lower addition of steam and at elevated pressure to values that are no longer acceptable for the overall process.

In a purely single-stranded production of synthesis gas based on a single autothermal reformer would therefore increase the capacity to increase the pressure, the steam addition can also be increased accordingly to keep the residual content of methane after reforming at the level of the conventional system and the synthesis gas compressor relieve. As the addition of water vapor increases, however, the need for expensive oxygen also increases, so that a reduction in the oxygen requirement and corresponding operating and investment costs in the case of a pure single-strand synthesis gas based on a single autothermal reformer would not be feasible. Because of the high proportion of air separation in the total cost of an ammonia plant based on autothermal reforming, this has a significant impact on economy, i. on the cost relations compared to conventional systems. Ultimately, this results in a larger limit capacity, from which an ammonia plant based on autothermal reforming has cost advantages over a conventional system.

It has surprisingly been found that all the advantages of the autothermal reforming can be utilized if the reforming is carried out in two steps at different pressure levels. The first step preferably uses both the advantage of a small amount of steam in the process gas to minimize the required amount of oxygen as well as an increased pressure to relieve the synthesis gas compressor.

An autothermal reformer in the context of the invention is a reformer in which the heat produced during the reforming by exothermic reactions is used for endothermic reactions, so that the reforming process takes place autothermally. In this case, the autothermal reformer preferably has a catalyst and a burner. Reactors for the autothermal partial catalytic oxidation of noble metal catalysts which have no burner are preferably not autothermal reformers in the sense of the invention.

- der erste autotherme Reformer in Schritt (b) bei einem Druck betrieben, der mindestens um 5 bar, bevorzugter mindestens um 10 bar, noch bevorzugter mindestens um 15 bar, am bevorzugtesten mindestens um 20 bar und insbesondere mindestens um 25 bar höher ist als der Druck, bei dem der zweite autotherme Reformer in Schritt (e) betrieben wird; und/oder
- der erste autotherme Reformer in Schritt (b) bei einem Druck von mindestens 30 bar betreiben, bevorzugt mindestens 35 bar oder mindestens 40 bar, bevorzugter mindestens 45 bar oder mindestens 50 bar, noch bevorzugter mindestens 55 bar oder mindestens 60 bar, am bevorzugtesten mindestens 65 bar oder mindestens 70 bar, und insbesondere mindestens 75 bar oder mindestens 80 bar, und/oder

– der zweite autotherme Reformer in Schritt (e) bei einem Druck von höchstens 60 bar betrieben, bevorzugt höchstens 55 bar oder höchstens 50 bar, bevorzugter höchstens 45 bar oder höchstens 40 bar, noch bevorzugter höchstens 38 bar oder höchstens 36 bar, am bevorzugtesten höchstens 34 bar oder höchstens 32 bar, und insbesondere höchstens 30 bar, höchstens 28 bar, höchstens 26 bar, höchstens 24 bar, höchstens 22 bar oder höchstens 20 bar.

In the method according to the invention is preferred

- The first autothermal reformer in step (b) operated at a pressure which is at least 5 bar, more preferably at least 10 bar, more preferably at least 15 bar, most preferably at least 20 bar and in particular at least 25 bar higher than that Pressure at which the second autothermal reformer is operated in step (e); and or
- The first autothermal reformer in step (b) operated at a pressure of at least 30 bar, preferably at least 35 bar or at least 40 bar, more preferably at least 45 bar or at least 50 bar, more preferably at least 55 bar or at least 60 bar, most preferably at least 65 bar or at least 70 bar, and in particular at least 75 bar or at least 80 bar, and or
- The second autothermal reformer in step (e) operated at a pressure of at most 60 bar, preferably at most 55 bar or at most 50 bar, more preferably at most 45 bar or at most 40 bar, more preferably at most 38 bar or at most 36 bar, most preferably at most 34 bar or at most 32 bar, and in particular at most 30 bar, at most 28 bar, at most 26 bar, at most 24 bar, at most 22 bar or at most 20 bar.

Preferably, the first autothermal reformer in step (b) is operated at a pressure which is 20 to 45 bar higher than the pressure at which the second autothermal reformer is operated in step (e). In this case, the first autothermal reformer in step (b) is preferably operated at such a high pressure that after deduction of all further pressure losses downstream of the first autothermal reformer, the resulting gas mixture can safely be fed to the subsequent stage of a multi-stage synthesis gas compressor subsequent ammonia synthesis, said Compression ratio, for example, preferably 2.5.

The pressure at which the first autothermal reformer is operated is preferably in the range of 30 to 80 bar. A pressure below 30 bar is not preferred because this would adversely affect the dimensioning of the second autothermal reformer upstream compressor. A pressure above 80 bar is not preferred since this would adversely affect the equilibrium position of the reaction taking place in the first autothermal reformer (steam reforming).

The pressure at which the second autothermal reformer is operated is preferably in the range of 30 to 60 bar. A pressure below 30 bar is basically possible, but has an unfavorable effect on the dimensioning of the second autothermal reformer. A pressure above 60 bar is not preferred because then for a given compression ratio of the first autothermal reformer would have to be operated at such high pressures at which the equilibrium position of taking place in the first autothermal reformer reaction (steam reforming) would be on the side of the reactants.

– wird bevorzugt das Oxidationsmittel in Form von reinem Sauerstoff oder in Form von mit Sauerstoff angereicherter Luft mit einem Gehalt an Sauerstoff von mindestens 90 Vol.-%, bevorzugter mindestens 92 Vol.-%, noch bevorzugter mindestens 94 Vol.-%, am bevorzugtesten mindestens 96 Vol.-% und insbesondere mindestens 98 Vol.-% bereitgestellt, wobei der benötigte Sauerstoff vorzugsweise aus einer Luftzerlegungsanlage stammt; und/oder
– werden bevorzugt dem Gasgemisch die Kohlenwasserstoffe in Form von Methan oder Erdgas zugesetzt, wobei das Erdgas ggf. bevorzugt zuvor entschwefelt wurde; und/oder
– weist bevorzugt das bereitgestellte Gasgemisch ein molares Wasserdampf/Kohlenstoff-Verhältnis von höchstens 3,6, höchstens 3,4 oder höchstens 3,2 auf, bevorzugt höchstens 3,0, höchstens 2,8 oder höchstens 2,6; bevorzugter höchstens 2,4, höchstens 2,2 oder höchstens 2,0; noch bevorzugter höchstens 1,8, unter Umständen ggf. auch höchstens 1,6, höchstens 1,4, höchstens 1,2, höchstens 1,0, höchstens 0,8, höchstens 0,6, höchstens 0,4 oder höchstens 0,2; und/oder
– weist bevorzugt das bereitgestellte Gasgemisch einen Gehalt an Stickstoff von höchstens 10 Vol.-% auf, bevorzugter höchstens 8 Vol.-%, noch bevorzugter höchstens 6 Vol.-%, am bevorzugtesten höchstens 4 Vol.-%, und insbesondere höchstens 2 Vol.-%

In step (a) of the method according to the invention

it is preferred that the oxidizing agent be in the form of pure oxygen or in the form of oxygen-enriched air containing at least 90% by volume of oxygen, more preferably at least 92% by volume, even more preferably at least 94% by volume, most preferably provided at least 96 vol .-% and in particular at least 98 vol -%, wherein the required oxygen preferably originates from an air separation plant; and or
- Are preferably added to the gas mixture, the hydrocarbons in the form of methane or natural gas, wherein the natural gas, if appropriate, preferably previously desulfurized; and or
The gas mixture provided preferably has a molar steam / carbon ratio of not more than 3.6, not more than 3.4 or not more than 3.2, preferably not more than 3.0, not more than 2.8 or not more than 2.6; more preferably at most 2.4, at most 2.2 or at most 2.0; more preferably at most 1.8, possibly even at most 1.6, at most 1.4, at most 1.2, at most 1.0, at most 0.8, at most 0.6, at most 0.4 or at most 0, 2; and or
The gas mixture provided preferably has a content of nitrogen of not more than 10% by volume, more preferably not more than 8% by volume, even more preferably not more than 6% by volume, most preferably not more than 4% by volume and in particular not more than 2% by volume .-%.

The molar water vapor / carbon ratio in the context of the invention is the molar ratio of molecules of water vapor to atoms carbon in the gas mixture, but only those carbon atoms of compounds which pure hydrocarbons, i. are free of oxygen. Carbon atoms of alcohols, aldehydes, etc. are not included accordingly.

Although a molar water vapor / carbon ratio of greater than 3.2 is technically possible, it is not preferred because it would result in more oxygen being consumed than is necessary and the yield of hydrogen would decrease. Therefore, according to the invention, a molar steam / carbon ratio of 3.2 preferably represents the upper limit of the economy. A molar steam / carbon ratio of less than 0.3 is not preferred, since otherwise carbon black would form, which would deactivate the catalyst.

– ein molares Wasserstoff/Kohlenstoffmonoxid-Verhältnis von höchstens 4,5 auf, bevorzugt höchstens 4,2, höchstens 3,9 oder höchstens 3,6, bevorzugter höchstens 3,3, höchstens 3,0 oder höchstens 2,7; noch bevorzugter höchstens 2,4, höchstens 2,1 oder höchstens 1,8; am bevorzugtesten höchstens 1,5, höchstens 1,2 oder höchstens 1,0; und insbesondere höchstens 0,8, höchstens 0,6 oder höchstens 0,4; und/oder
– einen Gehalt an Methan von mindestens 0,3 Vol.-% auf, bevorzugt mindestens 0,6 Vol.-%, mindestens 0,9 Vol.-% oder mindestens 1,2 Vol.-%, bevorzugter mindestens 1,5 Vol.-%, mindestens 1,8 Vol.-% oder mindestens 2,1 Vol.-%, noch bevorzugter mindestens 2,4 Vol.-%, mindestens 2,7 Vol.-% oder mindestens 3,0 Vol.-%; am bevorzugtesten mindestens 3,3 Vol.-%, mindestens 3,6 Vol.-% oder mindestens 3,9 Vol.-%; und insbesondere mindestens 4,2 Vol.-%, mindestens 4,5 Vol.-% oder mindestens 4,8 Vol.-%; und/oder
– einen Gehalt an Wasserstoff von mindestens 30 Vol -% auf, bevorzugt mindestens 32 Vol.-%, mindestens 34 Vol.-% oder mindestens 36 Vol.-%; bevorzugter mindestens 38 Vol.-%, mindestens 40 Vol.-% oder mindestens 42 Vol.-%; noch bevorzugter mindestens 44 Vol.-%, mindestens 46 Vol.-% oder mindestens 48 Vol.-%, am bevorzugtesten mindestens 50 Vol.-%, mindestens 52 Vol.-% oder mindestens 54 Vol.-%; und insbesondere mindestens 56 Vol.-%, mindestens 58 Vol.-% oder mindestens 60 Vol.-%; und/oder
– einen Gehalt an Kohlenstoffmonoxid im Bereich von 20 ± 19 Vol.-% auf, bevorzugter 20 ± 16 Vol.-%, noch bevorzugter 20 ± 13 Vol.-%, am bevorzugtesten 20 ± 9 Vol.-%, und insbesondere 20 ± 5 Vol.-%; und/oder
– einen Gehalt an Kohlenstoffdioxid im Bereich von 12 ± 11 Vol.-% auf, bevorzugter 12 ± 10 Vol.-%, noch bevorzugter 12 ± 8 Vol.-%, am bevorzugtesten 12 ± 6 Vol.-%, und insbesondere 12 ± 4 Vol -%; und/oder
– einen Gehalt an Stickstoff von höchstens 10 Vol.-% auf, bevorzugter höchstens 8 Vol.-%, noch bevorzugter höchstens 6 Vol.-%, am bevorzugtesten höchstens 4

– einen Gehalt an Wasserdampf von 30 ± 29 Vol.-% auf, bevorzugter 30 ± 25 Vol.-%, noch bevorzugter 30 ± 20 Vol.-%, am bevorzugtesten 30 ± 15 Vol.-%, und insbesondere 30 ± 10 Vol.-%;

wobei die Gehaltsangaben jeweils Feuchtkonzentrationen sind.The first synthesis gas obtained in step (b) of the process according to the invention preferably has

A molar hydrogen / carbon monoxide ratio of at most 4.5, preferably at most 4.2, at most 3.9 or at most 3.6; more preferably at most 3.3, at most 3.0 or at most 2.7, even more preferably at most 2.4, at most 2.1 or at most 1.8; most preferably at most 1.5, at most 1.2 or at most 1.0; and in particular not more than 0.8, not more than 0.6 or not more than 0.4; and or

A content of methane of at least 0.3% by volume, preferably at least 0.6% by volume, at least 0.9% by volume or at least 1.2% by volume; more preferably at least 1.5 vol.%, at least 1.8 vol.% or at least 2.1 vol.%; even more preferably at least 2.4 vol%, at least 2.7 vol%, or at least 3.0 vol%; at the most preferably at least 3.3 vol%, at least 3.6 vol% or at least 3.9 vol%; and in particular at least 4.2% by volume, at least 4.5% by volume or at least 4.8% by volume; and or

A hydrogen content of at least 30% by volume, preferably at least 32% by volume, at least 34% by volume or at least 36% by volume; more preferably at least 38% by volume, at least 40% by volume or at least 42% by volume; even more preferably at least 44% by volume, at least 46% by volume or at least 48% by volume; most preferably at least 50% by volume, at least 52% by volume or at least 54% by volume; and in particular at least 56% by volume, at least 58% by volume or at least 60% by volume; and or

A content of carbon monoxide in the range of 20 ± 19% by volume, more preferably 20 ± 16% by volume, more preferably 20 ± 13% by volume, most preferably 20 ± 9% by volume, and especially 20 ± 5% by volume, and or

A content of carbon dioxide in the range of 12 ± 11% by volume, more preferably 12 ± 10% by volume, more preferably 12 ± 8% by volume, most preferably 12 ± 6% by volume, and especially 12 ± 4% by volume, and or

A content of nitrogen of at most 10% by volume, more preferably at most 8% by volume, even more preferably at most 6% by volume, most preferably at most 4% by volume, and especially at most 2% by volume; and or

A water vapor content of 30 ± 29% by volume, more preferably 30 ± 25% by volume, more preferably 30 ± 20% by volume, most preferably 30 ± 15% by volume, and especially 30 ± 10% by volume .-%;

wherein the contents are each moist concentrations.

Unless expressly stated otherwise, all percentages in relation to gas mixtures containing water vapor are to be construed as wet concentrations

– einen Gehalt an Wasserstoff im Bereich von 38 bis 69 Vol.-% auf; und/oder
– einen Gehalt an Kohlenstoffmonoxid im Bereich von 7 bis 31 Vol.-% auf; und/oder
– einen Gehalt an Kohlenstoffdioxid im Bereich von 3 bis 19 Vol.-% auf.

Calculated dry, the first synthesis gas obtained in step (b) of the process according to the invention is preferred

A content of hydrogen in the range from 38 to 69% by volume; and or
A content of carbon monoxide in the range of 7 to 31% by volume; and or
A content of carbon dioxide in the range of 3 to 19% by volume.

The content of methane in the first synthesis gas can basically also be more than 4.8% by volume, in particular if a low molar steam / carbon ratio is set and a comparatively small amount of oxygen is fed to the first autothermal reformer, so that the Temperature in the POX zone of the reactor is comparatively low. However, methane contents of more than 4.8% by volume are not preferred since they have to be separated off in step (c) of the process according to the invention, so that subsequently a larger amount of gas must be recompressed to the pressure of the second autothermal reformer. This increases the operating costs.

Suitable measures to adjust the relative content of the individual gas components in autothermally produced first and second synthesis gas are known in the art, in particular oxygen, steam, hydrocarbon, temperature and pressure. If necessary, the influence of these parameters on the composition of the synthesis gas can be verified by suitable routine tests.

The first synthesis gas produced in the first autothermal reformer is poor or even unsuitable for a subsequent CO conversion because of its comparatively high CO partial pressure and the comparatively low content of water vapor. With the help of a pressure swing adsorption (PSA) but the hydrogen can be separated at a high pressure level and fed directly to the synthesis gas compressor. The pressure in the first autothermal reforming is therefore preferably selected so that the hydrogen can be fed directly to the synthesis gas compressor, preferably the second stage of a multistage synthesis gas compressor.

Preferably, in step (c) of the process according to the invention, the separation of the gas mixture comprising CO, CO_2 and CH_4 from the first synthesis gas (i) by pressure swing adsorption (PSA - Pressure Swing Adsorption) or (ii) by selective membrane permeation and subsequent pressure swing adsorption.

In pressure swing adsorption, the gas mixture comprising H_2, CO, CO_2 and CH_4 is physically separated from each other under pressure by adsorption. Preferably, porous materials (eg zeolites, activated carbon) are used as adsorbent. According to the invention, the release effect can be based on two different principles: equilibrium adsorption or molecular sieve action. The gas mixture is preferably introduced under elevated pressure into a fixed bed reactor, which is filled with the adsorbent, so that it is flowed through. CO, CO_2 and CH_4 from the gas mixture are now adsorbed and at the outlet of the bed H_2 can be removed. After a while, the adsorber bed is saturated and the process is switched by valves so that the outlet for H_2 is closed and an outlet for CO, CO_2 and CH_4 is opened. This is accompanied by a pressure reduction. At the lower pressure, the adsorbed CO, CO_2 and CH_4 are now desorbed again and can be recovered at the outlet. Two or more adsorbers alternately loaded and unloaded preferably allow continuous operation.

in a preferred variant of the method according to the invention, in step (c) the first synthesis gas is first fed to a membrane separation plant for separating carbon monoxide and carbon dioxide by selective membrane permeation. The membrane has the property that it lets carbon monoxide and carbon dioxide through much faster than hydrogen. The driving force for this separation process is the difference in the partial pressures of the component to be separated on the high and low pressure side of the membrane. Here, the pressure on the low pressure side of the membrane is set so that it is only slightly higher than the pressure of the hydrocarbons (natural gas) at the plant boundary. In the membrane separation plant, the first synthesis gas is separated into a hydrogen and methane-enriched retentate stream and a carbon monoxide and carbon dioxide-enriched permeate stream. The retentate stream is then fed to the separation of carbon monoxide, carbon dioxide and methane according to step (c), wherein the separation of carbon monoxide, carbon dioxide and methane then preferably also takes place by pressure swing adsorption. The resulting exhaust gas contains predominantly methane, previously not deposited carbon monoxide and carbon dioxide and in small quantities also hydrogen. It can be further used as fuel gas, e.g. in an auxiliary boiler for steam generation.

– einen Gehalt an Wasserstoff von mindestens 90 Vol.-%, bevorzugter mindestens 92 Vol.-%, noch bevorzugter mindestens 94 Vol.-%, am bevorzugtesten mindestens 96 Vol.-%, und insbesondere mindestens 98 Vol.-%; und/oder
– einen Gehalt an Stickstoff von höchstens 10 Vol.-% auf, bevorzugter höchstens 8 Vol.-%, noch bevorzugter höchstens 6 Vol.-%, am bevorzugtesten höchstens 4 Vol.-%, und insbesondere höchstens 2 Vol.-%.

After separating the gas mixture comprising carbon monoxide, carbon dioxide and methane in step (c), the first synthesis gas has been preferred

A hydrogen content of at least 90% by volume, more preferably at least 92% by volume, even more preferably at least 94% by volume, most preferably at least 96% by volume, and especially at least 98% by volume; and or
A content of nitrogen of at most 10% by volume, more preferably at most 8% by volume, more preferably at most 6% by volume, most preferably at most 4% by volume, and most preferably at most 2% by volume.

The main part of the hydrogen is contained after the separation of the gas mixture in the first synthesis gas. For its part, the separated gas mixture comprises CO formed for the most part in the reforming, unreacted CH_4 and further, comparatively small amounts of CO_2 and H_2. It has surprisingly been found that the further implementation of this stream is most advantageously carried out in a second autothermal reforming step in order to react both the residual methane and avoid problems with the CO conversion by the large partial pressure of the carbon monoxide. Possibly, after addition of further hydrocarbons, preferably of methane or natural gas, the separated gas mixture, which preferably originates from the pressure swing adsorption, fed to a second autothermal reformer and here also autothermally reformed with compressed air, possibly also moderately oxygen-enriched air as the oxidation medium. Due to the lower pressure in this reforming and a specifically greater addition of steam to the process gas results in this second autothermal reformer, a residual content of methane, which is comparable to that of a conventional plant.

The process according to the invention thus utilizes the advantages of a higher pressure level in the first autothermal reforming, but avoids a larger methane input into the preferably subsequent ammonia synthesis and greater stress on the subsequent process stages for the purification of the synthesis gas and also allows a significant relief of the synthesis gas compressor.

- wird bevorzugt dem Gasgemisch Luft oder mit durch Sauerstoff angereicherte Luft mit einem Gehalt an Sauerstoff von höchstens 90 Vol.-%, bevorzugter höchstens 80 Vol.-%, noch bevorzugter 70 Vol.-%, am bevorzugtesten höchstens 60 Vol.-% und insbesondere höchstens 50 Vol.-% zugesetzt; und/oder
- werden bevorzugt dem Gasgemisch Kohlenwasserstoffe in Form von Methan oder Erdgas zugesetzt, wobei das Erdgas ggf. bevorzugt zuvor entschwefelt wurde, und/oder
- weist bevorzugt das bereitgestellte Gasgemisch ein molares Wasserdampf/Kohlenstoff-Verhältnis von mindestens 3,2 auf, bevorzugt mindestens 3,4, mindestens 3,6 oder mindestens 3,8; bevorzugter mindestens 4,0, mindestens 4,2 oder mindestens 4,4; noch bevorzugter mindestens 4,6, mindestens 4,8 oder mindestens 5,0; am bevorzugtesten mindestens 5,2, mindestens 5,4 oder mindestens 5,6; und insbesondere mindestens 5,8, mindestens 6,0 oder mindestens 6,2; und/oder
- weist bevorzugt das bereitgestellte Gasgemisch einen Gehalt an Stickstoff von höchstens 70 Vol.-% auf, bevorzugter höchstens 60 Vol.-%, noch bevorzugter höchstens 50 Vol.-%, am bevorzugtesten höchstens 40 Vol.-%, und insbesondere höchstens 30 Vol.-%; und/oder
- weist bevorzugt das bereitgestellte Gasgemisch einen Gehalt an Stickstoff von mindestens 10 Vol.-% auf, bevorzugter mindestens 20 Vol.-%, noch bevorzugter mindestens 30 Vol.-%, am bevorzugtesten mindestens 40 Vol.-%, und insbesondere mindestens 50 Vol.-%.

in step (d) of the method according to the invention

Is preferably the gas mixture air or oxygen-enriched air with an oxygen content of at most 90 vol .-%, more preferably at most 80 vol .-%, more preferably 70 vol .-%, most preferably at most 60 vol .-% and in particular at most 50% by volume added; and or
Hydrocarbons in the form of methane or natural gas are preferably added to the gas mixture, the natural gas possibly having been previously desulphurized, and or
The gas mixture provided preferably has a molar steam / carbon ratio of at least 3.2, preferably at least 3.4, at least 3.6 or at least 3.8; more preferably at least 4.0, at least 4.2, or at least 4.4; more preferably at least 4.6, at least 4.8, or at least 5.0; most preferably at least 5.2, at least 5.4, or at least 5.6; and in particular at least 5.8, at least 6.0 or at least 6.2; and or
The gas mixture provided preferably has a nitrogen content of at most 70% by volume, more preferably at most 60% by volume, even more preferably at most 50% by volume, most preferably at most 40% by volume, and in particular not more than 30% by volume .-%; and or
The gas mixture provided preferably has a nitrogen content of at least 10 vol. %, more preferably at least 20% by volume, even more preferably at least 30% by volume, most preferably at least 40% by volume, and most preferably at least 50% by volume.

After the reaction in the second autothermal reformer is carried out according to the invention preferably a high-temperature conversion of carbon monoxide with steam to carbon dioxide and hydrogen. Therefore, the second autothermal reformer is preferably operated so that after steam reforming there is still enough water vapor in the second synthesis gas to enable the high temperature conversion of carbon monoxide to be efficiently carried out.

The molar steam / carbon ratio in the autothermal reforming in the second autothermal reformer in step (e) of the process according to the invention is preferably greater than the molar steam / carbon ratio in the autothermal reforming in the first autothermal reformer in step (b). Preferably, the relative difference of the molar steam / carbon ratio in step (e) to the molar steam / carbon ratio in step (b) is at least 0.1 or at least 0.2, more preferably at least 0.3 or at least 0.4 more preferably at least 0.5 or at least 0.6, most preferably at least 0.7 or at least 0.8 and in particular at least 0.9 or at least 1.0.

- ein molares Wasserstoff/Kohlenstoffmonoxid-Verhältnis von höchstens 4,5 auf, bevorzugt höchstens 4,2, höchstens 3,9 oder höchstens 3,6; bevorzugter höchstens 3,3, höchstens 3,0 oder höchstens 2,7; noch bevorzugter höchstens 2,4, höchstens 2,1 oder höchstens 1,8; unter Umständen ggf. auch höchstens 1,5, höchstens 1,2, höchstens 1,0, höchstens 0,8, höchstens 0,6 oder höchstens 0,4; und/oder
- einen Gehalt an Methan von höchstens 10 Vol.-%, höchstens 7,5 Vol.-%, höchstens 5,0 Vol.-% oder höchstens 4,8 Vol.-% auf, bevorzugt höchstens 4,5 Vol.-%, höchstens 4,2 Vol.-% oder höchstens 3,9 Vol.-%; bevorzugter höchstens 3,6 Vol.-%, höchstens 3,3 Vol.-% oder höchstens 3,0 Vol.-%; noch bevorzugter höchstens 2,7 Vol.-%, höchstens 2,4 Vol.-% oder höchstens 2,1 Vol.-%; am bevorzugtesten höchstens 1,8 Vol.-%, höchstens 1,5 Vol.-% oder höchstens 1,2 Vol.-%; und insbesondere höchstens 0,9 Vol.-%, höchstens 0,6 Vol.-% oder höchstens 0,3 Vol.-%; und/oder
- einen Gehalt an Wasserstoff von mindestens 50 Vol.-% auf, bevorzugt mindestens 52 Vol.-%, mindestens 54 Vol.-% oder mindestens 56 Vol.-%; bevorzugter mindestens 58 Vol.-%, mindestens 60 Vol.-% oder mindestens 62 Vol.-%, noch bevorzugter mindestens 64 Vol.-%, mindestens 66 Vol.-% oder mindestens 68 Vol.-%; am bevorzugtesten mindestens 70 Vol.-%, mindestens 72 Vol.-% oder mindestens 74 Vol.-%; und insbesondere mindestens 76 Vol.-%, mindestens 78 Vol.-% oder mindestens 80 Vol.-%; und/oder
- einen Gehalt an Kohlenstoffmonoxid im Bereich von 20 ± 19 Vol.-% auf, bevorzugter 20 ± 16 Vol.-%, noch bevorzugter 20 ± 13 Vol.-%, am bevorzugtesten 20 ± 9 Vol.-%, und insbesondere 20 ± 5 Vol.-%; und/oder
- einen Gehalt an Kohlenstoffdioxid im Bereich von 12 ± 11 Vol.-% auf, bevorzugter 12 ± 10 Vol.-%, noch bevorzugter 12 ± 8 Vol.-%, am bevorzugtesten 12 ± 6 Vol.-%, und insbesondere 12 ± 4 Vol.-%; und/oder
- einen Gehalt an Stickstoff von höchstens 10 Vol.-% auf, bevorzugter höchstens 8 Vol.-%, noch bevorzugter höchstens 6 Vol.-%, am bevorzugtesten höchstens 4 Vol.-%, und insbesondere höchstens 2 Vol.-%; und/oder
- einen Gehalt an Wasserdampf von 40 ± 30 Vol.-% auf, bevorzugter 40 ± 25 Vol.-%, noch bevorzugter 40 ± 20 Vol.-%, am bevorzugtesten 40 ± 15 Vol.-%, und insbesondere 40 ± 10 Vol.-%;

wobei die Gehaltsangaben jeweils Feuchtkonzentrationen sind.The second synthesis gas obtained in step (e) of the process according to the invention preferably has

A molar hydrogen / carbon monoxide ratio of at most 4.5, preferably at most 4.2, at most 3.9 or at most 3.6, more preferably at most 3.3, at most 3.0 or at most 2.7; even more preferably at most 2.4, at most 2.1 or at most 1.8, possibly also not more than 1,5, not more than 1,2, not more than 1,0, not more than 0,8, not more than 0,6 or not more than 0,4; and or
A content of methane of not more than 10% by volume, not more than 7,5% by volume, not more than 5,0% by volume or not more than 4,8% by volume, preferably not more than 4.5% by volume at most 4.2% by volume or at most 3.9% by volume; more preferably at most 3.6% by volume, at most 3.3% by volume or at most 3.0% by volume; even more preferably at most 2.7% by volume, at most 2.4% by volume or at most 2.1% by volume; most preferably at most 1.8 vol%, at most 1.5 vol% or at most 1.2 vol%; and in particular at most 0.9 vol.%, at most 0.6 vol.% or at most 0.3 vol.%; and or
A content of hydrogen of at least 50% by volume, preferably at least 52% by volume, at least 54% by volume or at least 56% by volume; more preferably at least 58% by volume, at least 60% by volume or at least 62% by volume; even more preferably at least 64% by volume, at least 66% by volume or at least 68% by volume; most preferably at least 70% by volume, at least 72% by volume or at least 74% by volume; and in particular at least 76% by volume, at least 78% by volume or at least 80% by volume; and or
A content of carbon monoxide in the range of 20 ± 19% by volume, more preferably 20 ± 16% by volume, more preferably 20 ± 13% by volume, most preferably 20 ± 9% by volume, and especially 20 ± 5% by volume; and or
A content of carbon dioxide in the range of 12 ± 11% by volume, more preferably 12 ± 10% by volume, more preferably 12 ± 8% by volume, most preferably 12 ± 6% by volume, and especially 12 ± 4% by volume; and or
A content of nitrogen of at most 10% by volume, more preferably at most 8% by volume, even more preferably at most 6% by volume, most preferably at most 4% by volume, and especially at most 2% by volume; and or
A content of water vapor of 40 ± 30% by volume, more preferably 40 ± 25% by volume, more preferably 40 ± 20% by volume, most preferably 40 ± 15% by volume, and especially 40 ± 10% by volume .-%;

wherein the contents are each moist concentrations.

– einen Gehalt an Wasserstoff im Bereich von 38 bis 69 Vol.-% auf; und/oder
– einen Gehalt an Kohlenstoffmonoxid im Bereich von 7 bis 31 Vol.-% auf, und/oder
– einen Gehalt an Kohlenstoffdioxid im Bereich von 3 bis 19 Vol.-% auf.

Calculated dry, the second synthesis gas obtained in step (e) of the process according to the invention is preferred

A content of hydrogen in the range from 38 to 69% by volume; and or
A content of carbon monoxide in the range of 7 to 31% by volume; and or
A content of carbon dioxide in the range of 3 to 19% by volume.

In particular, if the subsequent purification of the second synthesis gas is not carried out by CO_2 scrubbing and methanation, but by pressure swing adsorption or N_2 scrubbing, thereby the residual methane can be separated from the second syngas with synonymous. The separated methane can then be used together with the also separated carbon monoxide, carbon dioxide and excess nitrogen as fuel gas. In this variant of the method according to the invention, it is perfectly tolerable if the content of methane in the second synthesis gas is more than 5% by volume. If the subsequent purification of the second synthesis gas, however, by CO_2 scrubbing and methanation, so the content of methane in the second synthesis gas is preferably below 5 vol .-%.

A comparatively high content of water vapor in the second synthesis gas is preferred so that sufficient steam is available for the preferably subsequent high-temperature conversion of carbon monoxide. A content of water vapor before high-temperature conversion of, for example, 35 to 40% by volume is preferred. A content of water vapor of more than 40% by volume may also be relevant, but is not preferred. For a correspondingly high relative molar water vapor / carbon ratio at the entrance of the second autothermal reformer and thus a high content of water vapor in the second synthesis gas at the outlet of the second autothermal reformer more oxygen would be required, which would adversely affect the yield of hydrogen .

The residual content of methane in the first synthesis gas, which is obtained during the autothermal reforming in the first autothermal reformer in step (b), is preferably greater than the residual content of methane in the second synthesis gas, which in the autothermal reforming in the second autothermal reformer in step (e). Preferably, the relative difference of the residual content of methane of the first synthesis gas obtained in step (b) and the residual content of methane of the second synthesis gas obtained in step (e) is at least 0.4 vol% or at least 0.8 vol% more preferably at least 1.2 vol.% or at least 1.6 vol.%, more preferably at least 2.0 vol.% or at least 2.4 vol.%, most preferably at least 2.8 vol.% or at least 3.2% by volume and in particular at least 3.6% by volume or at least 4.0% by volume.

The content of carbon monoxide in the first synthesis gas, which is obtained in the autothermal reforming in the first autothermal reformer in step (b), is preferably greater than the content of carbon monoxide in the second synthesis gas, which in the autothermal reforming in the second autothermal reformer in step (e). Preferably, the relative difference in the content of carbon monoxide of the first synthesis gas obtained in step (b) and the content of carbon monoxide of the second synthesis gas obtained in step (e) is at least 0.4% by volume or at least 0.8% by volume. more preferably at least 1.2 vol.% or at least 1.6 vol.%, more preferably at least 2.0 vol.% or at least 2.4 vol.%, most preferably at least 2.8 vol.% or at least 3.2% by volume and in particular at least 3.6% by volume or at least 4.0% by volume.

The content of steam in the first synthesis gas, which is obtained in the autothermal reforming in the first autothermal reformer in step (b), is preferably smaller than the content of water vapor in the second synthesis gas, which in the autothermal reforming in the second autothermal reformer in step (e). Preferably, the relative difference in the content of water vapor of the second synthesis gas obtained in step (e) and the content of water vapor of the first synthesis gas obtained in step (b) is at least 5 vol.% Or at least 6 vol.%, More preferably at least 7 vol % or at least 8% by volume, more preferably at least 9% by volume or at least 10% by volume, most preferably at least 11% by volume or at least 12% by volume and in particular at least 13% by volume or at least 14% by volume.

(f) ein- oder zweistufiges Konvertieren von Kohlenstoffmonoxid, welches in dem in Schritt
(e) erhaltenen zweiten Synthesegas enthalten ist, zu Kohlenstoffdioxid,
(g) Abtrennen von Kohlenstoffdioxid, welches in dem in Schritt (f) erhaltenen zweiten Synthesegas enthalten ist; und
(h) abschließendes Reinigen des in Schritt (g) erhaltenen zweiten Synthesegases vorzugsweise durch Methanisierung oder Stickstoffwäsche.

The method according to the invention preferably comprises the additional steps

(f) one or two step conversion of carbon monoxide, which is in the step
(e) obtained second synthesis gas is included, to carbon dioxide;
(g) separating carbon dioxide contained in the second synthesis gas obtained in step (f); and
(h) finally purifying the second synthesis gas obtained in step (g), preferably by methanation or nitrogen scrubbing.

(f) ein- oder zweistufiges Konvertieren von Kohlenstoffmonoxid, welches in dem in Schritt

(e) erhaltenen zweiten Synthesegas enthalten ist, zu Kohlenstoffdioxid; und

(g') Abtrennen eines Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan vom zweiten Synthesegas durch Druckwechsel-Adsorption.
Alternatively, the method according to the invention comprises the additional steps

(f) one or two step conversion of carbon monoxide, which is in the step
(e) obtained second synthesis gas is included, to carbon dioxide; and
(g ') separating a gas mixture comprising carbon monoxide, carbon dioxide and methane from the second synthesis gas by pressure swing adsorption.

If the process according to the invention comprises the pressure swing adsorption according to step (g '), carbon monoxide, carbon dioxide and methane are completely separated off from the second synthesis gas by the pressure swing adsorption. Nitrogen is only partially removed, so that sufficient nitrogen remains in the second synthesis gas in order to adjust the required H_2 / N_2 ratio for the ammonia synthesis can. Hydrogen is practically not separated by the pressure swing adsorption. The exhaust stream of the pressure swing adsorption can be burned for example as a fuel gas in an auxiliary boiler. If the process according to the invention also comprises separation by pressure swing adsorption in step (c), the process according to the invention comprises a total of two pressure swing adsorptions.

The measures necessary for carrying out these steps are known to the person skilled in the art. In this regard, for example, reference may be made to A. Nielsen, I. Dybkjaer, Ammonia Catalysis and Manufacture, Springer Berlin 1995, chapter 6, pages 202-326 ,

The steps (a) to (h) of the method according to the invention are preferably carried out in succession, although the provision in step (a) at least partially coincides with the first autothermal reforming in step (b) and / or according to the provision in step (a). d) at least partially simultaneously with the first autothermal reforming in step (e) can be performed.

- einen Gehalt an Wasserstoff im Bereich von 40 ± 35 Vol.-% auf, bevorzugter 40 ± 30 Vol.-%, noch bevorzugter 40 ± 25 Vol.-%, am bevorzugtesten 40 ± 20 Vol.-%, und insbesondere 40 ± 15 Vol.-%; und/oder
- einen Gehalt an Stickstoff im Bereich von 60 ± 55 Vol.-% auf, bevorzugter 60 ± 50 Vol.-%, noch bevorzugter 60 ± 45 Vol.-%, am bevorzugtesten 60 ± 40 Vol.-%, und insbesondere 60 ± 35 Vol.-%.

After converting carbon monoxide in step (f), separating carbon dioxide in step (g) and finally purifying in step (h) or after separating carbon monoxide, carbon dioxide and methane in step (g '), the second synthesis gas prefers

A content of hydrogen in the range of 40 ± 35% by volume, more preferably 40 ± 30% by volume, more preferably 40 ± 25% by volume, most preferably 40 ± 20% by volume, and especially 40 ± 15% by volume; and or
A content of nitrogen in the range of 60 ± 55% by volume, more preferably 60 ± 50% by volume, more preferably 60 ± 45% by volume, most preferably 60 ± 40% by volume, and especially 60 ± 35% by volume.

The process according to the invention is preferably operated continuously. The process of the present invention preferably provides a total production of more than 3300 tpd of synthesis gas (total over the first synthesis gas and the second synthesis gas, preferably after separation in step (c) and final purification in step (h)), more preferably at least 3500 tpd synthesis gas more preferably at least 3800 t of synthesis gas and in particular at least 4000 t of synthesis gas.

The first autothermal reformer preferably has a capacity of at least 1000 tpd of syngas based on the immediate, unpurified reaction product of the first autothermal reformer of step (b), more preferably at least 1500 tpd, more preferably at least 2000 tpd, most preferably at least 2500 tpd, and especially At least 3000 tpd of syngas.

The second autothermal reformer preferably has a capacity of at least 1000 tpd of syngas based on the instant, unpurified reaction product of the second autothermal reforming in step (e), more preferably at least 1500 tpd, even more preferably at least 2000 tpd, most preferably at least 2500 tpd, and especially At least 3000 tpd of syngas.

Preferably, the capacity of the first autothermal reformer substantially corresponds to the capacity of the second autothermal reformer.

The hydrocarbon used in step (a) and optionally additionally in step (d) of the process according to the invention is preferably natural gas, which is optionally first desulfurized. The total consumption of natural gas is preferably provided as a natural gas stream, which is preferably divided into two partial streams: the first natural gas partial stream is added in step (a) to the gas mixture, which is then reformed in step (b) in the first autothermal reformer, and the second partial gas stream is added in step (d) to the gas mixture, which is subsequently reformed in step (e) in the second autothermal reformer. In a preferred embodiment, the relative weight ratio of the first partial gas stream to the second partial gas stream is less than 1: 1, more preferably less than 1: 1.5. In another preferred embodiment, the relative weight ratio of the first partial gas stream to the second partial gas stream is greater than 1: 1, more preferably greater than 1.5: 1. In another preferred embodiment, the relative weight ratio of the first partial gas stream to the second partial gas stream is in the range of 70:30 to 30:70, more preferably 60:40 to 40:60, and most preferably 55:45 to 45:55.

A further aspect of the invention relates to a process for the production of ammonia comprising the above-described process according to the invention for the production of synthesis gas, wherein the first synthesis gas and the second synthesis gas are fed together to an ammonia reactor.

Preferably, the first synthesis gas obtained in step (c) is compacted without further purification with the aid of a synthesis gas compressor to a pressure at which the ammonia reactor is operated. Preferably, the ammonia reactor is operated at a pressure of at least 150 bar, more preferably at least 170 bar, even more preferably at least 190 bar, most preferably at least 210 bar and especially at least 230 bar.

The second synthesis gas obtained in step (e) is preferably purified according to the additional steps (f), (g) and (h) or according to the additional steps (f) and (g '); then precompressed with the aid of a synthesis gas compressor initially to a pressure which is lower than the pressure at which the ammonia reactor is operated; and then compressed by means of another synthesis gas compressor to a pressure at which the ammonia reactor is operated. Preferably, the second synthesis gas is first at a pressure in the range using a syngas compressor precompressed from 100 ± 50 bar, more preferably 100 ± 40 bar, even more preferably 100 ± 30 bar, most preferably 100 ± 20 bar and especially 100 ± 10 bar; and then compressed using a further synthesis gas compressor to a pressure at which the ammonia reactor is operated, which is preferably at least 150 bar, more preferably at least 170 bar, more preferably at least 190 bar, most preferably at least 210 bar and in particular at least 230 bar.

The process of the present invention preferably provides a total production of more than 3300 tpc of ammonia, more preferably at least 3500 tpd, even more preferably at least 3700 tpd, most preferably at least 3900 tpd and especially at least 4000 tpd of ammonia.

- einen ersten autothermen Reformer zum Herstellen eines ersten Synthesegases umfassend Wasserstoff, Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan aus einem Gasgemisch umfassend Kohlenwasserstoffe, Wasserdampf und ein Oxidationsmittel, vorzugsweise Sauerstoff oder mit Sauerstoff angereicherte Luft;
- eine Anlage zum Abtrennen eines Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan von dem ersten Synthesegas;
- einen zweiten autothermen Reformer zum Herstellen eines zweiten Synthesegases umfassend Wasserstoff, Kohlenstoffmonoxid und Kohlenstoffdioxid aus einem Gasgemisch umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan.

– Mittel zum Überführen des von dem ersten Synthesegas abtrennten Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan zu dem zweiten autothermen Reformer,

wobei der erste autotherme Reformer für einen Druck ausgelegt ist, der höher ist als der Druck, für den der zweite autotherme Reformer ausgelegt ist.Another aspect of the invention relates to a device for the production of synthesis gas comprising

A first autothermal reformer for producing a first synthesis gas comprising hydrogen, carbon monoxide, carbon dioxide and methane from a gas mixture comprising hydrocarbons, water vapor and an oxidizing agent, preferably oxygen or oxygen-enriched air;
A plant for separating a gas mixture comprising carbon monoxide, carbon dioxide and methane from the first synthesis gas;
A second autothermal reformer for producing a second synthesis gas comprising hydrogen, carbon monoxide and carbon dioxide from a gas mixture comprising carbon monoxide, carbon dioxide and methane;
- Means for transferring the separated from the first synthesis gas gas mixture comprising carbon monoxide, carbon dioxide and methane to the second autothermal reformer;

wherein the first autothermal reformer is designed for a pressure that is higher than the pressure for which the second autothermal reformer is designed.

The device according to the invention is suitable for carrying out the process according to the invention for the production of synthesis gas. A further aspect of the invention therefore relates to the use of the apparatus according to the invention for the production of synthesis gas in the process according to the invention for the production of synthesis gas.

All preferred embodiments, which were described above in connection with the method according to the invention, apply analogously also with regard to the design and construction of the device according to the invention and are therefore not repeated in this respect.

Preferably, the plant for separating the gas mixture comprising carbon monoxide, carbon dioxide and methane from the first synthesis gas comprises a pressure swing adsorption plant. In a preferred embodiment, the pressure swing adsorption plant is preceded by a membrane separation plant, in which initially a large part of the carbon monoxide and carbon dioxide contained in the first synthesis gas is separated off as permeate stream. The retentate stream containing hydrogen as well as methane and uncut carbon monoxide and carbon dioxide is then fed to the pressure swing adsorption unit.

– eine Entschwefelungsanlage zum Entfernen von Schwefelverbindungen aus Kohlenwasserstoffen und Mittel zum Überführen der entschwefelten Kohlenwasserstoffe zum ersten autothermen Reformer oder einer dem autothermen Reformer vorgeschalteten Mischanlage; und/oder
– eine Luftzerlegungsanlage und Mittel zum Überführen von reinem Sauerstoff oder von mit Sauerstoff angereicherter Luft mit einem Gehalt an Sauerstoff von mindestens 90 Vol.-% zum ersten autothermen Reformer oder einer dem autothermen Reformer vorgeschalteten Mischanlage; und/oder
– eine ein- oder zweistufige Konvertierungsanlage zur Konvertierung von Kohlenstoffmonoxid, welches in dem zweiten Synthesegas enthalten ist, zu Kohlenstoffdioxid; und/oder
– eine Anlage zur Abtrennung von Kohlenstoffdioxid, welches in dem zweiten Synthesegas enthalten ist; und/oder
– eine Anlage zum Abtrennen eines Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan von dem zweiten Synthesegas, vorzugsweise durch Druckwechsel-Adsorption; und/oder
– eine Anlage zur abschließenden Reinigung des zweiten Synthesegases, vorzugsweise durch Methanisierung oder Stickstoffwäsche.

The device according to the invention preferably comprises

- A desulfurization plant for removing sulfur compounds from hydrocarbons and means for transferring the desulfurized hydrocarbons to the first autothermal reformer or upstream of the autothermal reformer mixing plant; and or
- An air separation plant and means for transferring pure oxygen or oxygen-enriched air containing at least 90 vol .-% of oxygen to the first autothermal reformer or upstream of the autothermal reformer mixing plant; and or
A one- or two-stage conversion plant for converting carbon monoxide contained in the second synthesis gas into carbon dioxide; and or
- An apparatus for the separation of carbon dioxide, which is contained in the second synthesis gas, and or
A system for separating a gas mixture comprising carbon monoxide, carbon dioxide and methane from the second synthesis gas, preferably by pressure swing adsorption; and or
- An installation for the final purification of the second synthesis gas, preferably by methanation or nitrogen scrubbing.

The air separation plant is preferably dimensioned so that it produces enough pure oxygen, as required in the method according to the invention. For example, the production of synthesis gas for an ammonia plant with a capacity of 3600 tpd requires 73 t / h of pure oxygen.

The sulfur compounds can be separated by conventional methods known to those skilled in the art. For example, the sulfur compounds can be adsorbed on Activated carbon or be separated on molecular sieves or by catalytic hydrogenation of the organic sulfur compounds and subsequent adsorption of the hydrogen sulfide formed on zinc oxide

– einen mehrstufigen Verdichter umfassend eine erste Verdichtungsstufe und eine nachgeschaltete zweite Verdichtungsstufe;
– Mittel zum Überführen des ersten Synthesegases aus der Anlage zum Abtrennen des Gasgemischs umfassend Kohlenstoffmonoxid, Kohlenstoffdioxid und Methan von dem ersten Synthesegas zur zweiten Verdichtungsstufe; und
– eine Anlage zur abschließenden Reinigung des zweiten Synthesegases, vorzugsweise durch Methanisierung, Druckwechsel-Adsorption oder Stickstoffwäsche, und Mittel zum Überführen des abschließend gereinigten zweiten Synthesegases zur ersten Verdichtungsstufe.

The device according to the invention preferably comprises

- A multi-stage compressor comprising a first compression stage and a downstream second compression stage;
- Means for transferring the first synthesis gas from the plant for separating the gas mixture comprising carbon monoxide, carbon dioxide and methane from the first synthesis gas to the second compression stage; and
A plant for the final purification of the second synthesis gas, preferably by methanation, pressure swing adsorption or nitrogen scrubbing, and means for transferring the finally purified second synthesis gas to the first compression stage.

Another aspect of the invention relates to an apparatus for the production of ammonia from synthesis gas comprising the inventive apparatus described above for the production of synthesis gas and an ammonia reactor.

The device according to the invention is suitable for carrying out the process according to the invention for the production of ammonia. A further aspect of the invention therefore relates to the use of the apparatus according to the invention for the production of ammonia in the process according to the invention for the production of ammonia.

The invention is based on the 1 exemplified. A person skilled in the art will recognize that, in the case of a device according to the invention, it is not absolutely necessary for all the imaged features to be realized simultaneously.

1 schematically illustrates a device according to the invention or the inventive method for the production of ammonia from natural gas (C_nH_{2n+2}). The natural gas is preferably first freed from the C_{2+} fraction and optionally in a desulfurization plant (5) desulfurizes. Subsequently, a first natural gas flow via line (a) to a compressor (12), wherein the natural gas to the operating pressure of the first autothermal reformer (1) is compressed. Behind the compressor (12) the natural gas stream is preferably mixed with water vapor and the mixture comprising natural gas and water vapor is the first autothermal reformer (1). An air separation plant (6) preferably provides pure oxygen or oxygen-enriched air, which is also the first autothermal reformer (1) is supplied. The mixing of natural gas and water vapor can alternatively in the first autothermal reformer (1) or outside the first autothermal reformer (1) in line (c) or in a first autothermal reformer (1) upstream mixing plant done. According to 1 First, the mixing of the first natural gas stream with water vapor in line (c) and then the addition of oxygen in the first autothermal reformer (1).

The autothermal reforming in the first autothermal reformer (1) provides a first synthesis gas, which is preferably in the heat exchanger (13) and then via line (d) of a plant (4) is supplied to separate CO, CO_2 and CH_4, wherein the separation of CO, CO_2 and CH_4 is preferably carried out by pressure swing adsorption. The thus purified first synthesis gas, which has an increased content of hydrogen, via line (e), preferably without further treatment, optionally after mixing with the required for the ammonia synthesis amount of compressed nitrogen, direct compression stage (11), which preferably forms the second stage of a multi-stage compressor, which comprises the upstream first compression stage (10) and the downstream second compression stage (11). From the second compression level (11), the first synthesis gas is added to the ammonia reactor (3).

The Annex to 4) separated gas mixture comprising CO, CO_2 and CH_4 is via lines (f) and (g) the compressor (14), which is the second autothermal reformer (2) is connected upstream. It is preferably first mixed with a second natural gas stream, which is introduced via line (b). The mixture of the second natural gas stream and the gas mixture comprising CO, CO_2 and CH_4 is then in the compressor (14) to the operating pressure of the second autothermal reformer (2) compacted. Subsequently, water vapor is added to the mixture. From the compressor (14), the gas mixture, possibly after preheating, the second autothermal reformer (2). Air or oxygen enriched air is injected into the compressor (15) to the operating pressure of the second autothermal reformer (2) and also the second autothermal reformer (2). Pure oxygen from the air separation plant (6) via line (s) directly to the second autothermal reformer (2) and / or the air in front of the compressor (15). The mixing of natural gas, gas mixture comprising CO, CO_2 and CH_4, and water vapor can alternatively in the second autothermal reformer (2) or outside the second autothermal reformer (2) in line (m) or in a second autothermal reformer (2) upstream mixing plant done. According to 1 First, the mixing of the second natural gas stream, gas mixture comprising CO, CO_2 and CH_4, and Steam in line (g) and then the addition of air into the second autothermal reformer (2). If the separation is in Annex (4) by pressure swing adsorption, this is in Appendix (4) separated gas mixture comprising CO, CO_2 and CH_4 at a pressure which is usually insufficient to bring it to the suction side of the compressor (14). In this case, an additional cycle compressor is preferably installed (in 1 not shown), which compresses the separated gas mixture back to the pressure of the natural gas at the plant boundary.

The autothermal reforming in the second autothermal reformer (2) provides a second synthesis gas, which is preferably in the heat exchanger (16) and then via line (h) of a one- or two-stage conversion plant (7) is supplied for the conversion of CO. The CO is converted to CO_2 and H_2 with the addition of H_2O and in this way the content of H_2 and CO_2 in the second synthesis gas is further increased and the CO content is reduced. After preferential cooling in the heat exchanger (17), the converted second synthesis gas is passed via line (i) of an installation (8th) for the removal of CO_2, preferably using suitable chemical or physical solvents (carbon dioxide scrubbing). The second synthesis gas, which now contains only residual amounts of CO and other impurities in addition to H_2 and N_2, is in an over line (k) plant (9) subjected to a final purification, preferably by methanation, pressure swing adsorption or N_2 scrubbing. Subsequently, the finally purified second synthesis gas of the first compression stage (10) in which it is precompressed before it is combined with the first synthesis gas stream and the second compression stage (11) is supplied from which it after compression to the ammonia reactor (3) is supplied.

2 schematically illustrates a further preferred variant according to the invention of the device or the method according to the invention for the production of ammonia from natural gas. Unlike the in 1 illustrated embodiment, the converted second synthesis gas after preferential cooling in the heat exchanger (17) via line (i) of a plant (10) is supplied to separate CO, CO_2 and CH_4, wherein the separation of CO, CO_2 and CH_4 is preferably carried out by pressure swing adsorption. The second synthesis gas purified in this way is purified via line (j), preferably without further treatment, if appropriate after mixing with the amount of compressed nitrogen required for the ammonia synthesis, directly in the first compression stage (10).

3 schematically illustrates a further preferred variant according to the invention of the device or the method according to the invention for the production of ammonia from natural gas. Unlike the in 1 and 2 illustrated embodiments, the first synthesis gas is preferably in the heat exchanger (13) and then via line (d) of a membrane separation plant (11) for separating CO and CO_2. In the membrane separation plant (11), the cooled first synthesis gas is separated into a hydrogen and methane-enriched retentate stream and a CO and CO_2 -enriched permeate stream. The permeate stream is sent via line (f) to the suction side of the compressor (14). The retentate flow is continued via line (o) of the system (4) for separating CO, CO_2 and CH_4, wherein the separation of CO, CO_2 and CH_4 is preferably carried out by pressure swing adsorption. The exhaust gas which is in Anage (4) is separated, contains predominantly methane, previously not deposited CO and CO_2 and in small quantities also H_2.

QUOTES INCLUDE IN THE DESCRIPTION

This list of the documents listed by the applicant has been generated automatically and is included solely for the better information of the reader. The list is not part of the German patent or utility model application. The DPMA assumes no liability for any errors or omissions.

Cited patent literature

WO 2004/083114 **[0008]**
EP 0999178 A1 **[0009]**
US 6444712 B1 **[0010]**
US 2013312384 A1 **[0011]**

Cited non-patent literature

A. Nielsen, I. Dybkjaer, Ammonia Catalysis and Manufacture, Springer Berlin 1995, Chapter 6, pages 202-326 **[0054]**

Urea Product Expansion by Newly Developed CO_2 Recovery Process from Primary Reformer Flue Gas

Urea production of 110% has been expanded by the newly developed CO_2 recovery process from Primary Reformer flue gas in ammonia plant.

Kansai Electric Power Co. INC. and Mitsubishi Heavy Industries, Ltd. have been collaborating on the development of the flue gas recovery technology since 1990. The first commercial plant for flue gas CO_2 recovery using the newly developed solvent (KS-1) has been operating commercially in Malaysia since October 1999. KS-1 solvent has been developed for low partial pressure of carbon dioxide such as the flue gas of the primary reformer, auxiliary boiler, gas turbine and so on.

In the Malaysian ammonia and urea complex plant, ammonia production was not balanced with CO_2 production due to the natural gas source with the rich methane. Therefore, the urea production was limited by the shortage of CO_2 production and the excess ammonia was accumulated in the storage tank or purge gas and the excess syn-gas was fired as reformer fuel. Petronas Fertilizer (KEDAH) SDN. BHD. Company had decided to install the newly developed CO_2 recovery system from the reformer flue gas to increase the urea production and to balance the ammonia production with the CO_2 production, increasing urea capacity from 1800 MTPD to over 2000 MTPD.

By applying this new technology, it is possible to match the ammonia production with CO_2 production for the full conversion to the granule urea product with recovery of the carbon dioxide from the flue gas independent of the natural gas source that is supplied. As a result, the heavier components of ethane, propane, butane will be extracted from the natural gas source at the upstream plant and the extracted gas will be used separately for the ethylene plants and propane supply, with the remaining natural gas containing the rich methane being supplied to the fertilizer and methanol plants.

This new technology will reduce the effluent CO_2 in the flue gas from the primary reformer and help the Kyoto Protocol for reducing CO_2 effluent gas.

Ryota Shimura
Mitsubishi Heavy Industries, LTD

Co-Author : Petronas Fertilizer (Kedah) Sdn Bhd

Introduction

Natural gas has been the primary feed source of the synthesis gas in ammonia and methanol plants opposed to naphtha feed. It is expected that the trend of using natural gas for the ammonia and methanol plants will steadily increase.

Usually ammonia produced in an ammonia plant is

Topsoe, Inc. – EX1003
Page 485 of 1210

converted to granular urea with the carbon dioxide which is also produced in the ammonia plant.

In case of using the natural gas feed source in the ammonia and urea complex plant, an excess of ammonia is normally produced since more ammonia is produced than carbon dioxide.

Therefore, the reformed hydrogen gas from the ammonia plant is used for the primary reformer fuel to prevent the excess ammonia production in natural gas feed plant. The excess ammonia can be converted to urea product if CO_2 gas is imported from the outside.

In this paper, it is mentioned that the urea production can be enhanced by the recovered CO_2 from the primary reformer flue gas of the ammonia plant using natural gas as feed source.

The new developed CO_2 recovery solvent (KS-1) is suitable for recovering the CO_2 gas from the reformer flue gas.

Conventional Ammonia Plant

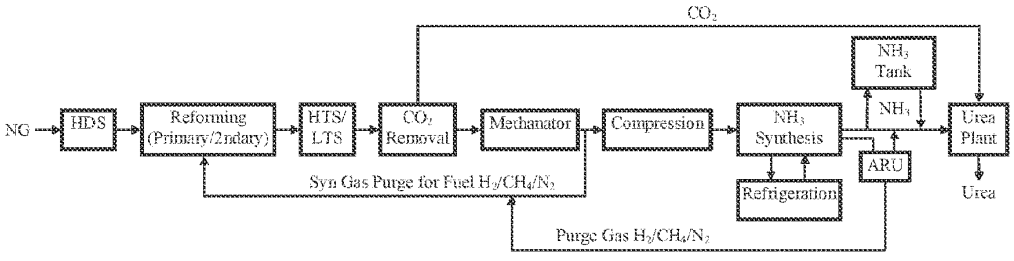
In an ammonia plant using natural gas feed, an excess of ammonia is normally produced since the hydrogen is produced more than the carbon dioxide due to the methane rich in natural gas.

However, it is not feasible to install ammonia export facilities such as the ammonia loading or the ammonia storage bottling because of the small quantity of the excess ammonia production.

Therefore, the purge gas extracted from the synthesis loop is sent to the ammonia recovery unit and only ammonia is recovered from the purge gas and the remaining purge gas including methane, nitrogen and extensive quantities of hydrogen is used for the reformer fuel in order to treat the excess hydrogen.

In case that excess ammonia is still being produced even when the purge gas including hydrogen is used for the reformer fuel, the excess synthesis gas is withdrawn from the outlet of methanator and then fired in the reformer with the purge gas until the CO_2 product is matched with the ammonia product for the urea plant.

This results in the front end facilities such as primary, secondary reformer, reactors, waste heat facilities and CO_2 removal facilities increasing in capacity compared to the synthesis loop facilities and also the higher energy consumption due to firing the hydrogen reformed from natural gas.



ARU: Ammonia Recovery Unit

Figure 1. Conventional Ammonia Plant

Topsoe, Inc. – EX1003
Page 486 of 1210

In addition, the product ammonia is stored in ammonia storage tank during stoppage of urea plant. It is difficult to convert the stored ammonia in the tank to urea product in normal operating condition because of the lack of CO_2.

In order to convert the ammonia in the ammonia storage tank to urea product, it is required to reduce the synthesis loop load with the normal front end operation and vent the excess syn-gas to flare upstream of the synthesis loop in order to produce the necessary CO_2 gas. (See Figure-1)

Advanced Ammonia and Urea Complex Plant with Flue Gas CO_2 Recovery

The excess ammonia can be converted to urea product by importing CO_2 gas from the outside of plant and the hydrogen gas from the synthesis purge gas can be recycled to the suction of the syn-gas compressor. However, it is very rare to have a CO_2 gas supply plant near the ammonia and urea complex plant.

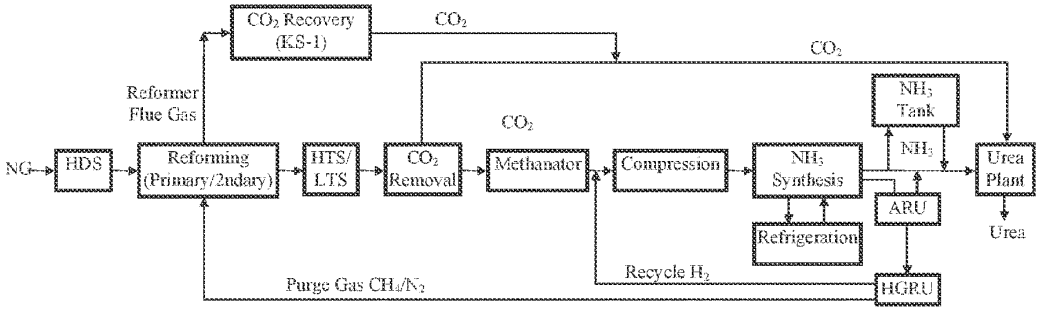
It is considered that CO_2 gas is extracted from the flue gas of the primary reformer in ammonia plant by the chemical absorption and the recovered CO_2 gas and excess ammonia is converted to urea product.

However, the conventional solvent is not suitable for absorbing the CO_2 gas from the flue gas in the primary reformer due to the low partial pressure of CO_2 in flue gas and the high energy consumption for the CO_2 regeneration.

Also, the degradation of amine in the CO_2 recovery system, higher amine consumption and corrosion trouble have been reported using conventional solvent like mono-ethanolamine.

Therefore, it is necessary to develop the new solvent for recovering the CO_2 gas in the reformer flue gas. It is found that the new CO_2 recovery solvent (KS-1) developed by Kansai Electric Power Company and Mitsubishi Heavy Industries, Ltd. is suitable for recovering CO_2 gas from the reformer flue gas.

The flow scheme of the advanced ammonia and urea complex plant with the CO_2 recovery process from the flue gas in the primary reformer is shown in Figure-2. This new developed scheme solves the problem of the shortfall of CO_2 gas and the excess ammonia production.



ARU: Ammonia Recovery Unit
HGRU: Hydrogen Recovery Unit

Figure 2. Advanced Ammonia & Urea Complex Plant with Flue Gas CO_2 Recovery

Topsoe, Inc. – EX1003
Page 487 of 1210

New CO_2 Recovery System

CO_2 absorption from the boiler flue gas or the gas turbine exhaust gas in the power plants by the chemical absorption methods requires the high energy for the regeneration of the absorbents containing CO_2 because of the low partial pressure of CO_2 in the flue gas.

Kansai Electric Power Company and Mitsubishi Heavy Industries, Ltd. have been collaborating on the development of flue gas CO_2 recovery technology since 1990 which is named Kansai Mitsubishi Carbon Dioxide Recovery (KMCDR) process.

A comprehensive range of available amines were examined and tested, with the new advanced KS-1 solvent developed without toxic, dramatically improving CO_2 absorbency, regeneration and low degradability.

This CO_2 recovery system is suitable for absorbing the low partial pressure of CO_2 gas such as the boiler flue gas and the gas turbine exhaust gas. This new developed solvent is being named KS-1 solvent.

The MHI advanced CO_2 removal system offers comprehensive advancements in process configuration and energy efficiencies over conventional systems.

Extracted flue gas is cooled down from 200 degC to 40-50 degC through the flue gas cooler and the exhaust cooled gas flows to the CO_2 absorber and the CO_2 gas in the flue gas is absorbed by KS-1 solvent in the CO_2 absorber while the remaining gas is exhausted from the top of the CO_2 absorber to atmosphere.

KS-1 solution absorbing CO_2 is pumped up to the CO_2 regenerator and CO_2 is regenerated by the steam reboiler at the bottom of the regenerator. The regenerated CO_2 product gas is cooled down at the overhead cooler at the top of regenerator flowing to the user such as urea plant, methanol plant and CO_2 gas plant. (See Figure -3)

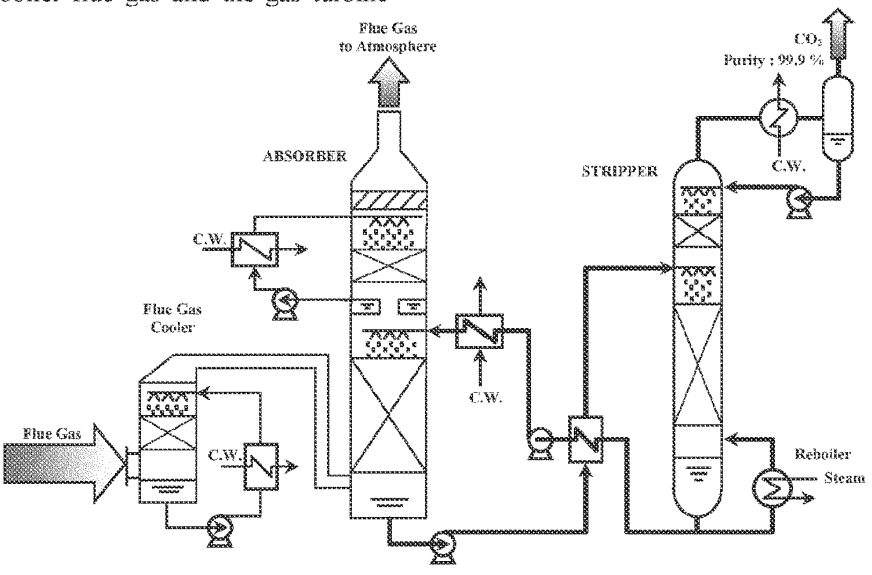


Figure 3. Flue Gas CO_2 Recovery System

Topsoe, Inc. – EX1003
Page 488 of 1210

Application of CO_2 Recovery Process from Flue Gas to Ammonia & Urea Complex Plant

Recently, it is requested to study that the source of the ammonia and urea complex plant is changed from naphtha to natural gas feed to improve the energy consumption by the owner of the fertilizer plant and a few projects have reached engineering stage.

In this study using the natural gas feed, the excess ammonia will be produced because of the lack of CO_2 production.

A conventional counter measure of CO_2 gas shortfall is that excess natural gas is reformed in the primary reformer in order to produce CO_2 gas matched with the urea production as described the above.

Alternative way is that the necessary CO_2 gas for urea production is recovered from the flue gas of primary reformer.

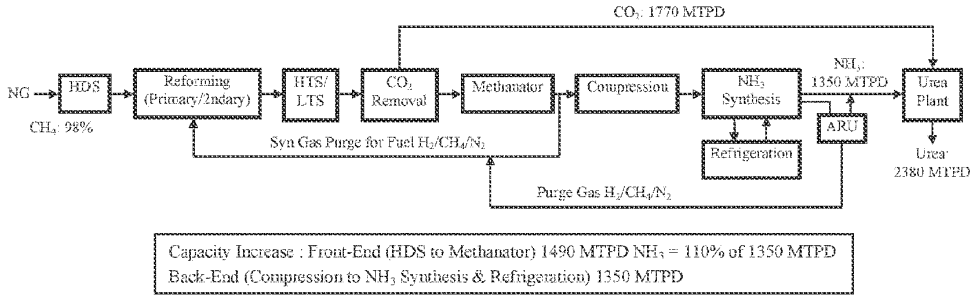
The study result of both cases is shown as follows.

The natural gas condition is similar to the gas source supplied from the liquid natural gas plant.

Natural gas source:
CH_4: 98%, C_2H_6: 1%, C_3H_8: 0.5%, N_2: 0.5%
Production:
Ammonia 1350 MTPD, Urea 2380 MTPD

CO_2 gas is needed to 1750 MTPD for the full conversion of the ammonia product to urea plant including the CO_2 gas loss in urea plant.

The above natural gas leads the lack of CO_2 because of methane rich in the natural gas. Which means excess hydrogen is produced from the natural gas for the necessity of CO_2 gas and is used as the primary reformer fuel. (See Figure-4).



ARU: Ammonia Recovery Unit

Figure 4. Larger Front-End Capacity Case

Alternatively in case of installation of the new CO_2 recovery system at the reformer stack, the necessary CO_2 gas of 160 MTPD is extracted from the flue gas in the primary reformer.

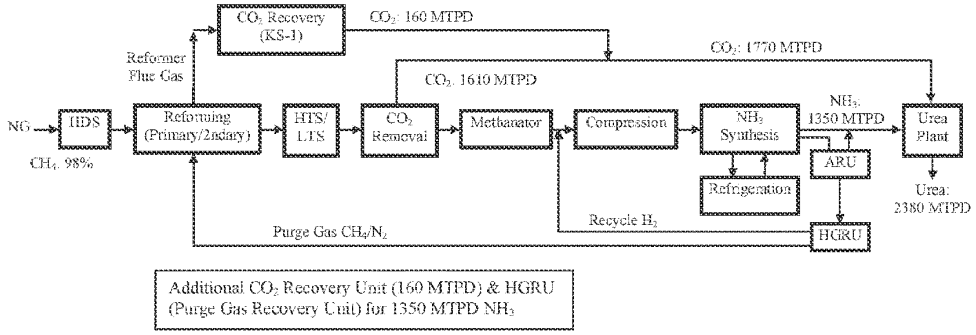
The CO_2 gas is mixed with the other CO_2 gas from ammonia plant and the mixed CO_2 gas is used as the source of the urea product. As a result, it is not necessary to fire the excess syn-gas in the reformer and the hydrogen in the purge gas is recovered by the additional hydrogen recovery unit at the outlet of the ammonia recovery unit and the recovered hydrogen is recycled by the suction of the syn-gas compressor. (See Figure-5)

Topsoe, Inc. – EX1003
Page 489 of 1210

The new flue gas CO_2 recovery system reduces the consumption of the process natural gas by 10 %. It means that the front-end facilities such as primary and secondary reformer, reactors, the waste heat facilities and CO_2 removal facilities can be reduced to 90% or the ammonia and urea production can increase to 110% if the ammonia synthesis system and urea & granulation plant have enough margin.

Considering the utility consumption in the flue gas CO_2 recovery plant such as the electricity of the flue gas blower, additional cooling water and the regeneration steam, the total unit energy consumption of ammonia plant reduces by -0.11 Gcal/MT-NH_3 (LHV Base) because of reducing the consumption of process natural gas dramatically. (See Table-1)

In addition, if this CO_2 recovery plant is installed in a methanol plant, the extracted CO_2 from the flue gas in the steam reformer is mixed to process natural gas or the synthesis gas and then methanol production can increases to 110 – 120% because CO and CO_2 gas is the source of the methanol. The unit operations energy consumption is the same as the original methanol plant even though the utility consumption of CO_2 recovery system and the CO_2 booster compressor is considered.



ARU: Ammonia Recovery Unit
HGRU: Hydrogen Recovery Unit

Figure 5. Flue Gas CO_2 Recovery Case

Table 1. Comparison of Energy Consumption

[Gcal/MT-NH_3]

	Larger Front-End	CO_2 Recovery
Process NG	Base	− 0.549
Fuel NG	Base	+ 0.316
Export Steam	Base	+ 0.124
Total	Base	− 0.109

Topsoe, Inc. – EX1003
Page 490 of 1210

First Commercial CO_2 Recovery Plant

The first commercial flue gas CO_2 recovery plant using KS-1 solvent for the ammonia and urea complex plant has been constructed in Petronas Fertilizer (Kedah) Sdn Bhd in Malaysia.

Petronas Fertilizer (Kedah) Sdn Bhd (PFK) has a complex for ammonia (1350 MTPD), urea (1750 MTPD), methanol (200 MTPD) and urea formaldehyde (17 MTPD) at Kedah in Malaysia. This plant has urea bagging and handling facilities and also ammonia export facilities including ammonia bottling, truck loading and rail loading. Therefore, the excess ammonia can be treated through these export facilities.

At first, PFK designed larger front-end facility in the ammonia plant in order to produce CO_2 gas matched with the ammonia production in case of supplying methane rich gas.

Moreover, considering the risk of stopping the ammonia export facilities by the unexpected plant stoppages in future, PFK continued to study the way of the treatment of the excess ammonia in the unexpected accidental conditions and finally decided not only to increase the front-end capacity but also to install the new CO_2 removal system which extracts 160 MTPD (Max. 200 MTPD) CO_2 gas from the primary reformer flue gas in ammonia plant.

In addition, PFK also made the decision of designing enough margin of the urea and granulation capacity considering the additional facility of CO_2 recovery system. This CO_2 recovery system leads to the full conversion of ammonia product to urea product and can treat the stored ammonia in the ammonia storage tank in any operating case. As a result, operating flexibility increases significantly in this plant.

In the PFK plant, CO_2 gas recovered from the flue gas of the steam reformer in the ammonia plant is mixed with the other CO_2 product from the Benfield system in the ammonia plant and delivered by suction of the CO_2 Compressor in the urea plant and then it is used for the source of the granule urea.

This CO_2 recovery plant leads the urea product expansion from 1800 MTPD to 2000 MTPD. The flue gas CO_2 recovery plant started on 20th October, 1999 and has operated continuously. Excellent performance of the process in terms of low steam consumption, very low solvent loss has been confirmed comparing the conventional solvent.

Main operation parameters of the flue gas CO_2 recovery plant are as follows;

- CO_2 Purity .....More than 99.9 vol% (Dry base). Impurities are nitrogen and oxygen
- CO_2 Recovery Ratio .....90 % at normal operation, however more than 97 %CO_2 recovery was attained by increasing steam consumption
- Steam Consumption..... 1.5 ton low pressure steam (@3.5K/G) / ton CO_2 recovered
- Amine Loss.....0.35 kg/ton CO_2 Recovered (See Figure -6, Table-2 and Table-3)

Table 2. Design Conditions of Flue Gas CO_2 Recovery Plant

- Flue Gas Source — Steam Reformer Flue Gas
- Flue Gas Flow Rate — 47,000 Nm^3/H
- Flue Gas Temperature — 168°C
- Flue Gas Composition

	(vol.%)
N_2	67.79
CO_2	8.08
O_2	0.85
Ar	1.00
H_2O	22.28
SOx	2.44(ppm)
NOx	200 (ppm)
Total	100.00

- CO_2 Recovery % — 90%

Topsoe, Inc. – EX1003
Page 491 of 1210

Table 3. Product CO_2 Condition

- CO_2 Flow Rate	3,400 Nm^3/H (160 MTPD) Max. 200 MTPD
- Recovered CO_2 Pressure	0.55Bar Gauge
- CO_2 Purity	More than 99.9 vol.% (Dry Base)

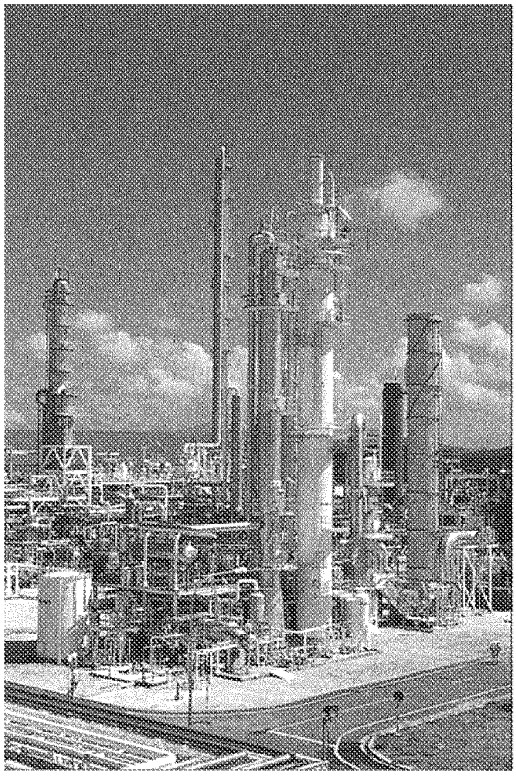


Figure 6. CO_2 Recovery Plant in Petronas Fertilizer (Keda) Sdn. Bhd.

Conclusion

This advanced developed CO_2 recovery system helps to a balance of the ammonia production and the urea production with natural gas as source.

This system can also recover the necessary CO_2 gas for treating the stored ammonia in the storage tank from the reformer flue gas. Which means the excess urea product can be produced from the stored ammonia in normal operating condition if the urea and granulation plant has excess margin.

This advanced system has been operating at Petronus Fertilizer in Malaysia since 1999 and in Japan for CO_2 product from 2005.

Two expansion urea projects are at construction stage in India and one expansion urea project is at engineering stage in Middle East with another at feasibility study stage with results highlighting considerable expansion potential for methanol gross.

The application of the new CO_2 recovery system to the EOR (enhanced oil recovery) are also being studied, where the recovered CO_2 gas from the power plant is injected in the oil field to increase the oil production.

In the future, it will be expected that the useful ethane, propane and butane are extracted from the natural gas at the well of natural gas and they are supplied to the ethylene plant, chemical plant, and propane gas plant with remaining natural gas containing rich methane is supplied to the fertilizer and methanol plant. At this time, this newly developed CO_2 recovery system helps the fertilizer and methanol plants. (See Figure-7)

In addition, this advanced technology can reduce effluent CO_2 gas to 90% in the flue gas from the primary reformer in ammonia and methanol plant and helps the Kyoto Protocol for reducing CO_2 effluent gas.

Topsoe, Inc. – EX1003
Page 492 of 1210

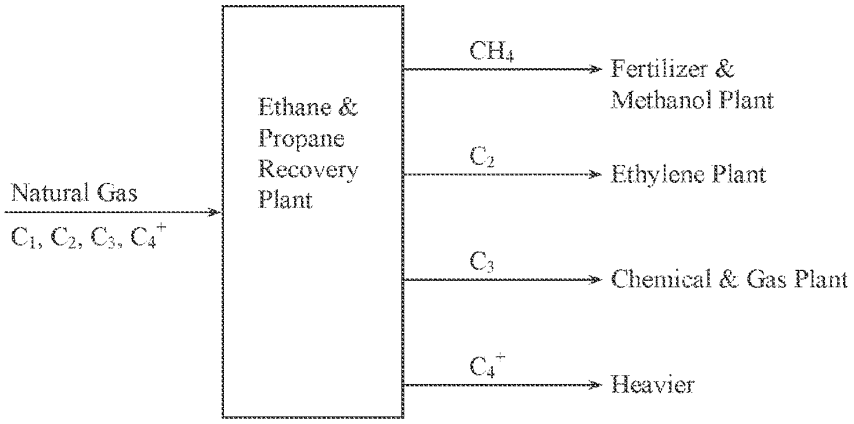


Figure 7. Natural Gas Distribution

References

Mimura, T., et al (1995) Energy Covers, Mgmt 36 (1995) p.397

Mimura, T., et al. 1996, Carbon Dioxide Removal, Cambridge, MA, USA. 9-11 September 1996, p.57

Mimura, T., Satsumi, S., Iijima, M. and Mitsuoka et al. (1999) Proceedings of the Fourth International Conference on Greenhouse Gas Control Technologies, Interlaken, Switzerland, (Editors: Reimer, P, Eliasson, B. and Wokaun, A.), Pergamon, p.71

Topsoe, Inc. – EX1003
Page 493 of 1210

Topsoe, Inc. – EX1003
Page 494 of 1210

Uhde



Autothermal reforming: a flexible syngas route with future potential

by

Dr. Klaus Noelker and Dr. Joachim Johanning

Uhde GmbH

Dortmund, Germany

Prepared for Presentation at

NITROGEN & SYNGAS 2010 International Conference

Bahrain

28 February – 3 March 2010

ABSTRACT

The autothermal reforming technology has been widely discussed in the past on conferences and in technical magazines. Compared to the steam methane reformer (SMR) with its multitude of tubes the autothermal reformer (ATR) offers a much simpler mechanical setup and superior operational robustness. The ATR can provide a wider syngas composition range than the SMR, especially significantly lower H_2:CO ratios.

Numerous ATRs are in operation worldwide. However, most of them operate as secondary reformers in ammonia and methanol plants in collaboration with steam reformers. Only a few true stand alone ATRs have been realized up to now. For ammonia and methanol plants the technology has so far been considered uneconomical. Natural gas based GTL plants, for which the ATR is the best choice, have not been built in large numbers as yet.

A comprehensive evaluation of the economic viability of an ATR based ammonia or methanol plant must take into consideration that the ATR requires oxygen. It also provides significantly less waste heat than the SMR for process media preheating and steam generation. So far, the additional operating costs for the utilities and the capital cost for the required equipment have eliminated the cost advantages of the stand alone ATR for ammonia plants and apparently also for methanol plants.

However, with ever growing plant capacities the competitiveness of ATR based plants is improving continuously. Mainly responsible for this are the different building-cost-to-capacity relationships of SMRs and air separation plants.

Uhde established an ATR development programme some years ago. A pilot plant has been built and is in operation since June 2009. There the applicability and robustness of the Uhde ATR concept is being validated.

The paper describes the pilot plant concept, its main design features, experiences made during erection and commissioning and outlines the extensive test program. Also, an ATR based ammonia process flowsheet is presented. Finally, an economic comparison between a conventional SMR-based ammonia plant with an ATR-based plant for a large capacity is discussed.

INTRODUCTION

Gas mixtures composed mainly of hydrogen and carbon monoxide are commonly addressed as synthesis gases. They are the base for important processes such as the syntheses of ammonia and methanol.

As required by the reactions which take place in the syntheses the syngases vary considerably in composition. Table 1 lists the most important processes and names the main requirements with respect to syngas composition.

Table 1: Synthesis gas composition requirements of downstream processes

process	synthesis gas composition requirements
ammonia	$(H_2 + CO) / N_2 \approx 3.0$
methanol	$(H_2 - CO_2) / (CO + CO_2) \approx 2.0$
hydrogen	max. H_2 content
gas-to-liquids	$H_2 : CO \approx 2.0$

Given their main constituents hydrogen and carbon monoxide synthesis gases can be processed from practically any carbon containing feedstock such as natural gas, naphtha, coal or petrol coke plus water via cracking and (steam) reforming. Coking has also been an important source.

Due to the heats of formation of the species involved all these processes are highly endothermic. The transfer of heat to the process gases to force the desired reactions can be effected via heat transfer through surrounding walls or by internal (autothermal) heat generation through partial combustion of the process gas.

A number of syngas generators are available, competing with each other for the different downstream processes. Table 2 names the most important syngas generator concepts and differentiates between externally and autothermally heated devices.

As Table 2 illustrates, most of the syngas generators operate on hydrocarbons as feedstocks. The coke oven basically extracts the volatile hydrocarbon components from the charged coal (dry distillation). It delivers a syngas composition not too different from the steam reformer, albeit with a significantly higher hydrocarbon content.

Table 2: Synthesis gas generator types

syngas generator	feedstock
external heating	
steam reformer	natural gas, naphtha
coke oven	coal
autothermal (internal) heating	
autothermal reformer	natural gas
partial oxidation reactor	natural gas
gasifier	coal, petrol coke

By nature, the syngas generators operating with autothermal heating have significantly higher CO and CO_2 contents in their syngases than the generators with external heating, i.e. much smaller H_2 : CO ratios. In syngas generators with external heating the carbon oxides are to be found in the flue gases of the external heating.

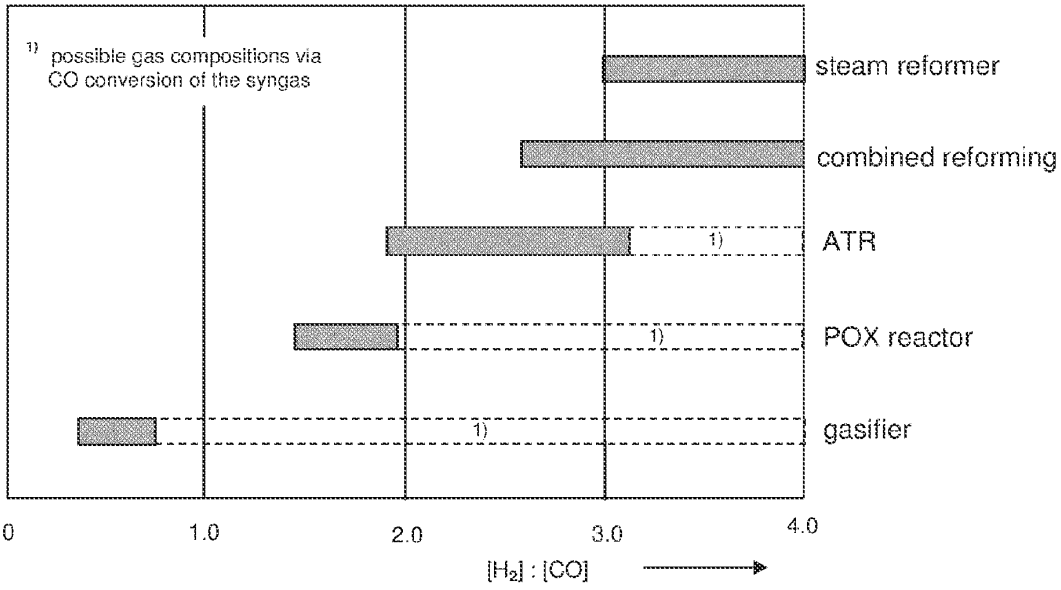


Fig. 1: Composition ranges provided by syngas generators

This feature is most significant in the gasifier, where practically no hydrogen is provided by the feedstock. The hydrogen has to come entirely from cracked water mole-

cules, which requires more energy compared to the cracking of hydrocarbons and hence is associated with higher CO and CO_2 production. This is illustrated by the graph shown in Figure 1. The figure shows the individual ranges of H_2 : CO ratios in the syngases which can be provided by the various syngas generators.

In general, matching the individual syngas-based processes with the syngas generators which can provide the required gas compositions straight away should give the most economical solutions. However, as discussed briefly below, the required gas compositions can not always be delivered by one syngas generator type on its own.

- Ammonia synthesis

  The ammonia synthesis requires an H_2 : N_2 ratio in the order of 3.0. Obviously, this could not be realized by a steam reformer on its own. However, it can be met easily by combined reforming using an air blown secondary reformer. The version where the secondary reformer provides just the stoichiometric amount of nitrogen required in the synthesis has been the dominant syngas generation concept in ammonia plants for the last fifty years.

  Other versions operating with an excess of nitrogen in the secondary reformer and a downstream process step to remove the surplus nitrogen have also been realized in considerable numbers. A stand alone ATR is also capable of feeding an ammonia synthesis. It has to be operated with oxygen-enriched air or pure oxygen combined with a subsequent process step to introduce the required amount of nitrogen.

- Methanol synthesis

  Steam reforming alone can not provide the syngas composition according to Table 1 best suited to the requirements of the methanol synthesis. A quite substantial purge from the synthesis or other means, e.g. a pressure swing absorption (PSA), are required to remove the surplus hydrogen. Pure autothermal reforming generates a syngas too low on hydrogen, requiring CO conversion and subsequent CO_2 removal.

  Again, combined reforming can generate the optimum gas composition for the methanol synthesis straight away, leading to a significantly better consumption figure for the plant. Other advantages such as a smaller steam reformer size and a higher operating pressure in the syngas generation section are also associated with combined reforming. Hence, although requiring pure oxygen, combined reforming appears to be the superior alternative for larger plant capacities.

- Hydrogen

  Hydrogen plants aim for maximum hydrogen production from a given amount of feedstock. Hence, most of these plants are based on steam reforming although several plants based on partial oxidation reactors are still in use. However, as ATR and POX reactors require pure oxygen, steam reforming is nowadays considered the more economic option. If this is valid for larger capacities in excess of 100,000 Nm^3/h, e.g. for heavy oil upgrader plants, remains to be seen.

- Gas-to-liquids
  As illustrated by Fig. 1 the ATR is the syngas generator best suited to Fischer-Tropsch (FT-) syntheses as it provides the required gas composition straight away. Besides using pure oxygen it is technically feasible to operate the ATR on plain air and feed the nitrogen containing syngas to the FT-synthesis. However, this obviously increases the flowrates in the entire process considerably and does not seem to be the most economic solution.

This brief excursion into the basics of syngas production shows that autothermal reforming has already been an established element of synthesis gas production for quite some time. It nevertheless wants to draw attention to the fact that – with the exception of the stand-alone ATR in GTL plants – all other autothermal reformers so far operate as secondary reformers on pre-reformed gas or mixtures of pre-reformed gas with natural gas. In addition, the effective steam-to-carbon ratios for these secondary reformers are also quite high.

Both the presence of considerable amounts of hydrogen in the pre-reformed gases and the high steam-to-carbon ratios substantially reduce the risk of soot formation in the ATR's combustion zones. Hence, operating experience gained with secondary reformers can not really be considered as a reliable basis for the design of "pure" ATR applications.

Recent years have brought a renewed interest in ATR based synthesis gas generation for ammonia plants. This is closely linked to further increases in plant capacity well beyond today's maximum of 3,300 mtpd realized by Uhde in the SAFCO IV and Ma'aden ammonia plants. As mentioned above in context with methanol plants, steam reformers are coming closer to their technical limits in this capacity range. The ATR technology appears to be a promising alternative here.

This paper presents Uhde's assessment of the economic viability of this approach and outlines what Uhde has done in recent years to prepare itself for this scenario.

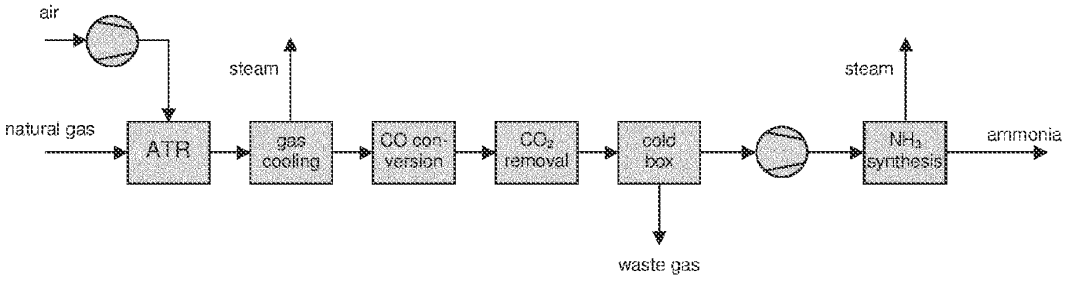
AMMONIA PLANTS BASED ON AUTOTHERMAL REFORMING

Flowsheet options

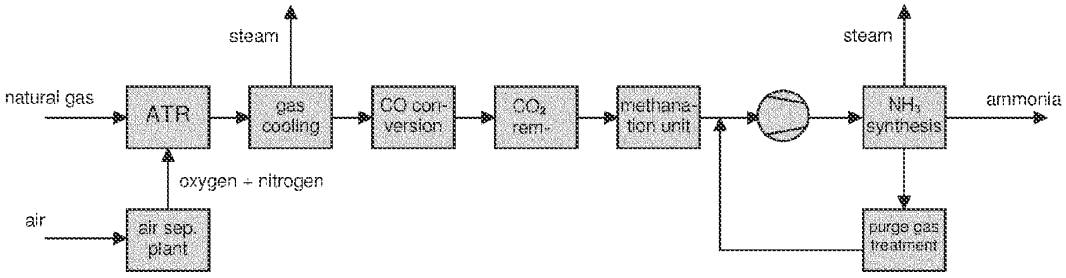
An autothermal reformer can be operated with the entire range of oxidator compositions between plain air and pure oxygen. The amount of oxygen which has to be provided by the oxidator is defined by the required reforming heat duty. It does not depend significantly on the overall oxidator composition. The process steps required downstream of the ATR for syngas preparation are however closely linked to the oxidator composition. Below, the consequences of the three most important oxidator compositions plain air, oxygen-enriched air with stoichiometric nitrogen content and pure oxygen on the process configurations as well as on equipment sizes are discussed briefly.

Fig. 2 contains simplified block flow diagrams of the process variations. Obviously, the numbers of process units are not significantly different between the three concepts.

Option 1 – plain air as oxidator



Option 2 – oxygen enriched air as oxidator



Option 1 – pure oxygen as oxidator

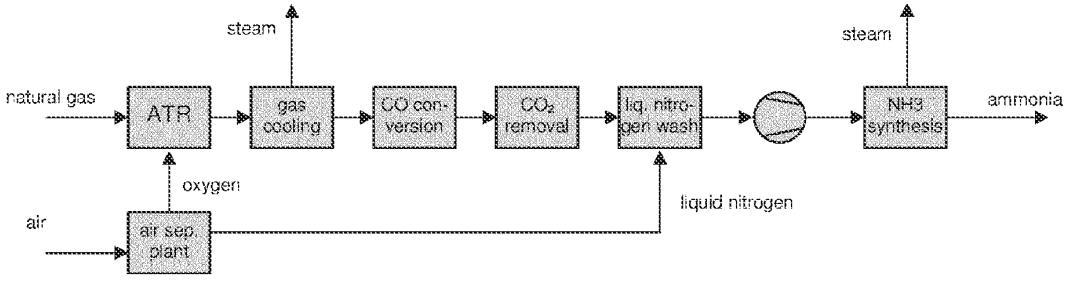


Fig. 2: Flowsheet options of ATR-based ammonia plants



- Option 1 – plain air

  Using plain air results in a large nitrogen surplus in the syngas. Hence, a cryogenic unit is required to extract the excessive nitrogen upstream of the syngas compressor or a very large purge stream from the ammonia synthesis. Obviously, this concept is associated with the largest flowrates and equipment sizes at least in the synthesis gas generation section.

- Option 2 – oxygen enriched air

  The option requires an air separation unit. The air flowrate is specifically selected to provide the correct amount of nitrogen for the ammonia synthesis. The oxygen coming in with the air and the added amount together meet the required reforming heat duty. Thus, the capacity of the air separation is minimized.

- Option 3 – pure oxygen

  In this process concept only marginal amounts of nitrogen depending on the oxygen purity are introduced into the ATR. Hence, flowrates in the synthesis gas generation section take on their smallest values. The nitrogen required in the ammonia synthesis is introduced into the syngas just upstream of the syngas compressor for example via a liquid nitrogen wash unit.

A natural advantage of the process concepts using final cryogenic units in the syngas preparation is the practically inert-free synthesis gas. Without accumulation of inerts the size of the equipment in the ammonia synthesis can be reduced in the order of 10 %.

Option 1 operates with significantly larger flowrates than option 2 in the syngas generation section. This may be compensated by a somewhat simpler cryogenic unit compared to the air separation, smaller flowrates in the synthesis and the missing purge gas treatment. Hence, the two options may have fairly similar investment costs.

Comparing option 3 with option 2 the following can be pointed out. The capacity of the air separation plant has to be about 40 % larger. A nitrogen wash unit is considerably more complicated than a methanation section. Whether this is fully compensated by the somewhat larger equipment of the versions 1 and 2 remains doubtful at least. Hence, option 3 is likely to have the highest investment costs among the three process versions discussed.

Economic comparison with steam reforming based plants

The economics of ATR based ammonia plants compared to plants using conventional tubular steam reformers has been addressed in a number of papers in recent years in more or less detail [1], [2]. The projections about possible investment cost reductions vary between 20% and none. With respect to operating costs an even larger range between 30 % reduction and none can be derived from the references. These assessments do not always reveal which cost components are taken into account and hence can not really be compared.



Uhde's assessment outlined below leads to the conclusion, that any definite figure is misleading since plant capacity is the decisive parameter. The break even point indeed appears to be in the area of 4000 mtpd as it has been reported by other authors. However, with the limited accuracy possible at this moment a range of uncertainty, at least in the order of ± 500 mtpd, should be expected.

An economic comparison between the two plant concepts must look at both operating and investment costs.

Operating cost

About 65 % of the specific energy consumption of a modern ammonia plant is transferred to the ammonia product as chemical energy. The remaining 35 % are needed to enforce the required process steps, i.e. via preheating and compression of the process media. The energy balance of an entire ammonia plant is fairly complex. As both parts are affected by the quite significant changes in the process, the consumption side as well as the available waste heat have to be looked at.

Table 3 contains a comparison of the consumption side. The table lists the most important energy consumers in ammonia plants for both plant concepts. The right hand side column of the table indicates the change in energy consumption which has to be expected for the respective process unit in the ATR-based plant. It has to be pointed out however that the individual energy consumptions of the consumers listed in the table differ significantly. By far the most important consumers are the reformer, the waste heat section/fired heater and the air separation.

The feed flowrate in the ATR-based plant is about 25 % larger compared to a steam reformer based plant as it contains between 50 and 60 % of the fuel flow for the reformer burners. Oxidation of this additional amount provides the heat for the reforming reactions. Due to the resulting increase in natural gas flowrate the related energy consumptions in the syngas generation section are likely to go up, though not always in the same order as indicated in Table 3.

Due to the larger process gas flowrate in the syngas generation section of the ATR-based plant more heat is available from this process stream. The surplus can be used to raise the additional steam required for the air separation.

The large amount of heat contained in the flue gas of the primary reformer is usually utilized for the process media preheating addressed in Table 3 as well as steam super heating. In the ATR-based plant this has to be supplied by a fired heater. Due to the increased steam production more heat for steam superheating has to be supplied by the fired heater in addition to the increased heat demand for feed and feed/steam preheating.

The heater operates with a smaller specific flue gas flowrate than the waste gas duct of the steam reformer. Hence, stack loss as well as heat duty for burner air preheating are reduced compared to the steam reformer.

In summary, our calculations carried out so far show an additional energy consumption for the ATR-based ammonia plant in the order of 6 % for the process version operating on enriched air (option 2). For the version operating on pure oxygen (option 3) a somewhat higher additional consumption in the order of 10 % has to be expected.

Table 3: Comparison of primary ammonia plant energy consumers

energy consumers		add. energy consumption
SMR-based plants	ATR-based plants	ATR plant [%]
reformer (feed + related fuel)	reformer feed	0
waste heat section (related fuel)	fired preheater	+ 15
feed compression	feed compression	+ 25
feed preheating	feed preheating	+ 25
feed/steam preheating	feed/steam preheating	+ 7
process air compression	air separation	+ 150 / + 188[1)]
process air preheating	process air preheating	0 [2)]
synthesis gas compression	synthesis gas compression	0
ammonia vapour compress.	ammonia vapour compress.	0

1) enriched air / pure oxygen
2) reduced preheating temperature with regard to higher oxygen content

Investment cost

No ATR-based ammonia plant has been built as yet. Hence, a comprehensive cost data base, comparable to that available for conventional plants, does not exist. Therefore, the qualitative analysis presented below is used to derive a cost relation between the two plant concepts.

Table 4 lists the main process steps in an ammonia plant and the respective units in the conventional plant based on steam reforming as well as in the ATR-based plant. The right hand side column of the table indicates whether the respective unit in an ATR based plant is expected to have lower (↓), equal (~) or higher (↑) investment costs. To keep the focus on the most relevant process units the ATR process concept based on enriched air is used for this comparison.

This qualitative approach illustrates that the two process steps “oxidator preparation” and “reforming” are decisive for the investment cost relation between the two plant

concepts. Minor cost differences can be expected for each other process step as equipment numbers, sizes and complexities vary moderately throughout the entire flowsheets. However, excluding the fundamentally different process steps "oxidator preparation" and "reforming" it can be expected that these differences will not all be in favour of one plant concept and hence equal each other out.

Table 4: Investment cost comparison per process step

process step	SMR plant	ATR plant	unit cost ATR : SMR
oxidator preparation	compressor	air separation	↑
desulphurization	preheater / reactor		~
process gas preheating	flue gas duct	fired heater	~
reforming	steam reformer	–	↓
	secondary reformer	ATR	~
process gas cooling	steam generator / superheater		~
CO conversion	2 converter / 2 BFW preheater		~
CO_2 removal	aMDEA, alternatively physical solvent		~
methanation	preheater / reactor		~
syngas compression	2-casing turbo compressor		~
ammonia synthesis	3 converter dual-pressure synthesis		~
refrigeration	compression type		~
purge gas treatment	hydrogen recovery		~ / ↓ 1)

1) option 2 "enriched air" / option 3 - "pure oxygen" with inert free syngas

The cost structure for a steam reformer has a fairly linear relationship between capacity and unit cost. With few exceptions material and construction costs are directly proportional to the number of tubes, i.e. unit capacity.

The cryogenic air separation is by nature a single train unit. Hence, contrary to the steam reformer, a considerable reduction of the specific investment cost with growing capacity can be expected. This characteristic is illustrated in Fig. 3. The steam reformer cost curve is derived from Uhde's respective database. The figures for air separation plants are derived from proposals provided by plant vendors.

The cost data have been deliberately related to the SAFCO IV reformer costs as it does not make sense to discuss absolute figures in this context. The actual costs depend very much on the region where the plant is to be built, specific requirements and the overall economic situation.

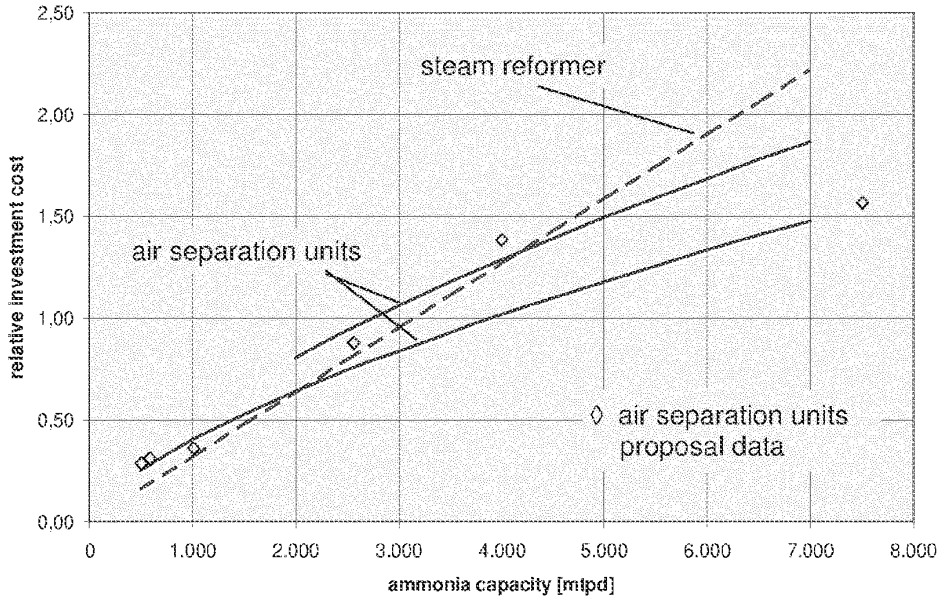


Fig. 3: Investment cost relation steam reformer vs. air separation plant

The figure illustrates that with the cost data available at present a single break-even capacity can hardly be determined. The cost figures of air separation units may be interpreted conservatively or optimistically by the continuous curves as shown in the figure. Obviously, there is a considerable capacity range of uncertainty. However, the figure indicates that – even with a conservative approach – beyond plant capacities of 4000 mtpd an ATR based plant is likely to have growing investment cost advantages compared to a steam reforming based plant.

UHDE'S ATR TECHNOLOGY

Description of Uhde's ATR test facility

The partial, i.e. substoichiometric combustion in autothermal reforming is in principal likely to generate soot. For any set of operating conditions defined by feed gas composition, pressure and steam-to-carbon ratio a minimum operating temperature exist below which soot is generated. Steam and hydrogen in principal reduce the soot forming potential, i.e. move the boundary move the boundary for soot-free operation to lower operating temperatures. The minimum temperature also depends on the burner design and the flow conditions in the combustion zone.



Uhde has extensive experience in the design of secondary reformers for ammonia plants. These vessels operate under similar pressure and temperature, but in the following two important aspects enjoy considerably milder conditions compared with pure autothermal reformers.

Secondary reformers process partly reformed gases which contain significant amounts of hydrogen and operate with quite high effective steam-to-carbon ratios. Hence, they do not provide a basis to determine the minimum possible operating temperatures with respect to soot formation. This temperature is directly related to the amount of oxygen supplied. Therefore, to minimize plant operating cost the ATR is to operate at the lowest possible operating temperature.

The heat generation rates of secondary reformers are relatively small. With the considerably higher heat generation in autothermal reformers, increased wear and tear on the burner and thermal insulation must be expected. They have to be taken care of by modified design features. Also catalyst bed design and size can be expected to vary.

To gain further insight into ATR operation and to produce the operational data required to adjust the design procedures, Uhde set up a development program several years ago. Subsequently to being successful in finding a cooperation partner in the russian company Kuibyshev Azot, a test facility was designed, built and commissioned at Kuibyshev Azot's production site.

Fig. 4 contains the process flowsheet of the test facility. The production site usually operates on fairly light natural gas with low contents of higher hydrocarbons and sulphur. Hence, to simulate heavier feedstocks, the test facility was equipped with a device to add propane to the incoming natural gas.

Provisions where also made for the addition of a hydrogen rich stream to the natural gas to simulate a pre-processed gas. With regard to the low sulphur content a further desulphurization of the incoming natural gas was considered unnecessary. It was also decided to take the required process steam from an external source. The heaters for natural, feed/steam mixture and oxidator are powered electrically.

At the ATR gas outlet a water quench is installed. Hence, only moderate gas temperatures are present outside the ATR pressure vessel. The ATR design capacity can be best characterized by a syngas flowrate at reactor outlet in the order of 1000 Nm^3/h at 30 bar operating pressure.

The test rig is equipped with optical light extinction measurement devices to detect soot in the gas phase as well as in the process condensate.

During the design phase of the ATR itself, considerable effort was spent to optimize the geometry of the combustion or partial oxidation (POX) zone, gas inlet velocity and swirl and to find the best position for the oxidator nozzles. CFD analysis has been employed extensively for this step. As a result of these studies two ATR reactor tops with completely different shapes of the combustion zone have been manufactured.

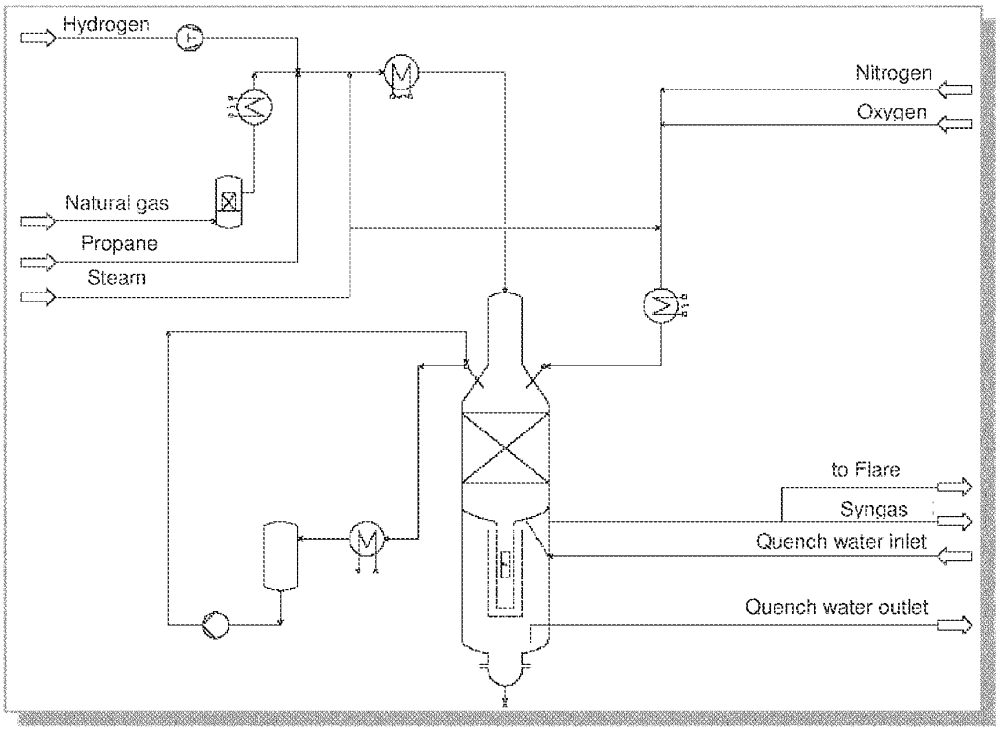


Fig. 4: Process flow diagram of the ATR test facility

With regard to the high design pressure and other restrictions it was decided early in the design phase to abandon the idea of installing an optical access to the combustion zone. Also, the number of nozzles which could be fitted to the reactor pressure vessel, is limited as each one is quite bulky due to the high design pressure.

Fig. 5 shows a CAD drawing of the test rig. The lower steel structures in the front contain the modules for burner cooling, hydrogen compression and feed preheating. The high steel structure at the back contains the ATR itself and the feed/ steam preheaters.

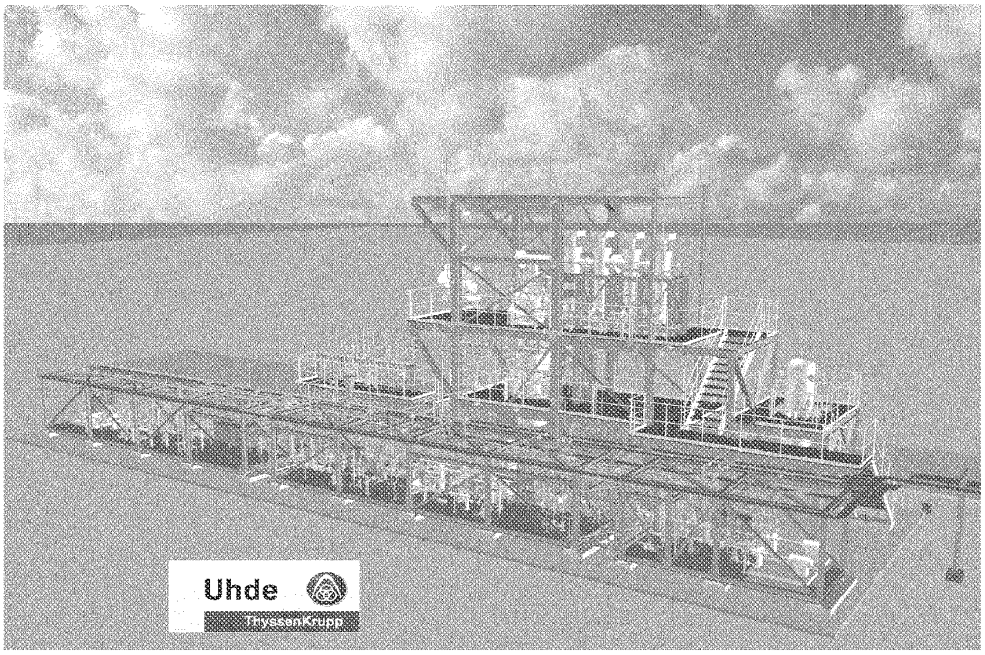


Fig. 5: CAD drawing of the ATR test rig

The process plant occupies an area of appr. 30 m by 11 m. The height of the central steel structure is about 10 m.

The main part of the test rig has been assembled on-site from prefabricated parts. This was considered more cost efficient than complete preassembly and transport of the relatively huge structure to the production site. The three modules in front were preassembled and transported as complete units.

Fig. 6 presents a photograph, showing the test facility in its final state of construction ready for startup. The picture contains a view on the facility from the opposite side compared to the CAD drawing in Fig. 5 with the main structure containing the ATR now in the front. On the right hand side of the picture the pipe rack for the utilities required by the test facility is visible.

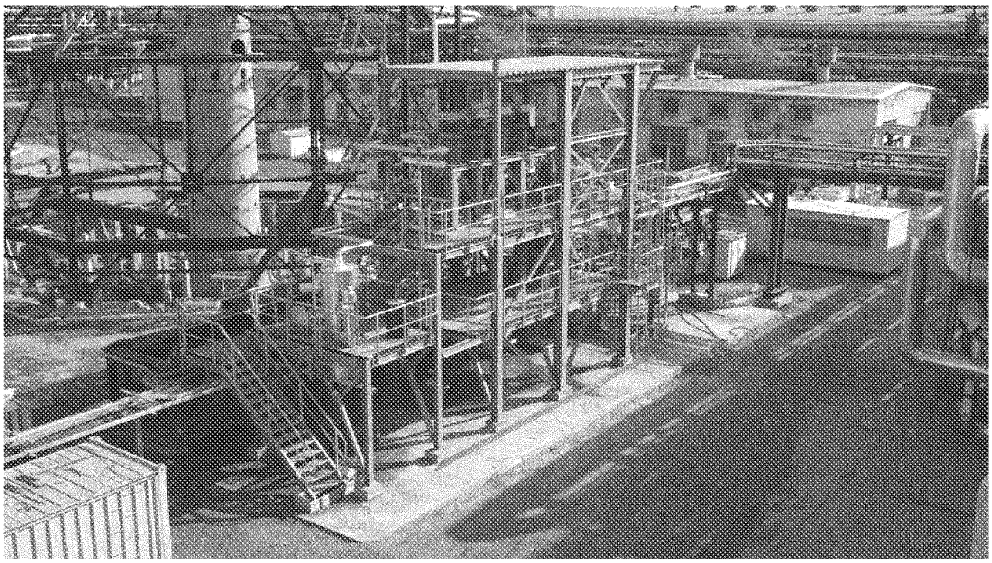


Fig. 6: View of the ATR test facility ready for startup

Experiences during erection and commissioning

To obtain building and operating permission for the test rig turned out to be a time consuming and relatively costly procedure. A safety study had to be carried out to show conformity of the plant's design and instrumentation with russian regulations. Also, a special documentation conforming with russian standards had to be generated from the plants engineering documents.

Transportation of the material to the construction site did not present any problems.

Assembly of the test rig presented no major problem and could be continued even through the cold season. It should be mentioned, however, that the winter of 2008 to 2009 was unusually mild. Subsequently to the thorough execution of pre-commissioning and commissioning procedures the ATR was ignited for the first time in June 2009.

Operation of the optical soot detection devices has shown that the lowest soot content which can be detected in the samples taken from the quench water offtake is in the order of 1-3 ppm wt. Quench water and process gas mass flowrates are not really linked but usually of the same order. Hence, the soot concentration determined in the quench water should correspond roughly to the concentration in the process gas.

The minimum measurable soot concentration in the process gas named by the manufacturer of the measuring device should be in the order of 80 mg/Nm³ (0.1 ppm wt.). During the test runs the onset of soot always became apparent at first in the quench water. Hence, the actual sensitivity of the measurement device appears to be at least one order of magnitude lower than pronounced.



The target in the test runs so far has been the detection of the soot formation boundary. Therefore, as soon as the onset of soot was detected, the run conditions have been readjusted immediately to take the reactor away from the critical region. Any prolonged operation in the critical region always demanded a considerably longer period under soot free conditions to get the soot out again.

Operational Results

Depending on the process an autothermal reformer is to serve as sole synthesis gas generator it has to meet certain

- outlet gas requirements
  - composition (e.g. $[CO + H_2]/N_2 \approx 3.0$ or $H_2 : CO \approx 2.0$)
  - pressure
  - methane content

To meet these requirements with the feedstock available at the respective production site and present the most economical solution with respect to investment and operating cost the following parameters have to be selected carefully:

- primary design parameters
  - combustion zone shape
  - combustion zone gas residence time
  - inlet velocity feed/steam mixture
  - inlet swirl feed/steam mixture
  - inlet velocity oxidator
  - number of oxidator nozzles
  - oxidator nozzles direction
  - space velocity catalyst bed
- operating parameters
  - steam-to-carbon ratio
  - combustion zone temperature (→ oxygen-to-carbon ratio)
  - oxidator composition

Obviously, it is economically infeasible, to investigate all of the above mentioned parameters in an experimental program. The number of test runs and individual pieces of equipment to be manufactured would be simply too large.

With the capabilities of modern CFD calculations this could be considerably reduced. As discussed in chapter 3.1 an optimization of the geometrical parameters around the combustion zone has been carried out to determine the most promising combinations for two different combustion zone shapes.

On this basis a still quite extensive test program has been devised to cover the relevant ranges of the parameters listed in Table 5.

Table 5: ATR test program

parameter	unit	lower limit	upper limit
feedstock higher hydrocarbon content	%	2	14
N_2 content oxidator	%	0	55
operating pressure	bar	20	30
steam-to-carbon ratio	–	0.5	3.0
combustion zone shape	–	A	B
rel. gas residence time comb. zone	%	50	100
combustion zone temperature	°C	1150	1250

As the first set of tests is specifically designed to determine the soot formation boundary, i.e. the minimum temperature for soot-free operation at given steam-to-carbon ratios, these tests were run without any catalyst in place to avoid damage to the catalyst.

These test runs carried out so far have delivered satisfying results. The performance of the ATR can be characterized by the three most important operating points depicted in Table 6. All points showed reasonable margins against the soot formation boundary despite rather unfavourable feedstock compositions, i.e. relatively high contents of higher hydrocarbons.

Operating point A represents the situation where an ATR generates a stoichio-metric syngas composition for an ammonia synthesis operating on oxygen enriched air and a steam-to-carbon ratio of 3.0.

In point B the ATR is operating on pure oxygen. With the steam-to-carbon ratio of 2.0 the conditions tend to ammonia or methanol plants.

Point C represents ATR operating conditions typical for a syngas unit in a gas-to-liquid plant based on Fischer-Tropsch synthesis with an H_2 : CO ratio in the syngas in the order of 2.0.

Since no catalyst had been in place during these test runs the syngas still contains noticeable methane contents. Also, the relatively large specific heat losses of the still rather small test facility lead to extra CO_2 generation compared to a large production plant. Hence, gas compositions at the reactor outlet are not really significant and have therefore not being included in the table.

Table 6: Operational results ot the test ATR

	Operating point

		A	B	C
Parameter	Unit	NH_3 syngas, enriched air	NH_3 syngas, pure oxygen	FT syngas
feed composition				
CH_4	mol%, dry	89.2	82.9	88.7
C_{2+}	mol%, dry	7.1	14.5	7.4
oxidator N_2 content	mol%, dry	42.1	5.0	5.0
steam-to-carbon ratio	----	3.0	2.0	0.7
outlet temp. oxidat. zone	°C	1200	1250	1238
oxygen-to-carbon ratio	----	0.85	0.74	0.60
syngas pressure	bar abs	28.0	28.0	28.0
outl. temp. catalyst zone	°C	1086		1100

CONCLUSION AND OUTLOOK

So far only a very limited number of true stand-alone autothermal reforming applications have been realized though the technology has been investigated extensively for more than a decade now. As discussed above, the well established combination of autothermal reformers with steam reformers does not count in this respect. The operating conditions of these secondary reformers are considerably less severe than those of a true stand alone ATR.

The analysis presented in this paper investigates the reasons for this and illustrates – with the main focus on ammonia plants – why the conventional syngas generation based on combined steam and autothermal reforming still dominates newly built plants. The analysis also shows that the cost advantage of the conventional concept against ATR-based syngas generation is shrinking with increasing plant capacity.

The capacity of world scale ammonia plants has grown substantially since the early beginnings and markedly in the past 50 years. Though it is technically and logistically more challenging to provide the equipment for large capacity plants there is no indication that the economy of scale does no longer work for today's world scale capacities.

As discussed before it is difficult to determine the actual break-even capacity, where investment costs of both plant versions become equal. However, there are substantial arguments that for capacities beyond 4000 mtpd the ATR-based plants will have increasing advantages.

Such capacities are also feasible with steam reformer based plants as Uhde has shown with a concept presented on the AIChE ammonia safety symposium 2004 [3]. However, the ATR allows to increase the pressure level in the syngas generation sec-

tion considerably beyond the current limit of appr. 45 bar for steam reforming based plants. Hence, with reduced volumetric flowrates in the syngas generation section it will be much easier to realize larger capacities.

Uhde intends to prepare itself for this scenario. The test program for the ATR will be completed during the next months. The operating data will provide the basis to identify the most promising design and to update the design tools.

The currently feasible maximum operating pressure for the tests covers ATR applications for hydrogen production as well as GTL plants. It also provides a reasonable basis to judge the ATR behaviour under ammonia plant conditions.

Once the test results have been fully evaluated and transferred to the design tools Uhde intends to start offering its ATR technology to customers. In the beginning the focus will be on plants with medium size syngas capacities, e.g. in a revamp project, to limit the upscaling factor from the test facility. In the long run, however, the prime target are larger plant capacities.

Since the consumption figures of ATR based ammonia plants are in the same order as those of steam reforming based plants, there will be no significant differences in the overall CO_2 balances. However, a natural advantage of the ATR-based plant is that a much larger part of the generated CO_2 is always contained in the syngas under high pressure. It is separated in the CO_2 removal section without additional equipment and marginal extra energy expenditure. This allows full conversion of the entire ammonia production into urea. A steam reforming plant would require an expensive removal system to extract the CO_2 from the atmospheric reformer flue gases.

A complete separation of the entire CO_2 could also be realized in the ATR-based plant with little extra investment and an only moderate increase of the plants consumption figure provided the fired heater would be fed with syngas instead of natural gas.

REFERENCES

[1] Davey, W; T. Wurzel; E. Filippi: MEGAMMONIA - the Mega-Ammonia Process for the New Century, Nitrogen & Syngas 2003.

[2] Dybkjaer, I.: New Reforming Concepts for Large Scale NH_3-Plants, AIChE Ammonia Safety Symposium 2005.

[3] Ruether, J; J. Larsen; D. Lippmann; D. Claes: 4000 mtpd Ammonia plant based on proven technology, AIChE Ammonia Safety Symposium 2005.

PTO/SB/59 (09-16)
Approved for use through 11/30/2021. OMB 0651-0064
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

REQUEST FOR SUPPLEMENTAL EXAMINATION TRANSMITTAL FORM

Address to:
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Attorney Docket No.:

Date:

1. ☑ This is a request for supplemental examination pursuant to 37 CFR 1.610 of patent number 11,286,168 issued March 29, 2022. 37 CFR 1.610(b)(1).

2. ☑ Supplemental examination of claim(s) 1-23 is requested. 37 CFR 1.610(b)(4).

3. ☑ a. The name(s) of the patent owner(s) (**not** the patent practitioner(s)) is (are):
CASALE SA

☐ b. A submission by the patent owner(s) in compliance with 37 CFR 3.73(c), which establishes that the patent owner(s) has (have) the entirety of the ownership in the patent for which supplemental examination is requested, is included. 37 CFR 1.610(b)(9).

4. ☐ a. A check in the amount of $_____ is enclosed to cover the fee for processing and treating a request for supplemental examination, the fee for reexamination ordered under 35 USC 257, and the fee for processing and treating each non-patent document over 20 sheets in length (37 CFR 1.20(k)(1 - 3));

☑ b. The Director is hereby authorized to charge all applicable fees as set forth in 37 CFR 1.20(k)(1 - 3) to Deposit Account No. 506181; or

☑ c. Payment by credit card. Form PTO-2038 is attached. 37 CFR 1.610(a).

5. ☑ Any refund should be made by ☐ check or ☑ credit to Deposit Account No. 506181. 37 CFR 1.26(c). If payment is made by credit card, refund must be to the credit card account.

6. ☑ A copy of the patent for which supplemental examination is requested, and a copy of any disclaimer or certificate issued for the patent are included. 37 CFR 1.610(b)(6).

7. ☐ CD-ROM or CD-R in duplicate, Computer Program (Appendix) or large table
☐ Landscape Table on CD

8. ☐ Nucleotide and/or Amino Acid Sequence Submission
If applicable, items a. – c. are required.

a. ☐ Computer Readable Form (CRF)
b. Specification Sequence Listing on:

i. ☐ CD-ROM (2 copies) or CD-R (2 copies); **or**
ii. ☐ paper

c. ☐ Statements verifying the identity of above copies

9. ☑ A list of no more than 12 items of information submitted as part of this request is provided in Part B of this form. Where appropriate, the list must meet the requirements of 37 CFR 1.98(b). 37 CFR 1.605(a), 1.610(b)(2).

This collection of information is required by 37 CFR 1.610. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 0.3 hours to complete, including

PTO/SB/59 (09-16)
Approved for use through 11/30/2021. OMB 0651-0064
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

10. ☑ A legible copy of each item of information listed in Part B of this form, and an English language translation of all necessary and pertinent parts of each non-English language item of information are included.

Copies of items of information that form part of the discussion within the body of the request (see 37 CFR 1.605(b)), and copies of U.S. patents and patent application publications, are not required. 37 CFR 1.610(b)(7).

11. ☑ A summary of the relevant portions of each non-patent document that is over 50 pages in length (other than the request) is included. The summary includes the required citations to the particular pages containing the relevant portions. 37 CFR 1.610(b)(8).

12. ☑ 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 requested, is included. 37 CFR 1.610(b)(5).

13. ☑ The below list includes all prior or concurrent post-patent Office proceedings (*ex parte* or *inter partes* reexamination, reissue, supplemental examination, post grant review, or *inter partes* review) involving the patent for which supplemental examination is being requested. 37 CFR 1.610(b)(3). An identifying number may be, e.g., a control no. or reissue application no. Any prior or concurrent post-patent Office proceedings not listed below are listed on a separate paper accompanying the request.

Type of Proceeding	Identifying Number	Filing Date

☐ See accompanying paper for a list of additional prior or concurrent post-patent Office proceedings involving the patent for which supplemental examination is requested. The paper should be a separate sheet titled "List of Prior or Concurrent Post-Patent Office Proceedings" and must provide the type, identifying number, and filing date of the post-patent Office proceeding.

14. Correspondence Address: Please recognize, or change, the correspondence address for the file of the patent for which supplemental examination is requested **and** for the supplemental examination proceeding to be:

☑ The address associated with Customer Number: 116407 **OR**

☐ Firm or Individual Name

Address

City	State	Zip
Country		
Telephone	Email	

15. **WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.**

/Jonathan Rowe/ — Authorized Signature

April 26, 2023 — Date

Jonathan Rowe — Typed/Printed Name

65,335 — Registration No.

PTO/SB/59 (09-16)
Approved for use through 11/30/2021. OMB 0651-0064
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

(Also referred to as FORM PTO-XXXX)

REQUEST FOR SUPPLEMENTAL EXAMINATION TRANSMITTAL FORM
PART B – LIST OF ITEMS OF INFORMATION – Page 1

Patent number for which supplemental examination is requested 11,286,168 Issue Date March 29, 2022

All items of information (no more than 12) submitted herewith as part of this request for supplemental examination of the above-identified patent are included in the following list:

U. S. PATENT DOCUMENTS

Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
1	US- 8,137,422 B2	03/20/2012	Licht, et al.	
2	US- 2004/0234426	11/25/2004	Reddy, et al.	
	US-			
	US-			
	US-			
	US-			
	US-			
	US-			
	US-			
	US-			
	US-			

FOREIGN PATENT DOCUMENTS

Cite No.[1]	Foreign Patent Document Country Code[3]-Number[4]-Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	T[2]
1	EP 2 817 260 B1	12/31/2014	Fillippi, et al.		
2	EP 1 648 817 B1	04/26/2006	Blumenfeld, et al.		
3	EP 2 266 922 A1	06/03/2009	Licht, et al.		
4	DE 10 2015 210 803 A1	06/12/2015	Gorval, et al.		
5	DE 10 2014 209 635 A1	05/21/2014	Gorval, et al.		

[1] Applicant's unique citation designation number (optional). [2] See Kinds Codes of USPTO Patent Documents at www.uspto.gov or MPEP 901.04. [3] Enter Office that issued the document, by the two-letter code (WIPO Standard ST.3). [4] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [5]Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [6] Applicant is to place a check mark here if English language Translation is attached.

PTO/SB/59 (09-16)
Approved for use through 11/30/2021. OMB 0651-0064
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

(Also referred to as FORM PTO-XXXX)

REQUEST FOR SUPPLEMENTAL EXAMINATION TRANSMITTAL FORM
PART B – LIST OF ITEMS OF INFORMATION – Page 2

Patent number for which supplemental examination is requested 11,286,168 Issue Date March 29, 2022

All items of information (no more than 12) submitted herewith as part of this request for supplemental examination of the above- identified patent are included in the following list:

OTHER DOCUMENTS

Cite No.[1]	Document Information (include, where appropriate, name of the author, title of the article, book, magazine, journal, serial, symposium, catalog, etc., publication date, page(s), volume-issue number(s), publisher, city and/or country where published. If a court document, identify the specific court, the designation (case citation or numeric designation), the title of the document, and the date submitted in court. If a declaration, include the type (e.g., 37 CFR 1.132 or 1.131), name of declarant, and the date of declaration. If an invoice or sales receipt, include the date issued and the name of the issuer (e.g., the name of the corporation or other place of business). If a discussion within the body of the request, include the pages of the request on which the discussion appears, and a description of the discussion (e.g., "discussion in request of why the claims are patentable under 35 U.S.C. 101, pages 7-11.") For all other materials, include, where appropriate, the title, author, date, and any descriptive information that would describe the document.)	T[2]
1	"Ammonia; Principles and Industrial Practice", Wiley-VCH, ISBN 3-527-29593-3 , January 1999, pp. 1-301	
2	Haussinger, et al., "Hydrogen, 3. Purification", Ullmann's Encyclopedia of Industrial Chemistry, Vol. 18, 2012, pp. 309-333	
3	Noelker, et al., " Autothermal reforming: a flexible syngas route with future potential", Prepared for Presentation at NITROGREN & SYNGAS 2010 International Conference, Bahrain, 28 February - 3 March 2010, pp. 1-20	
4	Shimura, "Urea Product Expansion by Newly Developed CO2 Recovery Process from Primary Reformer Flue Gas", Ammonia Technical Manual, Vol. 47, 2006, pp. 237-246	

[1] Applicant's unique citation designation number (optional). [2] Applicant is to place a check mark here if English language Translation is attached.

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Electronic Acknowledgement Receipt	
EFS ID:	47906483
Application Number:	96000424
International Application Number:	
Confirmation Number:	9950
Title of Invention:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE
First Named Inventor/Applicant Name:	1128618
Customer Number:	116407
Filer:	Jonathan P. Rowe/Holly Morton
Filer Authorized By:	Jonathan P. Rowe
Attorney Docket Number:	283386WOUS01_495230-44
Receipt Date:	26-APR-2023
Filing Date:	
Time Stamp:	13:55:17
Application Type:	Supplemental Examination
Patent Number:	

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)

1	Transmittal Letter	20230426_283386WOUS01_495230-44_CorrectedRequestForSupplementalExamination.pdf	340670 2442a3895d9da1f0cfd8134f8a0ce706e1cc8eb8	no	52
Warnings:					
Information:					
2	Copy of patent for which Supplemental Examination is requested	ExhibitA-US11286168.pdf	1323808 2e4c44c5208dd1090bb9a078edbd32e5c578ebd2	no	16
Warnings:					
Information:					
3	US Patent or Patent Application Publication - Supplemental Examination	ExhibitC-D2_US8137422.pdf	999027 9e80468a0ab1dbcadecaee929ee95f82efcb0d0b	no	14
Warnings:					
Information:					
4	Foreign Reference	ExhibitD-D3_EP2817260B1.pdf	253870 01277c49500c2aa23491776a75bb8fa0f3ed5e4a	no	15
Warnings:					
Information:					
5	Non Patent Literature	ExhibitF-D5_NPL_HydrogenPurification.pdf	3202765 f838d6b127f54230a2686a8dccc3e7ecc1849a75	no	26
Warnings:					
Information:					
6	US Patent or Patent Application Publication - Supplemental Examination	ExhibitG-D6_US20040234426A1.pdf	694390 040207922fbeaad289d1ceaeba9d32d414751eae	no	12
Warnings:					
Information:					
7	Foreign Reference	ExhibitH-D7_EP1648817B1.pdf	71635 1cb384b80027f0e4d217d53d95cefb995d70a655	no	8
Warnings:					
Information:					

8	Translation of Non-English Item of Information	ExhibitI-D7_EP1648817B1_EnglishTranslation.pdf	160370 dc3b687e20f0c1991839000f17e78efd072a8e80	no	3
Warnings:					
Information:					
9	Foreign Reference	ExhibitJ-D8_EP2266922A1.pdf	306342 1d95bfdf35955f461510d9528252d3c9e80aace6	no	20
Warnings:					
Information:					
10	Non Patent Literature	ExhibitK-D9_NPL_AmmoniaPrinciplesAndIndustrialPractice.pdf	16545733 f7b2e516c3247fa54f66d6454833dd1576e6a71e	no	305
Warnings:					
Information:					
11	Foreign Reference	ExhibitL-D10_DE102015210803A1.pdf	640721 7d73ce810cae1d4e718923f091c445b45799dfad	no	10
Warnings:					
Information:					
12	Translation of Non-English Item of Information	ExhibitM-D10_DE102015210803A1_EnglishTranslation.pdf	183508 41d7d3c18504a2aee22abbe0469744b5dbd576f9	no	4
Warnings:					
Information:					
13	Foreign Reference	ExhibitN-D11_DE102014209635A1.pdf	1438327 1af1d6fd78f484abfc61ee15398dd7c8df561941	no	19
Warnings:					
Information:					
14	Translation of Non-English Item of Information	ExhibitO-D11_DE102014209635A1_EnglishTranslation.pdf	215843 79bfe78a08568be350914011e792b1fb0ed9e9c4	no	10
Warnings:					
Information:					

15	Non Patent Literature	ExhibitE-D4_NPL_UreaProductExpansion.pdf	1805495 55d2468219994439e65b7b8b4eb3fd5b63894a80	no	10
Warnings:					
Information:					
16	Non Patent Literature	ExhibitB-D1_NPL_AutothermalReforming.pdf	3366390 c70b095dbe046256de46b3579bcd22a8ca5a9bfa	no	20
Warnings:					
Information:					
17	Miscellaneous Incoming Letter	20230426_283386WOUS01_495230-44_RequestForSupplementalExamination.pdf	485925 31ce1e3947f98b422adf22776487b501963a38e0	no	5
Warnings:					
Information:					
		Total Files Size (in bytes):	32034819		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

VIA *e*FILE

PATENT APPLICATION
Docket No. 283386WOUS01_495230-44

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of		)
	CASALE SA	)
Application No.:	96/000,424	)
Patent No.	11,286,168	) Art Unit
		) 1622
Filed:	August 13, 2019	)
Confirmation No.:	3128	)
For:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE	)
Examiner:	Jafar Parsa	)
Customer No.:	116407	)

CORRECTED REQUEST FOR SUPPLEMENTAL EXAMINATION

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

Pursuant to the provisions of 37 C.F.R. § 1.610, and responsive to a Notice of Noncompliant Supplemental Examination Request ("Notice") dated April 12, 2023, a request for supplemental examination ("Request") is taken herein for U.S. Patent No. 11,286,168 (Application No. 96/000,424). A Request For Supplemental Examination Transmittal Form is filed concurrently with this Request for Supplement Examination.

1. Remarks

The Patent Owner notes that the European counterpart (EP Patent No. 3583067B1) to U.S. Patent No. 11,286,168 was challenged via two Notices of Opposition both filed before the European Patent Office on June 8, 2022. These opposition proceedings remain pending before the European Patent Office, with the Patent Owner having filed a reply to the Notice of Opposition on November 3, 2022. Out of an abundance of caution, the Patent Owner is submitting this Request, which includes as the items of information to be considered the references cited in the Notice of Opposition. The Patent Owner believes the claims of U.S. Patent No. 11,286,168 remain patentable in light of the items of information presented herein.

The Patent Owner further notes an initial Request was filed on February 16, 2023 and assigned Application No. 96/000,424. The Notice was issued on April 12, 2023 and alleged three items of noncompliance in the Request. The Patent Owner submits a good faith effort is made herein to address the items alleged to be noncompliant in the Notice. Specifically, in Item I(1) on page 2 of the Notice, the PTO asserted that the Request "does not mention dependent claims 6, 13, 18 and 22-23" and "it is unclear how any of the items of information is applied to claims 6, 13, 18 and 22-23." The Patent Owner believes the original Request indicated that the Patent Owner relies upon the required explanation under 37 CFR 1.610(b)(5) of the manner of applying D1, D2, D3, D6, D7, and/or D8 to independent claims 1 and/or 21, provided below, as the required explanation under 37 CFR 1.610(b)(5) for at least dependent claims 6, 13, 18, 22, and 23. The Patent Owner has further highlighted (*e.g.* underlined) herein where the Patent Owner relies upon the required explanation of applying an item of information to an independent claim as the required explanation for at least dependent claims 6, 13, 18, 22, and 23.

In Item I(2) on pages 2-3 of the Notice, the PTO asserted that the "detailed explanation must reflect the opinion of the patent owner, and not that of a third party." Accordingly, as instructed by Supervisory Patent Reexamination Specialist Eileen D. Lillis in a phone call on April 20, 2023, the Patent Owner has removed the communication of a notice of opposition for European Application No. 18702977.2 as an Item of Information in this Request.

In Item I(3) on page 3 of the Notice, the PTO asserted that item of information D4 "is not applied to the limitations of the claims." The Patent Owner has applied D4 to the limitations of claim 1 herein.

In summary, the Patent Owner believes the Request is compliant with requirements for Supplemental Examination Request under 37 C.F.R. § 1.610.

2. Identification of the Number of the Patent

The number of the patent for which supplemental examination is requested is 11,286,168 ("the '168 Patent"), attached herewith as Exhibit A.

3. List of Items of Information

The list of items of information that are requested to be considered, reconsidered, or corrected includes:

- Noelker, et al., "Autothermal Reforming: A Flexible Syngas Route with Future potential," Prepared for Presentation at NITROGREN & SYNGAS 2010 International Conference, Bahrain, 28 February - 3 March 2010, pp. 1-20 ("D1"), attached herewith as Exhibit B.
- U.S. Patent No. 8,137,422 B2 to Licht, et al. ("D2"), attached herewith as Exhibit C.
- European Patent No. 2 817 260 B1 to Fillippi, et al. ("D3"), attached herewith as Exhibit D.
- Shimura, "Urea Product Expansion by Newly Developed CO2 Recovery Process from Primary Reformer Flue Gas," Ammonia Technical Manual, Vol. 47, 2006, pp. 237-246 ("D4"), attached herewith as Exhibit E.
- Häussinger, et al., "Hydrogen, 3. Purification", Ullmann's Encyclopedia of Industrial Chemistry, Vol. 18, 2012, pp. 309-333" ("D5"), attached herewith as Exhibit F.
- U.S. Patent Application Publication No. 2004/0234426 to Reddy, et al. ("D6"), attached herewith as Exhibit G.
- European Patent No. 1 648 817 B1 to Blumenfeld, et al. ("D7"), attached herewith as Exhibit H. An English translation of D7 is attached herewith as Exhibit I.
- European Patent No. 2 266 922 A1 to Licht, et al. ("D8"), attached herewith as Exhibit J.
- "Ammonia; Principles and Industrial Practice", Wiley-VCH, ISBN 3-527-29593-3, January 1999, pp. 1-301 ("D9"), attached herewith as Exhibit K.

- DE 10 2015 210 803 A1 to Gorval, et al. ("D10"), attached herewith as Exhibit L. An English translation of D10 is attached herewith as Exhibit M.
- DE 10 2014 209 635 A1 to Gorval, et al. ("D11"), attached herewith as Exhibit N. An English translation of D11 is attached herewith as Exhibit O.

4. List of Any Other Prior or Concurrent Post-Patent Office Proceedings Involving the '168 Patent

There are no other prior or concurrent post-patent Office proceedings involving the '168 Patent in the United States.

5. Identification of Each Claim of the '168 Patent For Which Supplemental Examination is Requested

Supplemental examination is requested of claims 1-23 (*i.e.*, all claims of the '168 Patent) is requested in light of D1-11.

6. Detailed Explanation of the Relevance and Manner of Applying Each Item of Information

A detailed explanation of the relevance and manner of applying D1-D11 is provided below. As provided in greater detail in the claim chart below:

- D1 may be relevant to independent claims 1 and 21 and dependent claims 3, 4, 8-10, and 14-17 (and the Patent Owner relies upon the required explanation under 37 CFR 1.610(b)(5) of the manner of applying D1 to independent claims 1 and 21, provided below, as the required explanation under 37 CFR 1.610(b)(5) for at least dependent claims 2, 5-7, 11-13, 18-20, 22, and 23);
- D2 may be relevant to independent claim 1 and dependent claims 3, 4, 8-11, and 20 (and the Patent Owner relies upon the required explanation under 37 CFR 1.610(b)(5) of the manner of applying D2 to independent claim 1, provided below, as the required explanation under 37 CFR 1.610(b)(5) for at least dependent claims 2, 5-7, and 12-19);
- D3 may be relevant to independent claim 1 and dependent claims 11, 14-16, and 19 (the Patent Owner relies upon the required explanation under 37 CFR 1.610(b)(5) of the manner of applying D3 to independent claim 1, provided

below, as the required explanation under 37 CFR 1.610(b)(5) for at least dependent claims 2-10, 12, 13, 17, 18, and 20);

- D4 may be relevant to independent claim 1 in view of D2 and/or D3;
- D5 may be relevant to dependent claim 7 in view of D1-D3;
- D6 may be relevant to independent claims 1 and 21 and dependent claims 2, 5, 8, and 9 (and the Patent Owner relies upon the required explanation under 37 CFR 1.610(b)(5) of the manner of applying D6 to independent claims 1 and 21, provided below, as the required explanation under 37 CFR 1.610(b)(5) for at least dependent claims 3, 4, 6, 7, 10-12, 22, and 23);
- D7 may be relevant to independent claims 1 and 21 and dependent claim 2 (and the Patent Owner relies upon the required explanation under 37 CFR 1.610(b)(5) of the manner of applying D7 to independent claims 1 and 21, provided below, as the required explanation under 37 CFR 1.610(b)(5) for at least dependent claims 3-20, 22, and 23);
- D8 may be relevant to independent claim 1 and dependent claims 3, 4, 8-11, 17, and 20 (and the Patent Owner relies upon the required explanation under 37 CFR 1.610(b)(5) of the manner of applying D8 to independent claim 1, provided below, as the required explanation under 37 CFR 1.610(b)(5) for at least dependent claims 2, 5-7, 12-16, 18, and 19);
- D9 may be relevant to dependent claims 7, 11, 12, and 14-16;
- D10 may be relevant to independent claim 1 in view of D7 and dependent claim 19;
- D11 may be relevant to independent claim 1 in view of D7.

A. D1 (Autothermal Reforming: A Flexible Syngas Route with Future Potential)

D1 may be relevant to independent claims 1 and 21 of the '168 Patent and dependent claims 3, 4, 8-10, and 14-17 as provided in the following claim charts. Because dependent claims 2, 5-7, 11-13, 18-20, 22, and 23 include all the limitations of independent claims 1 and 21, the Patent Owner relies upon the required explanation under 37 CFR 1.610(b)(5) of the manner of applying D1 to independent claims 1 and 21, provided below, as the required explanation under 37 CFR 1.610(b)(5) for dependent claims 2, 5-7, 11-13, 18-20, 22, and 23.

Claim 1 of the '168 Patent	**D1**
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;	**Table 3; Page 12:** "Description of Uhde's ATR Test Facility" Figure 2, Options 2 and 3.
treatment of said synthesis gas including at least a shift reaction of the carbon monoxide into CO2,	**Figure 2, Options 2 and 3**
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;	**Figure 2, Options 2 and 3**
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	No apparent corresponding disclosure.
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,	No apparent corresponding disclosure.
wherein the first stream forms the fuel fraction and the second stream is process gas intended for the	No apparent corresponding disclosure.

synthesis of ammonia.	

Claim 3 of the '168 Patent	**D1**
The process of claim 1, wherein said fuel fraction is between 1% and 40% of the total amount of said CO2-depleted syngas.	**Page 20:** "A complete separation of the entire CO2 could also be realized in the ATR-based plant with little extra investment and an only moderate increase of the plants consumption figure provided the fired heater would be fed with syngas instead of natural gas."

Claim 4 of the '168 Patent	**D1**
The process of claim 1, wherein said fuel fraction is between 10% and 30% of the total amount of said CO2-depleted syngas.	**Page 20:** "A complete separation of the entire CO2 could also be realized in the ATR-based plant with little extra investment and an only moderate increase of the plants consumption figure provided the fired heater would be fed with syngas instead of natural gas."

Claim 8 of the '168 Patent	**D1**
The process of claim 1, wherein said enriched air contains at least 50% oxygen.	**Page 19 Table:** (provided below)

Claim 9 of the '168 Patent	**D1**
The process of claim 1, wherein said enriched air contains at least 90% oxygen.	**Page 19 Table:** (provided below)

Page 19 Table: (provided below)

		A	B	C
Parameter	**Unit**	**NH_3 syngas, enriched air**	**NH_3 syngas, pure oxygen**	**FT syngas**
feed composition				
CH_4	mol%, dry	89.2	82.9	88.7
C_{2+}	mol%, dry	7.1	14.5	7.4
oxidator N_2 content	mol%, dry	42.1	5.0	5.0
steam-to-carbon ratio	----	3.0	2.0	0.7
outlet temp. oxidat. zone	°C	1200	1250	1238
oxygen-to-carbon ratio	---	0.85	0.74	0.60
syngas pressure	bar abs	28.0	28.0	28.0
outl. temp. catalyst zone	°C	1086		1100

Claim 10 of the '168 Patent	**D1**
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.	**Page 20:** "A complete separation of the entire CO2 could also be realized in the ATR-based plant with little extra investment and an only moderate increase of the plants consumption figure provided the fired heater would be fed with syngas instead of natural gas."

Claim 14 of the '168 Patent	**D1**
The process of claim 1, wherein the overall steam/carbon ratio in the	**Page 18:** Operating point A represents the situation where an ATR generates a stoichio-metric syngas

conversion step is greater than 2.0.	composition for an ammonia synthesis operating on oxygen enriched air and a steam-to-carbon ratio of 3.0. In point B the ATR is operating on pure oxygen. With the steam-to-carbon ratio of 2.0 the conditions tend to ammonia or methanol plants.

Claim 15 of the '168 Patent	**D1**
The process of claim 1, wherein the overall steam/carbon ratio in the conversion step is greater than 2.4.	**Page 18:** Operating point A represents the situation where an ATR generates a stoichio-metric syngas composition for an ammonia synthesis operating on oxygen enriched air and a steam-to-carbon ratio of 3.0. In point B the ATR is operating on pure oxygen. With the steam-to-carbon ratio of 2.0 the conditions tend to ammonia or methanol plants.

Claim 16 of the '168 Patent	**D1**
The process of claim 1, wherein the overall steam/carbon ratio in the conversion step is greater than 2.7.	**Page 18:** Operating point A represents the situation where an ATR generates a stoichio-metric syngas composition for an ammonia synthesis operating on oxygen enriched air and a steam-to-carbon ratio of 3.0. In point B the ATR is operating on pure oxygen. With the steam-to-carbon ratio of 2.0 the conditions tend to ammonia or methanol plants.

Claim 17 of the '168 Patent	**D1**
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.	**Page 20:** "A complete separation of the entire CO2 could also be realized in the ATR-based plant with little extra investment and an only moderate increase of the plants consumption figure provided the fired heater would be fed with syngas instead of natural gas."

Claim 21 of the '168 Patent	**D1**
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,	**Page 5:** The ammonia synthesis requires an H2: N2 ratio in the order of 3.0. Obviously, this could not be realized by a steam reformer on its own. However, it can be met easily by combined reforming using an air blown secondary reformer.
and a section for treatment of the synthesis gas by a shift reaction of carbon monoxide into carbon dioxide, and decarbonation;	**Figure 2, Options 2 and 3**
the method comprising: providing a flow of enriched air or oxygen and using said flow as oxidant, instead of air, for the secondary reformer;	**Table 3; Page 12:** "Description of Uhde's ATR Test Facility" Figure 2, Options 2 and 3.
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;	No apparent corresponding disclosure.
feeding said fuel fraction of the gas, which has a reduced CO2 content, as fuel for at least one furnace of the plant.	No apparent corresponding disclosure.

B. <u>D2 (U.S. Patent No. 8,137,422 B2)</u>

D2 may be relevant to independent claim 1 of the '168 Patent and dependent claims 3, 4, 8-11, and 20 as provided in the following claim charts, and may be further relevant to

independent claim 1 in view of D3 and D4 (described below). Because dependent claims 2, 5-7, and 12-19 include all the limitations of independent claim 1, the Patent Owner relies upon the required explanation under 37 CFR 1.610(b)(5) of the manner of applying D2 to independent claim 1, provided below, as the required explanation under 37 CFR 1.610(b)(5) for dependent claims 2, 5-7, and 12-19.

Claim 1 of the '168 Patent	**D2**
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;	**Col. 3, ll. 39-43:** "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." **Col. 5, ll. 57-59:** "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." **Col. 7, ll. 4-17:** "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."

	FIG. 2, 14
treatment of said synthesis gas including at least a shift reaction of the carbon monoxide into CO2,	**Col. 3, ll. 53-67:** "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."
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;	**Col. 4, ll. 13-22:** "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." **Col. 4, ll. 36-43:** "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."

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	**Col. 5, ll. 27-33:** "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."
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,	**Col. 5, ll. 12-14:** "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." **Col. 5, ll. 39-41:** "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."
wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia.	No apparent corresponding disclosure.

Claim 3 of the '168 Patent	**D2**
The process of claim 1, wherein said fuel fraction is between 1% and 40% of the total amount of said CO2-depleted syngas.	**Table 4**

Claim 4 of the '168 Patent	**D2**
The process of claim 1, wherein said fuel fraction is between 10% and 30% of the total amount of said	**Table 4**

CO2-depleted syngas.	

Claim 8 of the '168 Patent	**D2**
The process of claim 1, wherein said enriched air contains at least 50% oxygen.	**Col. 7, ll. 38-43:** "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."

Claim 9 of the '168 Patent	**D2**
The process of claim 1, wherein said enriched air contains at least 90% oxygen.	**Col. 7, ll. 38-43:** "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."

Claim 10 of the '168 Patent	**D2**
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.	**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 prereformer and/or an oxygen secondary reformer." **FIG. 1-3**

Claim 11 of the '168 Patent	**D2**
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.	**Col. 4, ll. 36-39:** 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. **Col. 4 ln. 56 – col 5. ln. 6: "**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. **Col. 5, ll. 27-33:** "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."

Claim 20 of the '168 Patent	**D2**
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.	**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 prereformer and/or an oxygen secondary reformer." **FIG. 2**

C. <u>D3 (EP 2817260B1)</u>

D3 may be relevant to independent claim 1 of the '168 Patent and dependent claims 11, 14-16, and 19 as provided in the following claim charts, and may be further relevant to independent claim 1 in view of D2 (described above) and D4 (described below). Because dependent claims 2-10, 12, 13, 17, 18, and 20 include all the limitations of independent claim 1, <u>the Patent Owner relies upon the required explanation under 37 CFR 1.610(b)(5) of the manner of applying D3 to independent claim 1, provided below, as the required explanation under 37 CFR 1.610(b)(5) for dependent claims 2-10, 12, 13, 17, 18, and 20</u>.

Claim 1 of the '168 Patent	**D3**
A process for synthesis of ammonia from natural gas, the process	**FIG. 2:** natural gas 10, ammonia 31

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;	**Paragraph [0048]**: "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."
treatment of said synthesis gas including at least a shift reaction of the carbon monoxide into CO2,	**Paragraph [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."
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;	**Paragraph [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."
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	No apparent corresponding disclosure.
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,	No apparent corresponding disclosure.
wherein the first stream forms the	

fuel fraction and the second stream is process gas intended for the synthesis of ammonia.	No apparent corresponding disclosure.

Claim 11 of the '168 Patent	**D3**
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.	**Paragraph [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." **Paragraph [0058]:** "Fig. 4 shows the optional CO2 removal units 23 and 24 for the embodiment of Fig. 3."

Claim 14 of the '168 Patent	**D3**
The process of claim 1, wherein the overall steam/carbon ratio in the conversion step is greater than 2.0.	**Paragraph [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."

Claim 15 of the '168 Patent	**D3**
The process of claim 1, wherein the overall steam/carbon ratio in the conversion step is greater than 2.4.	**Paragraph [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."

Claim 16 of the '168 Patent	**D3**
The process of claim 1, wherein the overall steam/carbon ratio in the conversion step is greater than 2.7.	**Paragraph [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."

Claim 19 of the '168 Patent	**D3**
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.	**Paragraph [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." **Paragraph [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."

D. <u>D4 (Urea Product Expansion by Newly Developed CO2 Recovery Process from Primary Reformer Flue Gas)</u>

D4 may be relevant to independent claim 1 of the '168 Patent as provided below in view of D2 and/or D3. In particular, the Introduction, Figure 1 (provided below), and Figure 4 (provided below) of D4 may be relevant to claim 1 of the '168 Patent in view of D2 and/or D3, as noted in the claim chart below.

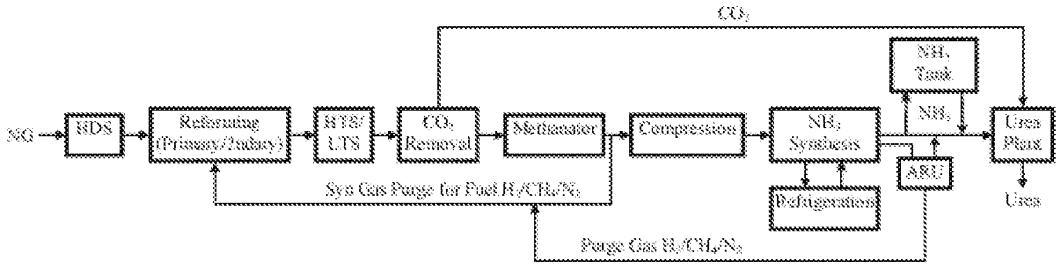


Figure 1. Conventional Ammonia Plant

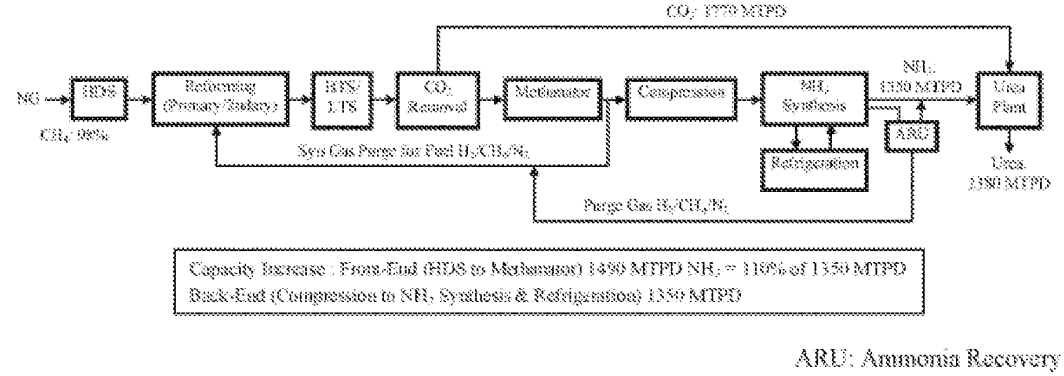


Figure 4. Larger Front-End Capacity Case

Claim 1 of the '168 Patent	**D4**
A process for synthesis of ammonia from natural gas, the process comprising:	Figures 1 and 4 (provided above): NG (natural gas) as an input in a conventional ammonia plant (Figure 1) and a larger front-end capacity case (Figure 4); NH_3 synthesis followed by ammonia recovery units of a conventional ammonia plant (Figure 1) and a larger front-end capacity case (Figure 4).
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;	No apparent corresponding disclosure: the hydrodesulphurization (HDS) stage is not followed by conversion of the charge of desulphurized natural gas with oxygen-enriched air or oxygen.
treatment of said synthesis gas including at least a shift reaction of the carbon monoxide into CO2,	Figures 1 and 4 (provided above): include a step of HTS (high temperature shift) / LTS (low temperature shift) between steps of reforming and CO2 removal in a conventional ammonia plant (Figure 1) and a larger front-end capacity case (Figure 4).
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;	Figures 1 and 4 (provided above): include a step of CO_2 removal after step of HTS/LTS and before a methanator, while the separated CO2 is directed to a urea plant in a conventional ammonia plant (Figure 1) and a larger front-end capacity case (Figure 4).
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	Figures 1 and 4 (provided above): include a flow of synthesis gas purge for fuel to reforming after the methanator in a conventional ammonia plant (Figure 1) and a larger front-end capacity case (Figure 4).
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,	Figures 1 and 4 (provided above): include a flow of synthesis gas purge for fuel after the methanator and a flow to a step of compression in a conventional ammonia plant (Figure 1) and a larger front-end capacity case (Figure 4).

wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia.	Figures 1 and 4 (provided above): include a flow of synthesis gas purge for fuel after the methanator and a flow to a step of compression before NH3 synthesis in a conventional ammonia plant (Figure 1) and a larger front-end capacity case (Figure 4).

E. D5 (Hydrogen, 3. Purification", Ullmann's Encyclopedia of Industrial Chemistry)

D5 may be relevant to dependent claim 7 of the '168 Patent in view of D1-D3 as provided in the following claim charts.

Claim 7 of the '168 Patent	**D5**
The process of claim 1, wherein said CO2-depleted syngas contains no more than 1000 ppm by volume of CO2.	**Page 327:** "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/m3] CO2)."

F. D6 (US Patent Application Publication No. 2004/0234426 A1)

D6 may be relevant to independent claims 1 and 21 and dependent claims 2, 5, 8, and 9 of the '168 Patent as provided in the following claim charts. Because dependent claims 3, 4, 6, 7, 10-20, 22, and 23 include all the limitations of independent claims 1 and 21, the Patent Owner relies upon the required explanation under 37 CFR 1.610(b)(5) of the manner of applying D6 to independent claims 1 and 21, provided below, as the required explanation under 37 CFR 1.610(b)(5) for dependent claims 3, 4, 6, 7, 10-20, 22, and 23.

Claim 1 of the '168 Patent	**D6**
A process for synthesis of ammonia from natural gas, the process comprising:	
conversion of a charge of	**Paragraph [0026]:** "Alternatively, or additionally as

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;	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." **Fig. 3**
treatment of said synthesis gas including at least a shift reaction of the carbon monoxide into CO2,	**Paragraph [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."
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;	**Paragraph [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."
separation of a part of said CO2-depleted synthesis gas as fuel	**Paragraph [0014]:** "In one particularly preferred aspect of the inventive subject matter, contemplated plants include an ammonia synthesis loop that receives an

fraction,	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."
wherein said fuel fraction is fed as fuel to at least one furnace	**Paragraph [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%."
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,	No apparent corresponding disclosure.
wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia.	No apparent corresponding disclosure.

Claim 2 of the '168 Patent	**D6**
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.	**Paragraph [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%."

Claim 5 of the '168 Patent	**D6**
further comprising a step for methanation of the synthesis gas and/or addition of nitrogen to the synthesis gas.	**Paragraph [0039]:** "A subsequent acid gas removal unit (here: carbon dioxide removal unit) 650 removes significant quantities of carbon dioxide, and methanator 660 downstream of the acid gas removal unit converts residual carbon monoxide and carbon dioxide to methane."

Claim 8 of the '168 Patent	**D6**
The process of claim 1, wherein said enriched air contains at least 50%	**Paragraph [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

oxygen.	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.

Claim 9 of the '168 Patent	**D6**
The process of claim 1, wherein said enriched air contains at least 90% oxygen.	**Paragraph [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.

Claim 20 of the '168 Patent	**D6**
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.	**Paragraph [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%.

Claim 21 of the '168 Patent	**D6**
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,	**Claim 8:** "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."
and a section for treatment of the synthesis gas by a shift reaction of carbon monoxide into carbon dioxide, and decarbonation;	**Paragraph [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."
the method comprising: providing a flow of enriched air or oxygen and using said flow as oxidant, instead of air, for the secondary reformer;	**Claim 8:** "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."
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;	**Paragraph [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."
feeding said fuel fraction of the gas, which has a reduced CO2 content, as fuel for at least one furnace of the plant.	No apparent corresponding disclosure.

G. D7 (EP 1648817B1)

D7 may be relevant to independent claims 1 and 21 and dependent claim 2 of the '168 Patent as provided in the following claim charts. Because dependent claims 3-20, 22, and 23 include all the limitations of independent claims 1 and 21, the Patent Owner relies upon the required explanation under 37 CFR 1.610(b)(5) of the manner of applying D7 to independent claims 1 and 21, provided below, as the required explanation under 37 CFR 1.610(b)(5) for dependent claims 2-20, 22, and 23.

Claim 1 of the '168 Patent	**D7**
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	No apparent corresponding disclosure.

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,	**Claim 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,
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;	**Claim 1:** wherein the carbon dioxide is removed from the converted gas stream (8) by means of a gas scrubber (7),
separation of a part of said CO2-depleted synthesis gas as fuel fraction,	**Fig. 1 and claim 1:** 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.
wherein said fuel fraction is fed as fuel to at least one furnace	**Fig. 1 and claim 1:** 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.
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,	**Fig. 1 and claim 1:** 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.
wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia.	**Fig. 1 and claim 1:** 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.

Claim 2 of the '168 Patent	**D7**
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.	**Claim 1:** and the scrubbed hydrogen-rich gas stream (10) is then separated in a pressure swing adsorption system (11)

Claim 21 of the '168 Patent	**D7**
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,	No apparent corresponding disclosure.
and a section for treatment of the synthesis gas by a shift reaction of carbon monoxide into carbon dioxide, and decarbonation;	**Claim 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,
the method comprising: providing a flow of enriched air or oxygen and using said flow as oxidant, instead of air, for the secondary reformer;	No apparent corresponding disclosure.
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;	**Fig. 1 and claim 1:** 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.
feeding said fuel fraction of the gas, which has a reduced CO2 content, as fuel for at least one furnace of the plant.	**Fig. 1 and claim 1:** 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.

H. D8 (EP 2266922A1)

D8 may be relevant to independent claim 1 and dependent claims 3, 4, 8-11, 17, and 20 of the '168 Patent as provided in the following claim charts, and may be further relevant to independent claim 1 in view of D3 and D4 (described above). Because dependent claims 2, 5-7, 12-16, 18, and 19 include all the limitations of independent claim 1, the Patent Owner relies upon the required explanation under 37 CFR 1.610(b)(5) of the manner of applying D8 to independent claim 1, provided below, as the required explanation under 37 CFR 1.610(b)(5) for dependent claims 2, 5-7, 12-16, 18, and 19.

Claim 1 of the '168 Patent	**D8**
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;	**Paragraph [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." **Paragraph [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." **Paragraph [0043]:** "FIG. 2 and FIG. 3 show additional optional features, for example a so-called prereformer 80, an oxygen sec-ondary reformer 20, and a second shift reactor 50." **Paragraph [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." **FIG. 2, 14**
treatment of said synthesis gas including at least a shift reaction of the carbon monoxide into CO2,	**Paragraph [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." **Paragraph [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"
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;	**Paragraph [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." **Paragraph [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. […]"
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	**Paragraph [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. […]“
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,	**Paragraph [0037]:** “[…] 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.” **Paragraph [0040]:** “[…] 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.”
wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia.	No apparent corresponding disclosure.

Claim 3 of the ‘168 Patent	**D8**
The process of claim 1, wherein said fuel fraction is between 1% and 40% of the total amount of said CO2-depleted syngas.	**Table 4**

Claim 4 of the ‘168 Patent	**D8**
The process of claim 1, wherein said fuel fraction is between 10% and 30% of the total amount of said CO2-depleted syngas.	**Table 4**

Claim 8 of the '168 Patent	**D8**
The process of claim 1, wherein said enriched air contains at least 50% oxygen.	**Paragraph [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."

Claim 9 of the '168 Patent	**D8**
The process of claim 1, wherein said enriched air contains at least 90% oxygen.	**Paragraph [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."

Claim 10 of the '168 Patent	**D8**
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.	**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 prereformer and/or an oxygen secondary reformer."

	FIG. 1-3

Claim 11 of the '168 Patent	**D8**
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.	**Paragraph [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. […]" **Paragraph [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. **Paragraph [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."

Claim 20 of the '168 Patent	**D8**
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.	**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 prereformer and/or an oxygen secondary reformer." **FIG. 2**

I. <u>D9 (Ammonia; Principles and Industrial Practice)</u>

D9 may be relevant to dependent claims 7, 11, 12, and 14-16 of the '168 Patent as provided in the following claim charts.

Claim 7 of the '168 Patent	**D9**
The process of claim 1, wherein said CO2-depleted syngas contains no more than 1000 ppm by volume of CO2.	**Table 33 (p. 136 of Exhibit K):** provided below.

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	62
(lean/semi-lean)	(47/53)	52/48	-
Reboiler duty	98	100	250
Specific energy, MJ/kmol CO_2	28.5	28	73

Claim 11 of the '168 Patent	**D9**
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.	**Pages 172-175 (text pages 166-169):** describes "Hydrogen Recovery by Cyrogenic [*sic*] Units."

Claim 12 of the '168 Patent	**D9**
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	**Pages 143-144 (text pages 137-138):** describes liquid nitrogen wash.

the second stream.	

Claim 14 of the '168 Patent	**D9**
The process of claim 1, wherein the overall steam/carbon ratio in the conversion step is greater than 2.0.	**Page 77 (text page 71):** "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."

Claim 15 of the '168 Patent	**D9**
The process of claim 1, wherein the overall steam/carbon ratio in the conversion step is greater than 2.4.	**Page 77 (text page 71):** "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."

Claim 16 of the '168 Patent	**D9**
The process of claim 1, wherein the overall steam/carbon ratio in the conversion step is greater than 2.7.	**Page 77 (text page 71):** "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."

J. D10 (DE 102015210803A1)

D10 may be relevant to a portion of claim 1 in view of D7 and dependent claim 19 of the '168 Patent as provided in the following claim chart.

Claim 1 of the '168 Patent	**D10**
conversion of a charge of	**Paragraph [0003]** (translated): The reforming 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;	hydrocarbonaceous feedstocks can usually be carried out either in a cracking furnace with external heating (steam reformer) or in an autothermal reformer (ATR) with an internal heating. Which of the two reforming technologies is the most economical depends on many parameters in each case, such as the desired ratio of H_2 to CO, plant capacity, product and educt prices, etc. Hydrocarbon-containing feedstocks include natural gas, LPG, biogas, butane, Gasoline or another type of hydrocarbon.

Claim 19 of the '168 Patent	**D10**
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.	**Paragraph [0020]** (translated): The S / C ratio is at the entrance of the autothermal reformer in the range of 0.1 to 2.5, more preferably in the range of 0.2 to 2.4, more preferably in the range of 0.3 to 2.3, in the range of 0.4 to 2.2, in the range of 0.5 to 2.1, in the range of 0.6 to 2.0, in the range of 0.7 to 1.9, in the range of 0.8 to 1, 8, in the range of 0.9 to 1.7, in the range of 1.0 to 1.6 in the range of 1.1 to 1.5 or in the range of 1.2 to 1.4.

K. <u>D11 (DE 102014209635A1)</u>

D11 may be relevant to a portion of claim 1 in view of D7 of the '168 Patent as provided in the following claim chart.

Claim 1 of the '168 Patent	**D11**
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;	**Paragraph [0006]** (translated): An alternative to two-stage reforming is the purely autothermal reforming of natural gas with the help of cheaper autothermal reformers (ATR). In order to provide the additional amount of oxygen required for this purpose, either oxygen from an air separation plant or a correspondingly larger amount of air is required. However, the cost of air separation or the provision of additional air and the removal of excess nitrogen are significant and, with plant

	capacities of up to 3,300 tpd of ammonia, compensate for the savings achieved by eliminating the steam reformer. However, devices for the separation of air and the separation of the excess nitrogen show a significant degression of the additional costs when increasing their capacity by increasing the components. With increasing capacity above 3300 tpd of ammonia, the increase in the components of plants based on purely autothermal reformers brings cost advantages compared to the two-stage reforming.

7. Optional Explanation Under 37 CFR 1.610(c)

As provided in 37 CFR 1.610(c), this Request also may include an explanation of how the claims are patentably distinguishable over the items of information and also an explanation of why each item of information does or does not raise a substantial new question of patentability.

A. D1 (Autothermal Reforming: A Flexible Syngas Route with Future Potential)

Patent Owner first notes that the public availability of D1 as prior art under 35 U.S.C. § 102(a)(2) to the '168 is questionable. Page 1 of D1 states that such report was prepared for Presentation at NITROGEN & SYNGAS 2010 International Conference, Bahrain, 28 February – 3 March 2010. However, D1 itself does not bear any indication of a publication. Also, there is no evidence that such scheduled lecture actually took place and, if it did, that D1 precisely reflects the content of that lecture.

Nonetheless, even assuming, *arguendo,* D1 is prior art 35 U.S.C. § 102(a)(2), claim 1 is patentably distinguishable from D1 and D1 does not raise a substantial new question of patentability. Fig. 2 of D1 appears to illustrate simplified block flow diagrams of process variations of ammonia plants based on autothermal reforming (ATR). In Option 2 of Fig. 2, a natural gas feed appears to be reformed in an ATR fired with oxygen-enriched air produced by an air separation unit (ASU). The effluent of the ATR appears to be subject to cooling, CO shift and CO2 removal and methanation. The so obtained ammonia make-up gas appears to be compressed and reacted in an ammonia synthesis loop. A stream purged from the ammonia loop appears to be treated to remove inert gas and to recover unreacted hydrogen which is reintroduced at the suction side of the compressor.

Option 3 of Fig. 2 appears to differ in that the ATR is fed with pure oxygen and the methanator is replaced by liquid nitrogen wash, using nitrogen from the ASU. Both Options 2 and 3 of Fig. 2 of D1 fail to disclose "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" of independent claim 1. Similarly, D1 fails to disclose "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," as recited in independent claim 21.

Patent Owner notes that D1 states, "[a] complete separation of the entire CO2 could also be realized in the ATR-based plant with little extra investment and an only moderate increase of the plants consumption figure provided the fired heater would be fed with syngas instead of natural gas." *D1*, p. 20. Based on Table 4, page 11 of D1, it is understood that said fired heater is a preheater of the process gas before an autothermal reformer (ATR). This, however, does not disclose the use of a portion of CO2-depleted ammonia make-up gas as fuel for a furnace of the plant, as such an interpretation goes beyond the disclosure of D1. To the contrary, this conclusive statement of D1, as a matter of fact, discloses no more than "syngas instead of natural gas." At page 20, D1 gives no further information on how to interpret the word "syngas". For a person of ordinary skill in the art, "syngas" denotes generally a gas which is the result of an artificial synthesis process, which could be, for example, the gasification of a liquid or solid fuel, in contrast with "natural gas" which is extracted from natural fields. Particularly in the context of D1, which discloses syngas *instead of* natural gas, a person of ordinary skill in the art would interpret the word "syngas" just to mean a fuel gas obtained by synthesis. D1 does not disclose that the syngas mentioned at page 20 is or can be the CO2-depleted process gas obtained after conversion and treatment of natural gas.

Furthermore, the introduction of D1 (page 3, lines 2-3) discloses that synthesis gases ("*syngases*") are gas mixtures composed mainly of hydrogen and carbon monoxide. D1 defines a synthesis gas in terms of the composition requirements for subsequent synthesis processes (Table 1, page 3) and of composition ranges provided by different generators (Fig. 1, page 4). In D1 the

expression "*syngas*" is never used to describe a CO2-depleted process gas. Hence, D1 is silent about a CO2-depleted synthesis gas as fuel fraction, as required by claim 1.

Furthermore, D1 is silent about splitting in a first stream and a second stream having the same composition. In D1, reference can be made to options 2 and 3 of page 7, appearing to disclose an ATR-based process for synthesis of ammonia from natural gas using oxygen enriched air (option 2) or pure oxygen (option 3; erroneously indicated as "option 1" after option 2) as oxidizer. In these options, D1 does not disclose to split the process gas into a first stream to form a fuel fraction and a second stream for synthesis of ammonia. As provided above, D1 appears only to provide a very generic indication about feeding a fired heater with syngas instead of natural gas.

Patent Owner further submits D2, D3, D4, D6, and/or D7 do not cure the deficiencies of D1. D2 and D7 appear to teach to take a portion of the process gas as a fuel for a reformer furnace, which is however absent in the ATR-based options 2 and 3 of D1. D3 does not disclose splitting a process gas into a fuel stream and a process stream having the same composition. D4 and D6 appear to relate to conventional reforming in a primary reformer and secondary reformer. Accordingly, no combination would teach the skilled person towards the subject matter of claim 1.

Accordingly, claims 1 and 21 are patentably distinguishable over D1, and D1 does not raise a substantial new question of patentability.

B. <u>D3 (EP 2817260B1)</u>

D3 appears to disclose a process for production of ammonia (31) wherein natural gas (10) is converted in an ATR or POX reactor (11); the ATR or POX reactor receives oxygen (12) from an air separation unit (13); the effluent of the ATR or POX reactor is treated (Fig. 2) in a medium-temperature shift reactor (15), CO2 removal unit (23) and PSA unit (17). The PSA unit produces a purified syngas (18) and a fuel gas (22). D3 appears to disclose that said fuel gas withdrawn from the PSA unit can be used as a fuel in a fired heater of the plant optionally after a further removal of CO2 ([0034]).

Claim 1 is distinguishable from D3 at least because D3 does not disclose "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," as recited in claim 1. Patent Owner further notes, that, as a matter of fact, D3 does not disclose separation of a part of the CO2-depleted gas as fuel fraction. In D3, the only fuel stream recycled in the process appears to be the tail gas (22) of the PSA unit. The purified syngas 18 of the PSA unit 17 of D3 appears to not split, does not appear to have the same composition of stream 22, and does not appear form the fuel fraction fed as fuel to at least a furnace.

Patent Owner further notes that D3, as a consequence of failing to discloses "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," D3 inevitably also fails to disclose "wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia," as further recited in independent claim 1, because these limitations refer to the streams defined previously in claim 1. Hence, D3 does not disclose at least "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."

Patent Owner respectfully submits that combining the teachings of D3 with the teaching of D2 and/or D4 would not cure the deficiencies of D2. Patent Owner notes that D2 appears to disclose a steam hydrocarbon reforming process for production of hydrogen (*see* D2 Abstract, claim 1) wherein a portion (74) of the hydrogen-containing product gas (72) is fed as a fuel stream to a reformer furnace (100). *See* D2, Figs. 1-3 and col. 5 lines 27-30. D3 further appears to disclose (*see* D3, [0018], lines 14-19) a process for producing ammonia synthesis gas from a hydrocarbon source comprises a conversion of said hydrocarbon source into a raw synthesis gas solely by means of an ATR or POX reactor and without a primary reforming stage. Paragraph [0019], line 36 of D3 underlines that the invention uses no primary reformer and no secondary reformer.

Accordingly, one of ordinary skill in the art would have no motivation to combine D2 with D3, realizing that D2 and D3 relate to very different processes. That said, even assuming, *arguendo,* one of ordinary skill in the art combined D2 with D3, the resulting combination would

not arrive any closer to the deficiencies of D3 relative to claim 1. For example, even assuming, *arguendo*, that one of ordinary skill in the art finds in D2 the teaching of sending a portion of CO2-depleted gas to a reformer furnace, such teaching would appear to one of ordinary skill in the art as inapplicable to D3, simply because D3 has no such furnace. D2 simply does not give the slightest hint to modify D3 in such a way to include "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."

A similar reasoning is applicable to the combination of D3 and D4. D4 (*see* D4, Fig. 1 or Fig. 4) appears to disclose ammonia plants with at least a primary/secondary reforming stage. D4 (*see* D4, Fig. 1) appears to disclose that a syngas purge taken after a methanator is sent to a reforming section including primary/secondary reformer. As commented above, this feature is incompatible with the ATR-based or POX-based process of D3.

In addition, D4 does not address the problem of reducing CO2 emissions in connection with ammonia synthesis. D4 appears to address a very specific issue in connection with an integrated ammonia-urea process. With reference to the Abstract of D4, paragraph 3, D4 appears to disclose that urea production in a Malaysian ammonia and urea complex plant was limited by a shortage of CO2 production and excess of ammonia, leading to an unbalance between NH3 and CO2, caused by a methane-rich natural gas source. According to page 238, right-handed column, third paragraph of D4, if excess ammonia is produced, the excess synthesis gas is withdrawn from the outlet of a methanator and then fired in the reformer with the purge gas until the CO2 product is matched with the ammonia product for the urea plant. Therefore, D4 appears to be basically concerned with the problem of how to balance a deficit in carbon dioxide production with respect to ammonia production for providing stoichiometrically required amounts for a downstream urea synthesis section (*see also* D4, page 239, left column, second paragraph). D4 only contains a very generic statement (*see* D4, Abstract, last paragraph) that its technology would reduce the effluent CO2 in the flue gas from the primary reformer; it does not address the problem of how to reduce CO2 emissions in a ATR or POX-based ammonia process like in D3.

With respect to dependent claim 11, the purge gas referenced in paragraph [0057] of D3 does not appear to be recycled as process gas does not appear to be subjected to a step of conversion of the natural gas into synthesis gas.

Accordingly, claim 1 is patentably distinguishable over D3, whether viewed alone or in combination with D2 and/or D4, and D3 in view of D2 and/or D4 does not raise a substantial new question of patentability.

C. D6 (US Patent Application Publication No. 2004/0234426 A1)

Patent Owner respectfully submits that D6 discloses different embodiments with reference to Fig. 2 and Fig. 3 (including a coldbox; see [0008]-[0009], [0023]-[0026]) and Fig. 6 (including a pressure swing absorption unit; see [0012], [0038]-[0040]).

Patent Owner respectfully submits that Fig. 6 of D6 (see [0037]-[0040]) appears to discloses a process for the synthesis of ammonia (692) from natural gas (602) based on primary reformer (610) and air-fired secondary reformer (620) followed by shift (640), carbon dioxide removal (650) and methanation (660). A portion (662A) of the process gas effluent from the methanator is sent to a PSA unit (685) which appears to produce a hydrogen-rich stream (662A') and a waste stream (662A"). Said hydrogen-rich stream (662A') is sent to the ammonia synthesis loop (690) via a compressor (680) like the remainder portion (662B) of the methanator effluent. The waste stream (662A") of the PSA unit is sent as fuel to the primary reformer together with a purge stream removed from the ammonia loop.

Patent Owner first notes that the embodiment of Fig. 6 lacks conversion ***with oxygen-rich air or with oxygen***. D6 has only one embodiment, namely that of Fig. 3, wherein oxygen from an ASU is fed – together with additional process air – to a reforming stage. In contrast, the embodiment of Fig. 6 uses process air with no added oxygen from an ASU. At least for this reason, the embodiment of Fig. 6 cannot be novelty-prejudicial for claim 1.

Patent Owner further notes that claim 1 requires the split of CO2-depleted gas into two streams *having the same composition,* one of which forms a fuel fraction and the other is process gas for ammonia synthesis. This is clearly absent from Fig. 6 of D6 because the stream 662A – resulting from the split of the methanator effluent – does not form a fuel fraction. In D6, a fuel fraction can be seen in stream 672 which includes the waste stream of the PSA unit and the purge taken from the ammonia loop, but this stream 672 does *not* result from splitting a CO2-depleted synthesis gas stream within the meaning of claim 1 or claim 21.

Furthermore, the stream 662A *itself* does not form the fuel fraction fed to at least a furnace because such stream is separated in the PSA unit 685 in the hydrogen rich stream 662A' and the waste stream 662A" comprising methane, hydrogen and nitrogen (see [0040]). Only waste stream 662A" is then fed to the burner of the primary reformer 610, so that said stream 662A" actually forms the fuel fraction. The stream 662A is not fed as fuel to at least one furnace and is not a first stream forming the fuel fraction in the meaning of claim 1.

The stream 662A "that is fed to the burner is a sub-fraction of stream 662A, in contrast to the other effluent stream 662A' of the PSA unit 685 defined as hydrogen rich stream. The stream 662A" is consequently a by-product of a further transformation / separation process performed on the CO2-depleted synthesis gas. In summary, Patent Owner cannot identify in D6-Fig. 6 the fuel fraction and the process gas stream having the same composition as required by claim 1. Hence, features of claim 1 are missing from D6. The deficiencies of D6 are not remedied by any of the remaining items of information presented herein.

Accordingly, claims 1 and 21 are patentably distinguishable over D6, and D6 does not raise a substantial new question of patentability.

D. <u>D7 (EP 1648817B1)</u>

Patent Owner respectfully submits D7 appears to disclose a process for the production of hydrogen featuring a steam reforming in a furnace (4), shift conversion (5), a gas scrubber (7) for CO2 removal and a PSA unit (11) for purification of the gas. D7 discloses that a portion of the process gas effluent from the gas scrubber is sent to the reformer as a fuel, together with the tail gas (17) of the PSA unit (Fig. 1, [0013]).

Patent Owner respectfully submits that D7 does not appear to disclose the production of ammonia from natural gas and does not appear to disclose that the conversion of the natural gas is performed with oxygen-enriched air or with oxygen. D7 appears to focus on the production of hydrogen. See claim 1 and [0013], lines 41-42 of D7; this latter passage appears to disclose a gas product stream (12) comprising a H2 content > 99 % vol.

Patent Owner respectfully notes that claim 1 recites, in part, "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." (Emphasis added). Claim 21 recites, in part, providing ***a flow of enriched air or oxygen*** and using said flow as oxidant, instead of air, for the secondary reformer." (Emphasis added). As provided in the '168 Patent,

using 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; it limits the flue loss of nitrogen; and/or it allows a high temperature for conversion of the natural gas to be maintained. Patent Owner respectfully submits the combination of D7 with any other items of information provided herein does not result in these advantages.

With specific respect to dependent claim 6, in claim 1 of D7, hydrogen appears to be branched off from the gas stream behind the gas scrubber, *i.e.*, downstream of the CO2 removal. D7 also does not appear to include a nitrogen addition step.

Even assuming, *arguendo*, the teachings of D7 were combined with the teachings of D6, Fig. 6 of D6 appears the only pertinent embodiment to the subject matter of claim 1 because the other embodiments do not comprise streams 662A, 662B having the same composition. However, the embodiment of Fig. 6 does not comprise a feed of oxygen from an air separation unit (*i.e.*, "with oxygen-enriched air or with oxygen," as recited in independent claim 1.

Even assuming, *arguendo*, the teachings of D7 were combined with the teachings of D9 (section 4.1.1, page 69, lines 20-22), D9 also is silent as to "oxygen-enriched air or with oxygen" because controlled amounts of air (and not oxygen-enriched air or oxygen) appear to be disclosed to be mixed with the effluent of the primary reformed in D9.

Even assuming, *arguendo*, the teachings of D7 were combined with the teachings of D10 (paragraph [0003]) and/or D11 (paragraph [0006]), such a combination does not address the above-referenced advantages of using oxygen-enriched air.

With specific respect to independent claim 21, D7 does not appear to teach or suggest "[a] method for ***revamping*** a plant…" as recited in independent claim 21.

Accordingly, claims 1 and 21 are patentably distinguishable over D7, and D7 does not raise a substantial new question of patentability.

E. D8 (EP 2266922A1)

Patent Owner respectfully submits D8 belongs to the same patent family of D2. Accordingly, Patent Owner respectfully notes that claim 1 recites, in part, "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" and "wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia." (Emphasis added). Claim 21 recites, in part, providing ***a flow of enriched air or***

oxygen and using said flow as oxidant, instead of air, for the secondary reformer." (Emphasis added). Accordingly, as provided above in relation to D2, claims 1 and 21 are patentably distinguishable over D8, and D8 does not raise a substantial new question of patentability.

F. D9 (Ammonia; Principles and Industrial Practice)

With respect to D9 and claims 14-16, Patent Owner respectfully submits that these claims depend from claim 1, which recites "***oxygen-enriched air or with oxygen***." (Emphasis added). D9 appears to reference controlled amounts of air that are **not** oxygen-enriched air or oxygen. D9, then cannot be combined with, for example, D1, for purposes of obviousness.

Accordingly, claims 14-16 are patentably distinguishable over D9 in view of the other items of information, and D9 does not raise a substantial new question of patentability.

8. Copy of the '168 Patent

The '168 Patent is attached herewith as Exhibit A.

9. Copy of Each Item of Information

Each item of information is attached herewith as Exhibits B-P.

10. Summary of Relevant Portions of Any Submitted Document Over 50 Pages In Length

D9 ("Ammonia; Principles and Industrial Practice", Wiley-VCH, ISBN 3-527-29593-3, January 1999, pp. 1-301) is over 50 pages in length. Pages 75-78 (text pages 69-72) may be relevant to claims 14-16. These pages describe thermodynamics, operation, pressure, steam/carbon ration. Table 33 on page 136 (text page 130) of D9 may be relevant to dependent claim 7. Table 33 provides examples of aMDEA process options in steam reforming ammonia plants. Pages 134-136 (text pages 128-130) of D9 describe ethanolamine-based systems that may be relevant to dependent claim 7. Pages 143-144 (text pages 137-138) of D9 may be relevant to dependent claim 12. These pages describe a liquid nitrogen wash. Pages 172-175 (text pages 166-169) of D9 may be relevant to dependent claim 11. These pages describe hydrogen recovery by cryogenic units. Table 39 on page 192 (text page 186) of D9 may be relevant to dependent claims 3 and 4. Table 39 provides a table pertaining to energy analysis of a low energy ammonia

plant. Pages 188-192 (text pages 182-186) of D9 describe minimum energy requirement for steam reforming process that may be relevant to dependent claims 3 and 4.

11. Identification of the Owner of the '168 Patent

The owner of the '168 Patent is Casale SA (Via Pocobelli 6, Lugano, Switzerland 6900).

B. CONCLUSION

In view of the foregoing, the Patent Owner believes the Request for Supplemental Examination for the '168 Patent is complete, and respectfully submits that the claims of the '168 Patent remain patentable in light of the items of information presented herein. A Request For Supplemental Examination Transmittal Form is filed concurrently with this Request for Supplement Examination.

The Commissioner is hereby authorized to charge payment of any of the following fees that may be applicable to this communication, or credit any overpayment, to Deposit Account No. 50-6181: (1) any filing fees required under 37 CFR § 1.16; (2) any patent application and reexamination processing fees under 37 CFR § 1.17; and/or (3) any post issuance fees under 37 CFR § 1.20. In addition, if any additional extension of time is required, which has not otherwise been requested, please consider this a petition therefor and charge any additional fees that may be required to Deposit Account No. 50-6181.

Dated this 26th day of April, 2023.

Respectfully submitted,

/Jonathan Rowe, Reg.# 65335/
Jonathan Rowe
Registration No. 65,335
Attorney for Patent Owner
Dorsey & Whitney LLP
Customer No. 116407
Telephone No. 801.933.7360

MSS:JPR

PTO/SB/59 (09-16)
Approved for use through 11/30/2021. OMB 0651-0064
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

REQUEST FOR SUPPLEMENTAL EXAMINATION TRANSMITTAL FORM

Address to:
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Attorney Docket No.:

Date:

1. ☑ This is a request for supplemental examination pursuant to 37 CFR 1.610 of patent number 11,286,168 issued March 29, 2022. 37 CFR 1.610(b)(1).

2. ☑ Supplemental examination of claim(s) 1-23 is requested. 37 CFR 1.610(b)(4).

3. ☑ a. The name(s) of the patent owner(s) (**not** the patent practitioner(s)) is (are):
CASALE SA

☐ b. A submission by the patent owner(s) in compliance with 37 CFR 3.73(c), which establishes that the patent owner(s) has (have) the entirety of the ownership in the patent for which supplemental examination is requested, is included. 37 CFR 1.610(b)(9).

4. ☐ a. A check in the amount of $_____ is enclosed to cover the fee for processing and treating a request for supplemental examination, the fee for reexamination ordered under 35 USC 257, and the fee for processing and treating each non-patent document over 20 sheets in length (37 CFR 1.20(k)(1 - 3));

☑ b. The Director is hereby authorized to charge all applicable fees as set forth in 37 CFR 1.20(k)(1 - 3) to Deposit Account No. 506181; or

☑ c. Payment by credit card. Form PTO-2038 is attached. 37 CFR 1.610(a).

5. ☑ Any refund should be made by ☐ check or ☑ credit to Deposit Account No. 506181. 37 CFR 1.26(c). If payment is made by credit card, refund must be to the credit card account.

6. ☑ A copy of the patent for which supplemental examination is requested, and a copy of any disclaimer or certificate issued for the patent are included. 37 CFR 1.610(b)(6).

7. ☐ CD-ROM or CD-R in duplicate, Computer Program (Appendix) or large table
☐ Landscape Table on CD

8. ☐ Nucleotide and/or Amino Acid Sequence Submission
If applicable, items a. – c. are required.

a. ☐ Computer Readable Form (CRF)
b. Specification Sequence Listing on:

i. ☐ CD-ROM (2 copies) or CD-R (2 copies); **or**
ii. ☐ paper

c. ☐ Statements verifying the identity of above copies

9. ☑ A list of no more than 12 items of information submitted as part of this request is provided in Part B of this form. Where appropriate, the list must meet the requirements of 37 CFR 1.98(b). 37 CFR 1.605(a), 1.610(b)(2).

This collection of information is required by 37 CFR 1.610. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.11 and 1.14. This collection is estimated to take 0.3 hours to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount

PTO/SB/59 (09-16)
Approved for use through 11/30/2021. OMB 0651-0064
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

10. ☑ A legible copy of each item of information listed in Part B of this form, and an English language translation of all necessary and pertinent parts of each non-English language item of information are included.

Copies of items of information that form part of the discussion within the body of the request (see 37 CFR 1.605(b)), and copies of U.S. patents and patent application publications, are not required. 37 CFR 1.610(b)(7).

11. ☑ A summary of the relevant portions of each non-patent document that is over 50 pages in length (other than the request) is included. The summary includes the required citations to the particular pages containing the relevant portions. 37 CFR 1.610(b)(8).

12. ☑ 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 requested, is included. 37 CFR 1.610(b)(5).

13. ☑ The below list includes all prior or concurrent post-patent Office proceedings (*ex parte* or *inter partes* reexamination, reissue, supplemental examination, post grant review, or *inter partes* review) involving the patent for which supplemental examination is being requested. 37 CFR 1.610(b)(3). An identifying number may be, e.g., a control no. or reissue application no. Any prior or concurrent post-patent Office proceedings not listed below are listed on a separate paper accompanying the request.

Type of Proceeding	Identifying Number	Filing Date

☐ See accompanying paper for a list of additional prior or concurrent post-patent Office proceedings involving the patent for which supplemental examination is requested. The paper should be a separate sheet titled "List of Prior or Concurrent Post-Patent Office Proceedings" and must provide the type, identifying number, and filing date of the post-patent Office proceeding.

14. Correspondence Address: Please recognize, or change, the correspondence address for the file of the patent for which supplemental examination is requested **and** for the supplemental examination proceeding to be:

☑ The address associated with Customer Number: 116407 **OR**

☐ Firm or Individual Name

Address

City	State	Zip
Country		
Telephone	Email	

15. **WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.**

/Jonathan Rowe/ — Authorized Signature

April 26, 2023 — Date

Jonathan Rowe — Typed/Printed Name

65,335 — Registration No.

PTO/SB/59 (09-16)
Approved for use through 11/30/2021. OMB 0651-0064
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

(Also referred to as FORM PTO-XXXX)

REQUEST FOR SUPPLEMENTAL EXAMINATION TRANSMITTAL FORM
PART B – LIST OF ITEMS OF INFORMATION – Page 1

Patent number for which supplemental examination is requested 11,286,168 Issue Date March 29, 2022

All items of information (no more than 12) submitted herewith as part of this request for supplemental examination of the above-identified patent are included in the following list:

U. S. PATENT DOCUMENTS

Cite No.[1]	Document Number Number-Kind Code[2] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear
1	US- 8,137,422 B2	03/20/2012	Licht, et al.	
2	US- 2004/0234426	11/25/2004	Reddy, et al.	
	US-			
	US-			
	US-			
	US-			
	US-			
	US-			
	US-			
	US-			
	US-			

FOREIGN PATENT DOCUMENTS

Cite No.[1]	Foreign Patent Document Country Code[3]-Number[4]-Kind Code[5] *(if known)*	Publication Date MM-DD-YYYY	Name of Patentee or Applicant of Cited Document	Pages, Columns, Lines, Where Relevant Passages or Relevant Figures Appear	T[2]
1	EP 2 817 260 B1	12/31/2014	Fillippi, et al.		
2	EP 1 648 817 B1	04/26/2006	Blumenfeld, et al.		
3	EP 2 266 922 A1	06/03/2009	Licht, et al.		
4	DE 10 2015 210 803 A1	06/12/2015	Gorval, et al.		
5	DE 10 2014 209 635 A1	05/21/2014	Gorval, et al.		

[1] Applicant's unique citation designation number (optional). [2] See Kinds Codes of USPTO Patent Documents at www.uspto.gov or MPEP 901.04. [3] Enter Office that issued the document, by the two-letter code (WIPO Standard ST.3). [4] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [5]Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [6] Applicant is to place a check mark here if English language Translation is attached.

PTO/SB/59 (09-16)
Approved for use through 11/30/2021. OMB 0651-0064
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it displays a valid OMB control number.

(Also referred to as FORM PTO-XXXX)

REQUEST FOR SUPPLEMENTAL EXAMINATION TRANSMITTAL FORM
PART B – LIST OF ITEMS OF INFORMATION – Page 2

Patent number for which supplemental examination is requested 11,286,168 Issue Date March 29, 2022

All items of information (no more than 12) submitted herewith as part of this request for supplemental examination of the above- identified patent are included in the following list:

OTHER DOCUMENTS

Cite No.[1]	Document Information (include, where appropriate, name of the author, title of the article, book, magazine, journal, serial, symposium, catalog, etc., publication date, page(s), volume-issue number(s), publisher, city and/or country where published. If a court document, identify the specific court, the designation (case citation or numeric designation), the title of the document, and the date submitted in court. If a declaration, include the type (e.g., 37 CFR 1.132 or 1.131), name of declarant, and the date of declaration. If an invoice or sales receipt, include the date issued and the name of the issuer (e.g., the name of the corporation or other place of business). If a discussion within the body of the request, include the pages of the request on which the discussion appears, and a description of the discussion (e.g., "discussion in request of why the claims are patentable under 35 U.S.C. 101, pages 7-11.") For all other materials, include, where appropriate, the title, author, date, and any descriptive information that would describe the document.)	T[2]
1	"Ammonia; Principles and Industrial Practice", Wiley-VCH, ISBN 3-527-29593-3 , January 1999, pp. 1-301	
2	Haussinger, et al., "Hydrogen, 3. Purification", Ullmann's Encyclopedia of Industrial Chemistry, Vol. 18, 2012, pp. 309-333	
3	Noelker, et al., " Autothermal reforming: a flexible syngas route with future potential", Prepared for Presentation at NITROGREN & SYNGAS 2010 International Conference, Bahrain, 28 February - 3 March 2010, pp. 1-20	
4	Shimura, "Urea Product Expansion by Newly Developed CO2 Recovery Process from Primary Reformer Flue Gas", Ammonia Technical Manual, Vol. 47, 2006, pp. 237-246	

[1] Applicant's unique citation designation number (optional). [2] Applicant is to place a check mark here if English language Translation is attached.

Topsoe, Inc. – EX1003
Page 579 of 1210

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

BIB DATA SHEET

CONFIRMATION NO. 9950

SERIAL NUMBER	FILING or 371(c) DATE RULE	CLASS	GROUP ART UNIT	ATTORNEY DOCKET NO.
96/000,424		423	3991	283386WOUS01_495230-44

APPLICANTS
DORSEY & WHITNEY/ UT GENERAL, Residence Not Provided;

INVENTORS
11286168, Residence Not Provided;
CASALE SA, SALT LAKE CITY,, UT;
PATENT OWNER, Residence Not Provided;

**** CONTINUING DATA ***************************
This application is a SER of 16/485,695 08/13/2019 PAT 11286168
which is a 371 of PCT/EP2018/052358 01/31/2018

**** FOREIGN APPLICATIONS ***************************
EUROPEAN PATENT OFFICE (EPO) 17156256.4 02/17/2017
EUROPEAN PATENT OFFICE (EPO) 17195305.2 10/06/2017

**** IF REQUIRED, FOREIGN FILING LICENSE GRANTED **** ** SMALL ENTITY **

Foreign Priority claimed ❑ Yes ❑ No 35 USC 119(a-d) conditions met ❑ Yes ❑ No Verified and Acknowledged _____ Examiner's Signature	❑ Met after Allowance _____ Initials	STATE OR COUNTRY	SHEETS DRAWINGS	TOTAL CLAIMS	INDEPENDENT CLAIMS

ADDRESS
Dorsey & Whitney / UT GENERAL
111 South Main Street
21st Floor
Salt Lake City, UT 84111-2176
UNITED STATES

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

FILING FEE RECEIVED		
0.00	FEES: Authority has been given in Paper No._____ to charge/credit DEPOSIT ACCOUNT No._____ for following:	❑ All Fees ❑ 1.16 Fees (Filing) ❑ 1.17 Fees (Processing Ext. of time) ❑ 1.18 Fees (Issue) ❑ Other _____ ❑ Credit

BIB (Rev. 05/07).



Assignment Query System

Close
Print
Main Page
Patents
Trademarks

Patent Assignment Abstract of Title

Total Assignments: 1

Application #: 16485695 **Filing Dt:** 08/13/2019 **Patent #:** 11286168 **Issue Dt:** 03/29/2022
PCT #: NONE **Intl Reg #:** **Publication #:** US20200055738 **Pub Dt:** 02/20/2020
Inventors: Francesco Baratto, Raffaele Ostuni
Title: PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE

Assignment: 1

Reel/Frame:	Received:	Recorded:	Mailed:	Pages:
050509 / 0723	09/27/2019	09/27/2019	09/30/2019	4

Conveyance: ASSIGNMENT OF ASSIGNORS INTEREST (SEE DOCUMENT FOR DETAILS).

Assignors: BARATTO, FANCESCO **Exec Dt:** 08/28/2019
OSTUNI, RAFFAELE **Exec Dt:** 08/28/2019

Assignee: CASALE SA
VIA POCOBELLI 6
LUGANO, SWITZERLAND 6900

Correspondent: DORSEY & WHITNEY LLP
111 SOUTH MAIN STREET
SUITE 2100
SALT LAKE CITY, UT 84111

Search Results as of: 05/02/2023 02:40 PM

If you have any comments or questions concerning the data displayed, contact PRD / Assignments at 571-272-3350. v.2.6
Web interface last modified: Jun 26, 2017 v.2.6

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
96/000,424	04/26/2023	11286168	283386WOUS01_495230-44	9950

116407 7590 05/11/2023
Dorsey & Whitney / UT GENERAL
111 South Main Street
21st Floor
Salt Lake City, UT 84111-2176

EXAMINER	
JOHNSON, JERRY D	

ART UNIT	PAPER NUMBER
3991	

MAIL DATE	DELIVERY MODE
05/11/2023	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.

Notice of Pre-AIA or AIA Status

The 11,268,168 patent was examined under the first inventor to file provisions of the AIA.

Decision on Supplemental Examination Request

A substantial new question of patentability affecting claims 1-23 of United States Patent Number 11,268,168 ("the '168 patent") to Baratto et al. is raised by the present Request for Supplemental Examination filed on April 26, 2023.

Request

Supplemental Examination is requested for claims 1-26 of the '168 patent in light of the following item of information:

(1) Noelker, et al., "Autothermal Reforming: A Flexible Syngas Route with Future potential," Prepared for Presentation at NITROGEN & SYNGAS 2010 International Conference, Bahrain, 28 February -3 March 2010, pp. 1-20. (Noelker)

(2) U.S. Patent No. 8,137,422 to Licht, et al. (Licht '422)

(3) European Patent No. 2 817 260 B1 to Fillippi, et al. (Fillippi)

(4) Shimura, "Urea Product Expansion by Newly Developed CO2 Recovery Process from Primary Reformer Flue Gas," Ammonia Technical Manual, Vol. 47, 2006, pp. 237-246. (Shimura)

(5) Häussinger, et al., "Hydrogen, 3. Purification", Ullmann's Encyclopedia of Industrial Chemistry, Vol. 18, 2012, pp. 309-333 (Haussinger)

(6) U.S. Patent Application Publication No. US 2004/0234426 to Reddy, et al. (Reddy)

(7) European Patent No. 1 648 817 B1 to Blumenfeld, et al. (Blumenfeld)

(8) European Patent No. 2 266 922 A1 to Licht, et al. (Licht '922)

(9) "Ammonia; Principles and Industrial Practice", Wiley-VCH, ISBN 3-527-29593-3, January 1999, pp. 1-301. (Ammonia)

(10) DE 10 2015 210 803 A1 to Gorval, et al. (Gorval '803)

(11) DE 10 2014 209 635 A1 to Gorval, et al. (Gorval '635)

Scope of Claims

The '168 patent contains claims 1-26 directed to a process for synthesis of ammonia from natural gas and a method for revamping a plant for synthesis of ammonia. Claims 1 and 21 are representative:

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 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.

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, downsteam 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.

Prosecution History

The '168 patent issued on March 29, 2022 from application Serial No. 16/485,695. A review of the prosecution history indicates that the '695 application was allowed because the prior art cited therein did not teach "the first and second streams having the same composition" (November, 18, 2021 Examiner's Statement of Reasons for Allowance).

Substantial New Question of Patentability

Noelker teaches autothermal reforming for ammonia synthesis comprising oxygen enriched air or pure oxygen as oxidator (Figure 2).

Licht '422 teaches steam-hydrocarbon reforming with reduced carbon dioxide emissions wherein a portion of the hydrogen-containing product gas is fed to the reformer furnace (col. 5, lines 27-56).

Fillippi teaches a process for producing ammonia synthesis gas from a hydrocarbon source in an autothermal reformer or in a partial oxidation reactor using oxygen or enriched air. ([0018], [0024]).

Shimura teaches a process for producing ammonia wherein excess synthesis gas is withdrawn from the outlet of the methanator and fired in the reformer (page 239, Figures 1 & 4).

Häussinger discusses processes of producing and purifying hydrogen.

Reddy teaches a process of producing ammonia wherein synthesis gas is withdrawn from the outlet of the methanator and is fed into the burner of the reformer ([0025], Figures 3 and 6).

Blumenfeld teaches a process of producing hydrogen from a methane-containing gas wherein CO2 depleted synthesis gas is separated by pressure swing adsorption into a product gas

stream and a waste stream and the waste stream is fed to the combustion chamber of the reformer (Claim 1, Figure 1).

Licht '922 is the corresponding European Patent Application of Licht '422.

Ammonia discusses the development and synthesis of ammonia.

Gorval '803 teaches a process for reforming a gas mixture comprising hydrocarbons, oxygen and water in an autothermal reformer at a steam/carbon molar ratio in the range of 0.1 to 2.5 (page 1)

Gorval '635 teaches a process for producing synthesis gas in an autothermal reformer (page 1).

There is a substantial likelihood that a reasonable examiner would consider Licht '422, Licht '922, Shimura and Reddy important in deciding whether or not claims 1-23 were patentable. Accordingly, Licht '422, Licht '922, Shimura and Reddy raise a substantial new question of patentability as to claims 1-23.

Signed:

/JERRY D JOHNSON/
Patent Reexam Specialist
Central Reexamination Unit 3991

/Alan Diamond/
Patent Reexamination Specialist
Central Reexamination Unit 3991

/Jean C. Witz/
Supervisory Patent Reexamination Specialist
Central Reexamination Unit 3991

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
96/000,424	04/26/2023	11286168	283386WOUS01_495230-44	9950

116407 7590 05/11/2023
Dorsey & Whitney / UT GENERAL
111 South Main Street
21st Floor
Salt Lake City, UT 84111-2176

EXAMINER	
JOHNSON, JERRY D	

ART UNIT	PAPER NUMBER
3991	

MAIL DATE	DELIVERY MODE
05/11/2023	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.

(12) SUPPLEMENTAL EXAMINATION CERTIFICATE

United States Patent (10) **Number: US 11,286,168 F1**
Barratto et al. (45) **Certificate Issued: May 11, 2023**

Control No.: 96/000,424 **Filing Date: Apr. 26, 2023**
Primary Examiner: Jerry D Johnson

A substantial new question of patentability affecting at least one claim of the patent is raised in the request for supplemental examination. See the Reasons for Substantial New Question of Patentability Determination in the file of this proceeding.Accordingly, ex parte re-examination will be ordered pursuant to 35 U.S.C 257.

(56) Items of Information

U.S. PATENT DOCUMENTS

8,137,422	3/2012	Licht et al.
2004/0234426	11/2004	Reddy et al.

FOREIGN PATENT DOCUMENTS

EP	2 817 260 B1	12/2014
EP	1 648 817 B1	4/2006
EP	2 266 922 A1	6/2009
DE	10 2015 210 803 A1	6/2015
DE	10 23014 209 6356 A1	5/2014

OTHER DOCUMENTS

"Ammonia; Principles and Industrial Practice", Wiley-VCH, ISBN 3-527-29593-3, January 1999, pp. 1-301.

Noelker, et al., "Autothermal Reforming: A Flexible Syngas Route with Future potential," Prepared for Presentation at NITROGEN & SYNGAS 2010 International Conference, Bahrain, 28 February -3 March 2010, pp. 1-20.

Shimura, "Urea Product Expansion by Newly Developed CO2 Recovery Process from Primary Reformer Flue Gas," Ammonia Technical Manual, Vol. 47, 2006, pp. 237-246.

Häussinger, et al., "Hydrogen, 3. Purification", Ullmann's Encyclopedia of Industrial Chemistry, Vol. 18, 2012, pp. 309-333.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
96/000,424	04/26/2023	11286168	283386WOUS01_495230-44	9950

116407 7590 06/28/2023
Dorsey & Whitney / UT GENERAL
111 South Main Street
21st Floor
Salt Lake City, UT 84111-2176

EXAMINER
JOHNSON, JERRY D

ART UNIT	PAPER NUMBER
3991	

MAIL DATE	DELIVERY MODE
06/28/2023	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.

Ex Parte Reexamination Ordered Pursuant to 35 U.S.C. 257	**Control No.**	**Patent Under Reexamination**	
	96/000,424	11286168	
	Examiner	**Art Unit**	**AIA (FITF) Status**
	Jerry D Johnson	3991	Yes

--The MAILING DATE of this communication appears on the cover sheet with the correspondence address--

The supplemental examination proceeding filed on 04/26/2023, concluded with the issuance of the supplemental examination certificate on 11 May 2023. The certificate indicated that one or more items of information submitted as part of the request for supplemental examination raises a substantial new question of patentability. See the Reasons for Substantial New Question of Patentability Determination in the file of this proceeding.

Accordingly, *ex parte* reexamination of claim(s) 1-23 of U.S. Patent No. 11,268,168 is ordered. See 35 U.S.C. 257(b) and 37 CFR 1.625(b). This *ex parte* reexamination proceeding is hereby initiated by the mailing of this order. *Ex parte* reexamination under 35 U.S.C. 257 will be conducted in accordance with 37 CFR 1.530 through 1.570, which govern *ex parte* reexamination, subject to the exceptions enumerated in 37 CFR 1.625(d), and, in addition, to the exception that a patent owner's statement, including any amendment, under 37 CFR 1.530(a)-(c) may not be filed. For this reason, no amendment in an *ex parte* reexamination proceeding ordered under 35 U.S.C. 257 may be filed until after the mailing of a first Office action on the merits.

This reexamination proceeding has been assigned to the art unit listed above. All future correspondence should be directed to the assigned art unit and should be identified by the control number listed above, which is identical to the control number assigned to the now-concluded supplemental examination proceeding.

/JEAN C WITZ/ Supervisory Patent Examiner, Art Unit 3991	/ALAN D DIAMOND/ Patent Reexam Spec., CRU 3991	/JERRY D JOHNSON/ Patent Reexam Spec., CRU 3991

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
96/000,424	04/26/2023	11286168	283386WOUS01_495230-44	9950

116407 7590 07/07/2023

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

EXAMINER	
JOHNSON, JERRY D	

ART UNIT	PAPER NUMBER
3991	

MAIL DATE	DELIVERY MODE
07/07/2023	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.

Office Action in Ex Parte Reexamination	**Control No.** 96/000,424	**Patent Under Reexamination** 11286168	
	Examiner Jerry D Johnson	**Art Unit** 3991	**AIA (FITF) Status** Yes

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

a. ☐ Responsive to the communication(s) filed on _____.
☐ A declaration(s)/affidavit(s) under **37 CFR 1.130(b)** was/were filed on _____.

b. ☐ This action is made FINAL.

c. ☐ A statement under 37 CFR 1.530 has not been received from the patent owner.

A shortened statutory period for response to this action is set to expire 2 month(s) from the mailing date of this letter. Failure to respond within the period for response will result in termination of the proceeding and issuance of an *ex parte* reexamination certificate in accordance with this action. 37 CFR 1.550(d). **EXTENSIONS OF TIME ARE GOVERNED BY 37 CFR 1.550(c).** If the period for response specified above is less than thirty (30) days, a response within the statutory minimum of thirty (30) days will be considered timely.

Part I THE FOLLOWING ATTACHMENT(S) ARE PART OF THIS ACTION:

1. ☑ Notice of References Cited by Examiner, PTO-892.
2. ☐ Information Disclosure Statement, PTO/SB/08.
3. ☐ Interview Summary, PTO-474.
4. ☐ _____.

Part II SUMMARY OF ACTION

1a. ☑ Claims 1-23 are subject to reexamination.
1b. ☐ Claims _____ are not subject to reexamination.
2. ☐ Claims _____ have been canceled in the present reexamination proceeding.
3. ☑ Claims 13 and 18 are patentable and/or confirmed.
4. ☑ Claims 1-12,14-17 and 19-23 are rejected.
5. ☐ Claims _____ are objected to.
6. ☐ The drawings, filed on _____ are acceptable.
7. ☐ The proposed drawing correction, filed on _____ has been (7a) ☐ approved (7b) ☐ disapproved.
8. ☑ Acknowledgment is made of the priority claim under 35 U.S.C. 119(a)-(d) or (f).
   a) ☑ All b) ☐ Some* c) ☐ None of the certified copies have
   1 ☐ been received.
   2 ☐ not been received.
   3 ☑ been filed in Application No. 16/485,695.
   4 ☐ been filed in reexamination Control No. _____.
   5 ☐ been received by the International Bureau in PCT application No. _____.
   * See the attached detailed Office action for a list of the certified copies not received.
9. ☐ Since the proceeding appears to be in condition for issuance of an *ex parte* reexamination certificate except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte* Quayle, 1935 C.D. 11, 453 O.G. 213.
10. ☐ Other: _____

cc: Requester (if third party requester)

Notice of Pre-AIA or AIA Status

The 11,268,168 patent was examined under the first inventor to file provisions of the AIA.

Status of Proceedings

A request pursuant to 35 U.S.C. §257(a) for supplemental examination of claims 1-23 of U.S. Patent 11,268,168 ("the '168 patent") to Baratto et al. was filed April 26, 2023. A Substantial New Question of Patentability (SNQ) affecting at least one claim of the '168 patent was identified in the Reasons for SNQ Determination mailed May 11, 2023. A Supplemental Examination Certificate stating that *ex parte* reexamination will be ordered pursuant to 35 U.S.C. §257 issued on May 11, 2023.

In accordance with 37 CFR §1.625(d), this *ex parte* reexamination will be conducted in accordance with 37 CFR §§ 1.530 through 1.570, with a few exceptions enumerated in 37 CFR §1.625(d)(1) – (d)(4).

Scope of Claims

The '492 patent contains claims 1-23. Claims 1 and 21 are representative:

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 compositions, wherein the first stream

forms the fuel fraction and the seconds stream is process gas intended for the synthesis of ammonia.

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.

While the preamble of independent claim 1 recites "A process for synthesis of ammonia from natural gas", claim 1 does not require that ammonia is produced. In fact, claim 1 specifically states "the second stream is process gas intended for the synthesis of ammonia." According, the preamble "A process for synthesis of ammonia from natural gas" is an intended result and not a limitation of the claim.

35 USC § 102

The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

A person shall be entitled to a patent unless –

(a)(1) the claimed invention was patented, described in a printed publication, or in public use, on sale, or otherwise available to the public before the effective filing date of the claimed invention.

35 USC § 103

The following is a quotation of 35 U.S.C. 103 which forms the basis for all obviousness rejections set forth in this Office action:

> A patent for a claimed invention may not be obtained, notwithstanding that the claimed invention is not identically disclosed as set forth in section 102, if the differences between the claimed invention and the prior art are such that the claimed invention as a whole would have been obvious before the effective filing date of the claimed invention to a person having ordinary skill in the art to which the claimed invention pertains. Patentability shall not be negated by the manner in which the invention was made.

In the event the determination of the status of the application as subject to AIA 35 U.S.C. 102 and 103 (or as subject to pre-AIA 35 U.S.C. 102 and 103) is incorrect, any correction of the statutory basis for the rejection will not be considered a new ground of rejection if the prior art relied upon, and the rationale supporting the rejection, would be the same under either status.

I. Claims 1-4, 8-11, 17 and 20 are rejected under 35 U.S.C. 102(a)(1) as being anticipated by U.S. Patent No. 8,137,422 to Licht et al. (Licht '422).

Licht '422 teaches a process for producing a hydrogen-containing product gas with reduced carbon dioxide emissions compared to conventional hydrogen production processes. The process may optionally include reforming in a prereformer and/or an oxygen secondary reformer (abstract). The process comprising (a) introducing a process stream comprising steam and at least one hydrocarbon selected from, *inter alia*, methane and natural gas (column 3, line 41) in a reformer furnace to form a reformate stream comprising hydrogen, carbon monoxide, methane and steam; (b) reacting the reformate steam in the presence of a shift catalyst to form a second process stream comprising carbon dioxide, hydrogen, carbon monoxide and methane; (c) scrubbing the second process stream with a wash steam to form a carbon dioxide-depleted stream and a carbon dioxide-loaded wash steam; (d) separating the carbon dioxide-depleted stream to form hydrogen-containing product gas and by-product gas comprising methane and carbon monoxide; (e) introducing a portion of the by-product gas into the process steam at a location upstream of the reformer; and (f) combusting a fuel gas comprising a portion of the hydrogen-

containing product gas in the reformer furnace, optionally a portion of the by-product gas, and optionally a supplementary fuel in the reformer furnace (column 1, lines 31-67). The fuel portion may be between 10% and 30% of the total amount of the CO_2 depleted syngas (Table 4). The process includes introducing an oxygen-rich gas into the reformate stream (column 2, lines 13-17) wherein the oxygen-rich gas has an oxygen concentration of 98 to 100 percent by volume (column 7, lines 38-40).

II. Claims 5 and 6 are rejected under 35 U.S.C. 103 as being unpatentable over Licht '422 as applied to claims 1-4, 8-11, 17 and 20 above, and further in view of U.S. Patent Application Publication No. US 2004/0234426 to Reddy et al. (Reddy).

Licht '422 differs from claims 5 and 6 in not teaching a methanation process step.

Reddy teaches that in a typical ammonia plant configuration, after carbon dioxide is removed, residual carbon monoxide and carbon dioxide are almost completely eliminated in a methanator ([0003], [0024]-[0025]).

It would have been obvious to one having ordinary skill in the art before the effective filing date of the claimed invention to include a step for methanation in the process of Licht '422 so as to remove residual carbon monoxide and carbon dioxide in the synthesis gas and improve the output of the process. As to claim 6, it would have been obvious to separate the fuel fraction of Licht '422 prior to the methanation process so as to reduce the demand on the methanation process and eliminate methanation of synthesis gas that is consumed as fuel.

III. Claims 7, 12 and 14-16 are rejected under 35 U.S.C. 103 as being unpatentable over Licht '422 as applied to claims 1-4, 8-11, 17 and 20 above, and further in view of "Ammonia: Principles and Industrial Practice" (hereafter "Ammonia").

Licht '422 differs from the claims in not disclosing the CO_2 concentration in the carbon dioxide-depleted stream, nitrogen wash of the carbon dioxide-depleted stream, or the steam/carbon (S/C) ratio in the conversion step.

Ammonia, Table 33 on page 136, discloses that CO_2 concentration in the carbon dioxide-depleted stream is reduced to 0.1% in a purified synthesis gas. Ammonia, pages 143-144 teaches that a liquid nitrogen wash is used to remove impurities and also to supply some or all of the nitrogen required for ammonia synthesis. On page 77, Ammonia teaches that "[m]odern 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."

It would have been obvious to one having ordinary skill in the art before the effective filing date of the claimed invention to use a S/C ratio of around 3.0; to reduce the CO_2 concentration in the carbon dioxide-depleted stream to 0.1%; and to include a liquid nitrogen gas wash to remove impurities and to supply some or all of the nitrogen required for ammonia synthesis in a process as taught by Licht '422 because Ammonia discloses that the claimed S/C ratio, CO_2 concentration, and liquid nitrogen wash are conventionally used in the art.

IV. Claims 1, 11, 14, 15, 16 and 19 are rejected under 35 U.S.C. 103 as being unpatentable over of EP 2 817 260 (EP '260) in view of Licht '422.

EP '422 teaches a process for synthesis of ammonia from natural gas by partial oxidation in an oxygen-fired reactor with steam which is either an autothermal reformer or a partial

oxidation reactor [0048]. The reactor effluent is directed to a medium temperature shift reactor to remove residual carbon oxides and methane [0050]. Upstream removal of CO2 is an option feature, in a first option, CO2 is removed from shift reactor effluent prior to a PSA unit. In a second option, CO2 is removed from the fuel gas to obtain a purified fuel gas [0054]. The air and/or steam, or the mixture thereof, is conventionally heated prior to reaction with the natural gas feedstock (see U.S. Patent 4,725,380 cited in [0013] of the '168 patent).

EP '269 differs from the claims in not teaching that the fuel gas is used as fuel in at least one furnace of the plant.

Licht '422 teaches using purified fuel gas from a hydrogen synthesis as fuel and because the fuel gas comprises hydrogen in an amount greater than conventional reformer furnace fuels, the flue gas will contain a reduced amount of carbon dioxide compared to conventional reformer furnaces (column 5, lines 34-38).

It would have been obvious to one having ordinary skill in the art before the effective filing date of the claimed invention to use the fuel gas taught by EP '269 to preheat the air and/or steam, or the mixture thereof, prior to reaction with the natural gas feedstock in the reactor, so as to reduce the amount of carbon dioxide produced compared to conventional fuels as taught by Licht '422.

V. Claims 21 and 23 are rejected under 35 U.S.C. 103 as being unpatentable over the admitted prior art in view of Licht '422.

Under the section "PRIOR ART", the '168 patent teaches that in prior art ammonia synthesis plants, desulphurized natural gas undergoes reforming, resulting in a gas containing essentially hydrogen, carbon monoxide and carbon dioxide. 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 above described ammonia plant results in significant emissions of CO2 into the atmosphere (column 1, lines 10-42).

Licht '422 teaches there is growing pressure to reduce carbon dioxide emissions from industrial processes and that a large hydrogen production plant may be considered a significant source of carbon dioxide (column 1, lines 5-10).

Licht '422 teaches a process for producing a hydrogen-containing product gas with reduced carbon dioxide emissions compared to conventional hydrogen production processes. The process may optionally include reforming in a prereformer and/or an oxygen secondary reformer (abstract). The process comprising (a) introducing a process stream comprising steam and at least one hydrocarbon selected from, *inter alia*, methane and natural gas (column 3, line 41) in a reformer furnace to form a reformate stream comprising hydrogen, carbon monoxide, methane and steam; (b) reacting the reformate steam in the presence of a shift catalyst to form a second process stream comprising carbon dioxide, hydrogen, carbon monoxide and methane; (c) scrubbing the second process stream with a wash steam to form a carbon dioxide-depleted stream and a carbon dioxide-loaded wash steam; (d) separating the carbon dioxide-depleted stream to form hydrogen-containing product gas and by-product gas comprising methane and carbon monoxide; (e) introducing a portion of the by-product gas into the process steam at a location upstream of the reformer; and (f) combusting a fuel gas comprising a portion of the hydrogen-containing product gas in the reformer furnace, optionally a portion of the by-product gas, and optionally a supplementary fuel in the reformer furnace (column 1, lines 31-67). The fuel

portion may be between 10% and 30% of the total amount of the CO_2 depleted syngas (Table 4). The process includes introducing an oxygen-rich gas into the reformate stream (column 2, lines 13-17) wherein the oxygen-rich gas has an oxygen concentration of 98 to 100 percent by volume (column 7, lines 38-40). Because the fuel gas 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 (column 5, lines 34-38).

It would have been obvious to one having ordinary skill in the art before the effective filing date of the claimed invention to modify an existing, prior art ammonia synthesis plant as taught by the '168 patent's admitted prior art, to a process providing enriched air or oxygen for secondary reforming wherein a fuel fraction of the product gas is fed to the reformer furnace so as to reduce the CO2 production of the plant as taught by Licht '422.

VI. Claim 22 is rejected under 35 U.S.C. 103 as being unpatentable over the admitted prior art in view of Licht '422 as applied to claims 21 and 23 above, and further in view of EP '260.

The admitted prior art in view of Licht '422 differs from claim 22 in not teaching using nitrogen from the air separation unit to obtain the desired hydrogen to nitrogen ratio in an ammonia synthesis process.

EP '260 teaches producing a nitrogen stream from the air separation unit (ASU) which is used to adjust the hydrogen to nitrogen ratio in the process [0025].

It would have been obvious to one having ordinary skill in the art before the effective filing date of the claimed invention to use an ASU in a process as taught by Licht '422 to adjust the hydrogen to nitrogen ratio in a process of synthesizing ammonia as taught by the admitted prior art in view of Licht '422.

Claims Allowed

Claims 13 and 18 are allowed. The following is a statement of reasons for the indication of allowable subject matter: The cited prior art does not teach heating and using the CO2-depleted stream for mechanical work as in claim 13, or regulation of the conversion section by modulating the quantity of fuel fraction directed to the conversion section along with exporting a portion of the fuel fraction from the process as in claim 18.

Conclusion

In order to ensure full consideration of any amendments, affidavits or declarations, or other documents as evidence of patentability, such documents must be submitted in response to this Office action. Submissions after the next Office action, which is intended to be a final action, will be governed by the requirements of 37 CFR 1.116, after final rejection and 37 CFR 41.33 after appeal, which will be strictly enforced.

Duty to Disclose

The patent owner is reminded of the continuing responsibility under 37 CFR 1.565(a) to apprise the Office of any litigation activity, or other prior or concurrent proceeding, involving Patent No. 11,286,168 throughout the course of this reexamination proceeding.

Correspondence

Any inquiry concerning this communication or earlier communications from the specialist should be directed to Jerry Johnson whose telephone number is 571-272-1448. The specialist can normally be reached on Monday through Thursday from 5:30 am to 3:00 pm and

Fridays from 5:30 am to 9:30 am. If the attempts to reach the specialist are unsuccessful, the specialist's supervisor, Jean Witz can be reached by dialing 571-272-0927.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

All correspondence relating to this ex parte reexamination proceeding should be directed:

By EFS: Registered users may submit via the electronic filing system EFS-Web at https://efs.uspto.gov/efile/myportal/efs-registered

By Mail to: Mail Stop *Ex Parte* Reexam
Central Reexamination Unit
Commissioner for Patents
United States Patent & Trademark Office
P.O. Box 1450
Alexandria, VA 22313-1450

By FAX to: (571) 273-9900
Central Reexamination Unit

By hand: Customer Service Window
Randolph Building
401 Dulany Street
Alexandria, VA 22314

Signed:

/JERRY D JOHNSON/
Patent Reexamination Specialist
Central Reexamination Unit 3991

/Alan Diamond/
Patent Reexamination Specialist
Central Reexamination Unit 3991

/Jean C. Witz/
Supervisory Patent Reexamination Specialist
Central Reexamination Unit 3991

Notice of References Cited	Application/Control No. 96/000,424	Applicant(s)/Patent Under Reexamination 11286168	
	Examiner Jerry D Johnson	Art Unit 3991	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	CPC Classification	US Classification
*	A	US-4725380-A	02-1988	Pinto; Alwyn	C01B3/48	252/376
	B					
	C					
	D					
	E					
	F					
	G					
	H					
	I					
	J					
	K					
	L					
	M					

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	CPC Classification
	N					
	O					
	P					
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

Index of Claims	Application/Control No.	Applicant(s)/Patent Under Reexamination
	96/000,424	11286168
	Examiner	**Art Unit**
	Jerry D Johnson	3991

✓	Rejected	-	Cancelled	N	Non-Elected	A	Appeal
=	Allowed	÷	Restricted	I	Interference	O	Objected

CLAIMS

☐ Claims renumbered in the same order as presented by applicant ☐ CPA ☐ T.D. ☐ R.1.47

CLAIM		DATE								
Final	Original	07/06/2023								
	1	✓								
	2	✓								
	3	✓								
	4	✓								
	5	✓								
	6	✓								
	7	✓								
	8	✓								
	9	✓								
	10	✓								
	11	✓								
	12	✓								
	13	=								
	14	✓								
	15	✓								
	16	✓								
	17	✓								
	18	=								
	19	✓								
	20	✓								
	21	✓								
	22	✓								
	23	✓								

Doc Code: ECOMM.AUTH/ECOMM.WTDW
Doc Description: Internet Communications Authorization/Internet Communications Authorization Withdrawal

PTO/SB/439 (11-15)

AUTHORIZATION FOR INTERNET COMMUNICATIONS IN A PATENT APPLICATION OR REQUEST TO WITHDRAW AUTHORIZATION FOR INTERNET COMMUNICATIONS		
	Application No.	96/000,424
	Filing Date	April 26, 2023
	First Named Inventor	11286168
	Art Unit	3991
	Examiner Name	Jerry D. Johnson
	Practitioner Docket No.	283386WOUS01_495230-44

To: Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

I. To authorize permission for Internet Communications.

☒ Recognizing that Internet communications are not secure, I hereby authorize the USPTO to communicate with the undersigned and practitioners in accordance with 37 CFR 1.33 and 37 CFR 1.34 concerning any subject matter of this application via video conferencing, instant messaging, or electronic mail. I understand that a copy of these communications will be made of record in the application file. (MPEP 502.03)

II. To withdraw authorization for Internet Communications.

☐ The authorization given on _____, to the USPTO to communicate with the undersigned and any practitioner in accordance with 37 CFR 1.33 and 37 CFR 1.34 concerning any subject matter of this application via Internet communications such as video conferencing, instant messaging, or electronic mail is hereby withdrawn. I understand that the withdrawal is effective when approved rather than when received.

I am the

☐ applicant.

☒ attorney or agent of record. Registration number 50258.

☐ attorney or agent acting under 37 CFR 1.34. Registration number _____.

/Marcus S. Simon, Reg.# 50258/ — Signature

July 26, 2023 — Date

Marcus S. Simon — Typed or printed name

801-933-7360 — Telephone Number

NOTE: This form must be signed in accordance with 37 CFR 1.33. See 37 CFR 1.4 for signature requirements and certifications. Juristic entities must be represented by a patent practitioner (see 37 CFR 1.31, which is applicable to any paper filed on or after September 16, 2012, that is presented on behalf of a juristic entity, regardless of application filing date). Submit multiple forms if more than one signature is required, see below*.

☒ * Total of 1 forms are submitted.

Privacy Act Statement

The **Privacy Act of 1974 (P.L. 93-579)** requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether disclosure of these records is required by the Freedom of Information Act.
2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.
3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.
4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).
5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.
6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).
7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (*i.e.*, GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.
8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspection or an issued patent.
9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

Electronic Acknowledgement Receipt	
EFS ID:	48353353
Application Number:	96000424
International Application Number:	
Confirmation Number:	9950
Title of Invention:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE
First Named Inventor/Applicant Name:	11286168
Customer Number:	116407
Filer:	Marcus S. Simon/Samantha Mayo
Filer Authorized By:	Marcus S. Simon
Attorney Docket Number:	283386WOUS01_495230-44
Receipt Date:	26-JUL-2023
Filing Date:	26-APR-2023
Time Stamp:	15:25:21
Application Type:	Supplemental Examination
Patent Number:	

Payment information:

Submitted with Payment	no

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)

1	Miscellaneous Incoming Letter	20230726_283386WOUS01_495230-44_Internet-Communication-Authorization-Form.pdf	186425 71889d3efa5b8f22e31d25c4cf4c92e19fd9b63d	no	2
Warnings:					
Information:					
			Total Files Size (in bytes):	186425	

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

VIA *e*FILE

PATENT APPLICATION
Docket No. 283386WOUS01_495230-44

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re patent of		)
	CASALE SA	)
Control/Serial No.:	96/000,424	)
Patent No.	11,286,168	) Art Unit
Issued:	March 29, 2022	) 3991
Confirmation No.:	9950	)
For:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE	)
Examiner:	Jerry Johnson	)
Customer No.:	116407	)

PETITION FOR EXTENTION OF TIME UNDER 37 CFR § 1.550(c)

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

This is a request under the provisions of 37 CFR § 1.550(c) to extend the time period for filing a reply to the Office Action in the above-identified *ex parte* reexamination. The current *ex parte* reexamination was instituted as a result of a supplemental examination request filed by the patent owner and, therefore, is considered to be a patent owner requested *ex parte* reexamination in which "no cause" extensions of time may be requested. *MPEP § 2265.V.*

An Office Action in the above Ex Parte Reexamination was issued on July 7, 2023, having a shortened statutory period for reply set to expire September 7, 2023, subject to extensions of time under 37 CFR § 1.550(c).

A two (2) month extension of time to increase the period for reply from September 7, 2023, to November 7, 2023, is being requested herewith. The required fee under 37 CFR § 1.17(g) is being paid herewith to permit timely filing of the response.

No additional fees are believed to be due. However, should any fees be due, the Commissioner is hereby authorized to charge payment of any of the following fees that may be applicable to this communication, or credit any overpayment, to Deposit Account No. 50-6181.

Dated this 23rd day of August, 2023.

Respectfully submitted,

/Marcus S. Simon, Reg.# 50258/
MARCUS S. SIMON
Registration No. 50,258
Attorney for Applicant
Dorsey & Whitney LLP
Customer No. 116407
Telephone No. 801.933.7360

MSS: JR: sm

Electronic Patent Application Fee Transmittal

Application Number:	96000424
Filing Date:	26-Apr-2023
Title of Invention:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE
First Named Inventor/Applicant Name:	11286168
Filer:	Marcus S. Simon/Samantha Mayo
Attorney Docket Number:	283386WOUS01_495230-44

Filed as Small Entity

Filing Fees for Supplemental Examination

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
Pages:				
Claims:				
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
PETITION FEE-37CFR 1.17(G)(GROUPII)	2463	1	88	88
Miscellaneous:				
		Total in USD ($)		**88**

Electronic Acknowledgement Receipt	
EFS ID:	48480736
Application Number:	96000424
International Application Number:	
Confirmation Number:	9950
Title of Invention:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE
First Named Inventor/Applicant Name:	11286168
Customer Number:	116407
Filer:	Marcus S. Simon/Samantha Mayo
Filer Authorized By:	Marcus S. Simon
Attorney Docket Number:	283386WOUS01_495230-44
Receipt Date:	23-AUG-2023
Filing Date:	26-APR-2023
Time Stamp:	14:50:47
Application Type:	Supplemental Examination
Patent Number:	

Payment information:

Submitted with Payment	yes
Payment Type	DA
Payment was successfully received in RAM	$88
RAM confirmation Number	E20238ME51328293
Deposit Account	506181
Authorized User	Samantha Mayo
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:	

37 CFR 1.16 (National application filing, search, and examination fees)

37 CFR 1.17 (Patent application and reexamination processing fees)

37 CFR 1.19 (Document supply fees)

37 CFR 1.20 (Post Issuance fees)

37 CFR 1.21 (Miscellaneous fees and charges)

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Petition for review by the Office of Petitions	20230823_283386WOUS01_495230-44_Petition-for-Extension-of-Time.pdf	22819 7d282af69ac00677f9a9d188cc44387c1a7fea7d	no	2
Warnings:					
Information:					
2	Fee Worksheet (SB06)	fee-info.pdf	37882 c0778963137c72523fc012613d8280a1d5527d8a	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	60701		

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

New Applications Under 35 U.S.C. 111

If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.

National Stage of an International Application under 35 U.S.C. 371

If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.

New International Application Filed with the USPTO as a Receiving Office

If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
96/000,424	04/26/2023	11286168	283386WOUS01_495230-44	9950

116407 7590 08/25/2023

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

EXAMINER
JOHNSON, JERRY D

ART UNIT	PAPER NUMBER
3991	

MAIL DATE	DELIVERY MODE
08/25/2023	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.

Decision on Petition for Extension of Time in Reexamination	**Application No.** 96/000,424	**Applicant(s)** 11,286,168 B2	
	Examiner Jerry D. JOHNSON	**Art Unit** 3991	

1. THIS IS A DECISION ON THE PETITION FILED 08/23/23.

2. THIS DECISION IS ISSUED PURSUANT TO:
   - A. ☐ 37 CFR 1.550(c) – The time for taking any action by a patent owner in a third party requested *ex parte* reexamination proceeding will be extended only for sufficient cause and for a reasonable time specified.
   - B. ☒ 37 CFR 1.550(c) – The time for taking action by a patent owner in a patent owner requested *ex parte* reexamination proceeding will only be extended for more than two months for sufficient cause and for a reasonable time specified.
   - C. ☐ 37 CFR 1.956 – The time for taking any action by a patent owner in an *inter partes* reexamination proceeding will be extended only for sufficient cause and for a reasonable time specified.

   The petition is before the Central Reexamination Unit for consideration.

3. FORMAL MATTERS: Patent Owner requests that the time period for filing a response to the Non-Final Office action mailed on 07/07/23, which set a two (2) month period for response (due 09/07/23), be extended by an additional two (2) months (due 11/07/23).
   - A. Petition fee per 37 CFR §1.17(g)):
     - i. ☒ Petition includes authorization to debit a deposit account.
     - ii. ☐ Petition includes authorization to charge a credit card account.
     - iii. ☐ Other: _____.
   - B. ☐ Proper certificate of service was provided. (Not required in reexamination where patent owner is requester.)
   - C. ☒ Petition was timely filed.
   - D. ☒ Petition properly signed.

4. DECISION (See MPEP 2265 and 2665)
   - A. ☒ Granted or ☐ Granted-in-part for ***two (2) additional months***. (See 37 CFR 1.550(c) and 37 CFR 1.956).
     - i. ☒ Other/comment: See CONCLUSION below.
   - B. ☐ Dismissed because:
     - i. ☐ Formal matters (See unchecked box(es) (A, B, C and/or D) in section 4 above).
     - ii. ☐ Petitioner failed to provide a factual accounting of reasonably diligent behavior by all those responsible for preparing a response to the outstanding Office action within the statutory time period.
     - iii. ☐ Petitioner failed to explain why, in spite of the action taken thus far, the requested additional time is needed.
     - iv. ☐ The statements provided fail to establish sufficient cause to warrant extension of the time for taking action (See attached).
     - v. ☐ The petition is moot.
     - vi. ☐ Other/comment: _____

5. CONCLUSION: **The 08/23/23 "PETITION FOR EXTENSION OF TIME UNDER 37 CFR § 1.550(c)" is hereby granted under the "no cause" standard. See MPEP 2265, Roman Numeral V, A. Therefore, the time period for filing a response to the 07/07/23 Non-Final Office action is extended by two (2) additional months from 09/07/23 to the end of the day on Tuesday, 11/07/23**.

6. Telephone inquiries with regard to this decision should be directed to either QAS Stephen J. Stein at 571-272-1544 or SPRS Gay Ann Spahn at 571-272-7731 in the CRU.

/Gay Ann Spahn/
Supervisory Patent Reexamination Specialist
Central Reexamination Unit

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
Address: COMMISSIONER FOR PATENTS
P.O. Box 1450
Alexandria, Virginia 22313-1450
www.uspto.gov

APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
96/000,424	04/26/2023	11286168	283386WOUS01_495230-44	9950

116407 7590 08/25/2023
Dorsey & Whitney / UT GENERAL
111 South Main Street
21st Floor
Salt Lake City, UT 84111-2176

EXAMINER
JOHNSON, JERRY D

ART UNIT	PAPER NUMBER
3991	

MAIL DATE	DELIVERY MODE
08/25/2023	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.

Ex Parte Reexamination Interview Summary	Control No.	Patent Under Reexamination	
	96/000,424	11286168	
	Examiner	Art Unit	AIA (FITF) Status
	Jerry D Johnson	3991	Yes

All participants (USPTO personnel, patent owner, patent owner's representative):

(1) Jerry Johnson	(3) Marcus Simon
(2) Alan Diamond; Jean Witz	(4) John Rowe

Date of Interview: 21 August 2023

Type: a) ☑ Telephonic b) ☐ Video Conference
c) ☐ Personal (copy given to: 1) ☐ patent owner 2) ☐ patent owners representative)

Exhibit shown or demonstration conducted: d) ☐ Yes e) ☑ No.
If Yes, brief description: _____

Agreement with respect to the claims f) ☐ was reached. g) ☑ was not reached. h) ☐ N/A.
Any other agreement(s) are set forth below under "Description of the general nature of what was agreed to..."

Claim(s) discussed: 1-23 .

Identification of prior art discussed: Licht et al., EP 2 817 260 .

Description of the general nature of what was agreed to if an agreement was reached, or any other comments:
See Continuation Sheet .

(A fuller description, if necessary, and a copy of the amendments which the examiner agreed would render the claims patentable, if available, must be attached. Also, where no copy of the amendments that would render the claims patentable is available, a summary thereof must be attached.)

A FORMAL WRITTEN RESPONSE TO THE LAST OFFICE ACTION MUST INCLUDE PATENT OWNER'S STATEMENT OF THE SUBSTANCE OF THE INTERVIEW. (See MPEP § 2281). IF A RESPONSE TO THE LAST OFFICE ACTION HAS ALREADY BEEN FILED, THEN PATENT OWNER IS GIVEN **ONE MONTH** FROM THIS INTERVIEW DATE TO PROVIDE THE MANDATORY STATEMENT OF THE SUBSTANCE OF THE INTERVIEW
(37 CFR 1.560(b)). THE REQUIREMENT FOR PATENT OWNERS STATEMENT CAN NOT BE WAIVED.
EXTENSIONS OF TIME ARE GOVERNED BY 37 CFR 1.550(c).

/JEAN C WITZ/ Supervisory Patent Examiner, Art Unit	/Alan Diamond/ Patent Reexam Spec., CRU 3991	/JERRY D JOHNSON/ Patent Reexam Specialist, CRU 3991

cc: Requester (if third party requester)

Continuation of Description of the general nature of what was agreed to if an agreement was reached, or any other comments: Discussed the proposed amendments in the interview agenda. The examiners noted that Licht et al. teaches a secondary reforming reactor which is an autothermal reactor (col. 7, lines 17-28) and that the use of a prereformer is optional (column 5, line 57 to column 6. line 3). It was also noted that the process of EP '260 does not include a primary reformer.

VIA FACSIMILE

PATENT APPLICATION
Docket No. 283386WOUS01_495230-44

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of	CASALE SA	)
		)
Serial No.:	96/000,424	) Art Unit
		) 3991
Filed:	March 29, 2022	)
		)
For:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2IN ATMOSPHERE	)
		)
Confirmation No.:	3128	)
		)
Customer No.:	116407	)
		)
Examiner:	Jerry Johnson	)

INTERVIEW AGENDA AND PROPOSED AMENDMENTS

Dear Examiner Johnson:

Thank you for agreeing to a telephonic interview on August 21, 2023 at 1:00 pm, (ET) to discuss the above-identified patent application. Please find enclosed proposed amendments to be discussed during the interview.

Please contact me if you have any questions. I look forward to speaking with you.

Dated this 11th day of August, 2023.

Respectfully submitted,

/Marcus S. Simon, Reg.# 50258/
MARCUS S. SIMON
Registration No. 50,258
Attorney for Applicant
Dorsey & Whitney LLP
Customer No. 116407
Telephone: 801.933.7360

PROPOSED AMENDMENTS TO THE CLAIMS

Claim 1 Amendment Proposal - Main

1. (Proposed to be Amended) 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;

addition of nitrogen to the synthesis 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.

It is proposed that claim 1 be amended to incorporate a portion of granted dependent claim 5. In the Office Action, the PTO acknowledged Licht (U.S. Patent No. 8,137,422) does not disclose "addition of nitrogen to the synthesis gas." Even assuming, *arguendo*, either of Reddy (U.S. Patent Application Publication No. 2004/0234426) or EP 2817260 ("EP '260") disclose "addition of nitrogen to the synthesis gas," one of ordinary skill in the art would not be motivated to combine such a teaching with the system of Licht. As Licht is directed to hydrogen production, one of ordinary skill in the art would have no motivation to add nitrogen to a system focused on hydrogen production. At a minimum, such a modification would render the system of Licht unsatisfactory for its intended purpose.

Claim 1 Amendment Proposal – Auxiliary #1

1. (Proposed to be Amended) 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;

addition of nitrogen to the synthesis 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,

wherein the conversion of the charge of desulphurized natural gas includes a step of autothermal reforming or a step of partial oxidation.

It is alternatively proposed that claim 1 be amended to incorporate a portion of granted dependent claim 5 and a portion of granted dependent claim 19. As provided above, the PTO has not demonstrated that the cited references disclose "addition of nitrogen to the synthesis gas."

With respect to granted dependent claim 19, the PTO acknowledged that Licht does not disclose "wherein the conversion of the charge of desulphurized natural gas includes a step of autothermal reforming or a step of partial oxidation," but asserted that EP 2817260 ("EP '260") teaches "a process for synthesis of ammonia from natural gas by partial oxidation in an oxygen-fired reactor with steam which is either an autothermal reformer or a partial oxidation reactor [0048]." *Office Action*, p. 6-7. Even assuming, *arguendo*, EP '260 discloses a step of autothermal reforming or a step of partial oxidation, the alleged disclosures are steps without a primary reformer. For example, paragraph [0018], lines 17-19; paragraph [0019]; and claim 1 of EP '260 expressly describe partial oxidation "without a step of primary reforming." Applicant notes the secondary reformer in Licht is not an autothermal reformer. Accordingly EP'260 teaches away from being combined with Licht because EP '260 discloses that there is no primary reformer,

Topsoe, Inc. – EX1003
Page 624 of 1210

while Licht appears to disclose the hydrogen-containing product gas is used as fuel precisely in the primary reformer that must be absent from EP '260.

Claim 1 Amendment Proposal – Auxiliary #2

1. (Proposed to be Amended) 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;

addition of nitrogen to the synthesis 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;

wherein the conversion of the charge of desulphurized natural gas includes a step of autothermal reforming or a step of partial oxidation; and

wherein an amount of the desulphurized natural gas is provided as trim fuel, said trim fuel accounting for not more than 15% of a total combustion heat of the at least one furnace.

It is alternatively proposed that claim 1 be amended to incorporate a portion of granted dependent claim 5, a portion of granted dependent claim 19, and a portion of granted dependent claim 17. As provided above, the PTO has not demonstrated that the cited references disclose "addition of nitrogen to the synthesis gas" and "the conversion of the charge of desulphurized natural gas includes a step of autothermal reforming or a step of partial oxidation."

With respect to granted dependent claim 17, it is not apparent in the Office Action where the PTO addressed the limitations of granted dependent claim 17. Moreover, the PTO appears to not have addressed the alternative limitation of "an amount of natural gas is provided as trim fuel, said trim fuel accounting for not more than 15% of the total combustion heat." Instead, Licht appears to be silent about the trim fuel and its relation to total combustion heat. Even

assuming, *arguendo*, the supplementary fuel (18) of Licht is considered to be a trim fuel, the supplementary fuel is used only in relation to the problem of reducing CO2 emissions in the atmosphere. To solve this problem, Licht appears to propose replacing natural gas with ***hydrogen***. Licht does not teach or suggest using trim fuel to perform a rapid control of the furnace in order to quickly raise or lower the load, as is the effect of providing an amount of the desulphurized natural gas as trim fuel, said trim fuel accounting for not more than 15% of a total combustion heat of the at least one furnace.

Claim 1 Amendment Proposal – Auxiliary #3

1. (Proposed to be Amended) 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;

addition of nitrogen to the synthesis 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;

wherein the conversion of the charge of desulphurized natural gas includes a step of autothermal reforming or a step of partial oxidation; and

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 furnaces for pre-heating the charge of an autothermal reformer; or partial oxidation reactor or natural-gas desulphurization section.

It is alternatively proposed that claim 1 be amended to incorporate a portion of granted dependent claim 5, a portion of granted dependent claim 19, and a portion of granted dependent

Topsoe, Inc. – EX1003
Page 626 of 1210

claim 10. As provided above, the PTO has not demonstrated that the cited references disclose "addition of nitrogen to the synthesis gas" and "the conversion of the charge of desulphurized natural gas includes a step of autothermal reforming or a step of partial oxidation."

With respect to granted dependent claim 10, it is not apparent in the Office Action where the PTO addressed the limitations of granted dependent claim 10. The proposed amendment to claim 1 has removed "one or more burners of a primary steam reformer" from the subject matter of granted claim 10. Accordingly, the PTO has not demonstrated the cited references teach or suggest "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 furnaces for pre-heating the charge of an autothermal reformer; or partial oxidation reactor or natural-gas desulphurization section."

Claim 1 Amendment Proposal – Auxiliary #4

1. (Proposed to be Amended) 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;

addition of nitrogen to the synthesis 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;

wherein the conversion of the charge of desulphurized natural gas includes a step of autothermal reforming or a step of partial oxidation;

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 furnaces for pre-

heating the charge of an autothermal reformer; or partial oxidation reactor or natural-gas desulphurization section; and

conversion of the charge of desulphurized natural gas and steam is performed without any primary reforming.

It is alternatively proposed that claim 1 be amended to incorporate a portion of granted dependent claim 5, a portion of granted dependent claim 19, a portion of granted dependent claim 10, and the limitation "conversion of the charge of desulphurized natural gas and steam is performed without any primary reforming," not previously claimed in the granted claims. Support for this limitation is found in at least col. 7, ll. 21-22. As provided above, the PTO has not demonstrated that the cited references disclose "addition of nitrogen to the synthesis gas" and "the conversion of the charge of desulphurized natural gas includes a step of autothermal reforming or a step of partial oxidation." Moreover, "conversion of a charge of desulphurized natural gas and steam is performed without any primary reforming" excludes the possible combination of Licht and EP '260.

Claim 1 Amendment Proposal – Auxiliary #5

1. (Proposed to be Amended) 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;

addition of nitrogen to the synthesis 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;

wherein the conversion of the charge of desulphurized natural gas includes a step of autothermal reforming preceded by a pre-reforming;

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 furnaces for pre-heating the charge of an autothermal reformer; or natural-gas desulphurization section; and

wherein conversion of the charge of desulphurized natural gas and steam is performed without any primary reforming.

It is alternatively proposed that claim 1 be amended to incorporate a portion of granted dependent claim 5, a portion of granted dependent claim 19, a portion of granted dependent claim 10, the limitation "conversion of the charge of desulphurized natural gas and steam is performed without any primary reforming" (not previously claimed in the granted claims), the limitation "preceded by a pre-forming" (not previously claimed in the granted claims). Support for this limitation is found in at least col. 6, ll. 17-20. As provided above, the PTO has not demonstrated that the cited references disclose "addition of nitrogen to the synthesis gas" and "the conversion of the charge of desulphurized natural gas includes a step of autothermal reforming or a step of partial oxidation." Moreover, "conversion of a charge of desulphurized natural gas and steam is performed without any primary reforming" excludes the possible combination of Licht and EP '260. Furthermore, the step of autothermal reforming preceded by a pre-reforming further distinguishes claim 1 from the cited references.

VIA *e*FILE

PATENT APPLICATION
Docket No. 283386WOUS01_495230-44

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re patent of		)
	CASALE SA	)
Control/Serial No.:	96/000,424	)
Patent No.	11,286,168	) Art Unit
Issued:	March 29, 2022	) 3991
Confirmation No.:	9950	)
For:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE	)
Examiner:	Jerry Johnson	)
Customer No.:	116407	)

AMENDMENT "A" AND RESPONSE UNDER 37 C.F.R. § 1.530 – 1.570

VIA *e*FILE AMENDMENT
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

In response to the *Ex Parte* Reexamination Office Action dated July 7, 2023, please amend the above-identified application as follows:

Amendments to the Claims are reflected in the listing of claims which begins on page 2 of this paper.

Patent Owner's Statement of the Interview begins on page 8 of this paper.

Remarks/Arguments begin on page 9 of this paper.

AMENDMENTS TO THE CLAIMS

The listing of claims will replace all prior versions and listings of claims in the application:

Listing of Claims:

1. (Amended) 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 including an autothermal reformer downstream from a pre-reformer and without a primary reformer therebetween;

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

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

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

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

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

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

10. (Amended) 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] the autothermal reformer [or partial oxidation reactor] or natural-gas desulphurization section.

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

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

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

17. (Original) 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. (Original) 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. (Amended) 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] <u>conversion of the charge of desulphurized natural gas and steam into the synthesis gas in the autothermal reformer</u> is performed with a steam/carbon ratio not greater than 2.

20. (Canceled)

21. (Amended) 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, directly downstream of decarbonation, for use as fuel fraction, and allocating a remaining process fraction of the synthesis gas for ammonia conversion in a synthesis section, wherein the part of the synthesis gas separated for use as the fuel fraction is separated upstream from the synthesis section;

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

22. (Original) 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. (Previously Presented) The method of claim 21, wherein the section for treatment of the synthesis gas by the shift reaction of carbon monoxide includes methanation.

24. (New) 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 including a non-catalytic partial oxidation reactor;

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 comprises 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 that is directed to a synthesis section for synthesis of ammonia;

purification of the CO2-depleted synthesis gas with a dryer and a liquid nitrogen wash after the shift reaction; and

addition of nitrogen to the CO2-depleted synthesis gas after the shift reaction.

25. (New) The process of claim 24, wherein the part of the CO2-depleted synthesis gas that is separated as the fuel fraction is separated before the purification of the CO2-depleted synthesis gas with the dryer and the liquid nitrogen wash after the shift reaction.

26. (New) 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 without a primary reformer;

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,

wherein the fuel fraction of the synthesis gas feeds one or more of a steam production and/or superheating furnace or one or more furnaces for pre-heating the charge of an autothermal reformer or natural-gas desulphurization section.

PATENT OWNER'S STATEMENT OF THE INTERVIEW

Patent Owner and the undersigned express their appreciation to the Examiners for conducting a telephone interview with the undersigned on August 21, 2023. Multiple proposed amendments to independent claim 1 were discussed in the interview as set forth in the interview agenda sent to the Examiner and of record in the electronic file history at the PTO. No agreement was reached regarding patentable subject matter during the interview.

REMARKS

A. BACKGROUND

The present Amendment is in response to the Office Action dated July 7, 2023 by the U.S. Patent and Trademark Office ("PTO"). Claims 1-23 are subject to reexamination in view of cited art.[1]

By this Amendment, claim 20 is canceled, claims 1, 10, 19, 20, and 21 are amended, and new claims 24-26 are added. No new matter is presented with the amendments and new claim presented herein. Claims 1-19 and 21-26 are now pending in view of the above amendments.

Reconsideration of the application is respectfully requested in view of the above amendments to the claims and the following remarks. For the Examiner's convenience and reference, Patent Owner's remarks are presented in the order in which the corresponding issues were raised in the Office Action.

Please note that the following remarks are not intended to be an exhaustive enumeration of the distinctions between any cited references and the claimed subject matter. Rather, the distinctions identified and discussed below are presented solely by way of example to illustrate some of the differences between the claimed subject matter and the cited references. In addition, Patent Owner requests that the Examiner carefully review any references discussed below to ensure that Patent Owner's understanding and discussion of the cited references, if any, are consistent with the Examiner's understanding.

B. CLAIM AMENDMENTS

Patent Owner further submits that the claim amendments and new claims presented herein narrow the scope of the claims of the patent, and are, therefore, in compliance with 35 U.S.C. § 305. Patent Owner respectfully submits that independent claim 1 has been narrowed to recite that the conversion section includes "an autothermal reformer downstream from a pre-reformer and without a primary reformer there between." To be consistent with this narrowing amendment of independent claim 1, dependent claims 10 and 19 are amended herein to remove language now presented in independent claim 1 or in conflict with the narrowing amendment to independent claim 1. Patent Owner notes that MPEP 1412.03(II) states that:

[1] Although the prior art status of the cited art is not being challenged at this time, Patent Owner reserves the right to challenge the prior art status of the cited art at any appropriate time, should the need arise. Accordingly, any arguments and amendments made herein should not be construed as acquiescing to any prior art status of the cited art.

> …a claim which has been *broadened in a reissue as compared to its scope in the patent* is not a broadened reissue claim if it is narrower than, or equal in scope to, any other claim which appears in the patent. A common example of this is where dependent claim 2 is broadened via the reissue (other than the addition of a process step to convert an intermediate to a final product), but independent claim 1 on which it is based is not broadened. Because a dependent claim is construed to contain all the limitations of the claim upon which it depends, claim 2 must be at least as narrow as claim 1 and is thus not a broadened reissue claim.

(Emphasis in original.) As the MPEP states that "[i]f a claim is considered to be a broadening claim for purposes of reissue, it is likewise considered to be a broadening claim in reexamination" (*see* MPEP 2258(III)(A)), Patent Owner believes the amendments to dependent claims 10 and 19 are not broadening in view of the narrowing amendment to claim 1.

Patent Owner further notes the new independent claims 24 and 26 include all the limitation of original claim 1, as well as additional limitations that narrow the scope of new independent claims 24 and 26 relative to original independent claim 1. Accordingly, Patent Owner believes new independent claims 24 and 26 do not enlarge the scope of the claims of the patent.

C. REJECTIONS UNDER 35 U.S.C. §§ 102 AND 103

I. REJECTION UNDER 35 U.S.C. § 102

a. REJECTION I

Claims 1-4, 8-11, 17, and 20 stand rejected under 35 U.S.C. § 102(a) as allegedly being anticipated by U.S. Patent No. 8,137,422 to Licht et al. ("Licht").

The PTO has not established a *prima facie* case of anticipation against currently amended independent claim 1 because the PTO has not demonstrated, at a minimum, that Licht discloses expressly or inherently *each* and *every* limitation of claim 1. For example, at a minimum, the PTO has not demonstrated that Licht discloses "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 including an autothermal reformer downstream from a pre-reformer and without a primary reformer therebetween***… wherein said fuel fraction is ***fed as fuel to at least one furnace***," as recited in currently amended independent claim 1. (Emphasis added).

In rejecting claim 1, the PTO asserts that Licht teaches a process including "introducing a process stream comprising steam and at least one hydrocarbon selected from, *inter alia,* methane and natural gas (column 3, line 41) in a reformer furnace to form a reformate stream comprising

hydrogen, carbon monoxide, methane and steam." *Office Action*, p. 4. During the interview with the Examiners, it was further asserted that Licht "teaches a second reforming reactor which is an autothermal reactor (col. 7, lines 17-28) and that use of a pre-reformer is optional (column 5, line 57 to column 6, line 3). *Examiner Interview Summary*, Continuation Sheet.

Patent Owner respectfully submits that currently amended independent claim 1 now recites, in part, "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 including an autothermal reformer downstream from a pre-reformer and without a primary reformer therebetween***." (Emphasis added). Referring to FIG. 2 of Licht (provided below for reference), the PTO has asserted that reference 80 is a prereformer and reference 20 is a secondary reformer/autothermal reformer.

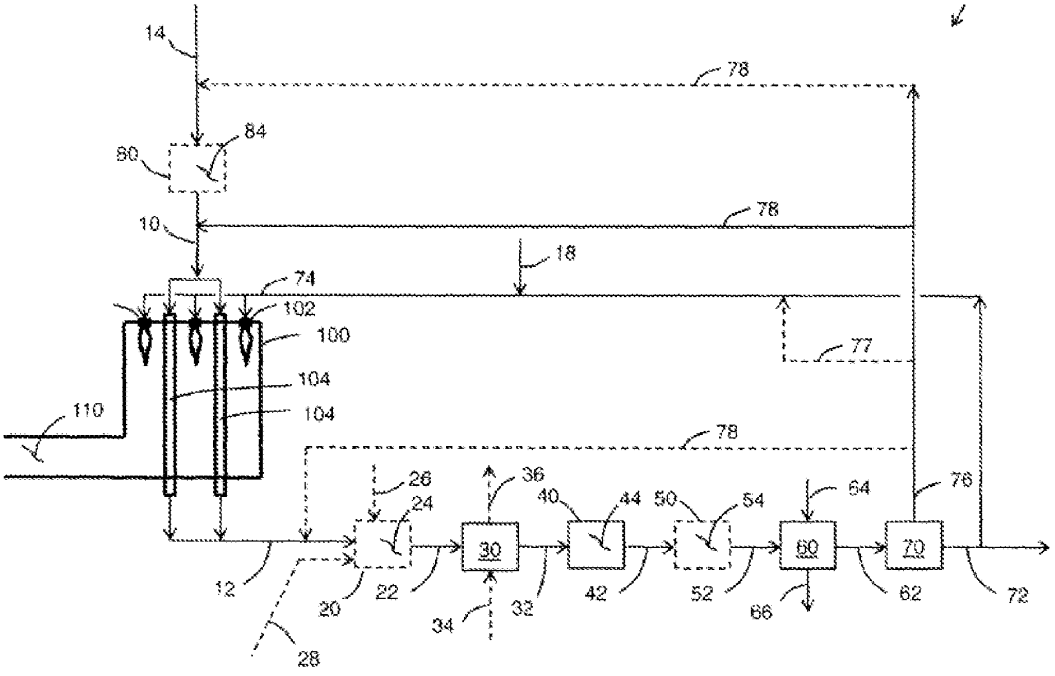


FIG. 2

Even assuming, *arguendo*, the secondary reformer discloses an autothermal reformer as characterized by the PTO, Patent Owner respectfully submits that Licht does not disclose "a conversion section including an autothermal reformer downstream from a pre-reformer and without a primary reformer therebetween." To the contrary, Licht appears to require a reformer furnace of a primary reformer positioned downstream from the prereformer and upstream from the alleged autothermal reformer. Accordingly, Licht does not disclose "a conversion section including an autothermal reformer downstream from a pre-reformer and ***without a primary***

reformer therebetween." Patent Owner further notes that the systems and processes of Licht would not operate as intended without the reformer furnace described throughout the specification of Licht.

Patent Owner respectfully submits the claimed conversion section "including an autothermal reformer downstream from a pre-reformer and without a primary reformer therebetween" provides benefits not found in the cited references and conventional systems. For example, Patent Owner found specific benefits of the system of claim 1, and the specification provides data comparing different options of ammonia plants. *See* '168 Patent, col. 14, l. 48-col. 15, l. 28 and Table 1. In the provided examples, option (1) is a plant with a primary reformer and an air-fed secondary reformer, option (2) is a plant with a primary reformer and an air-fed secondary reformer and also with capturing of the CO2 from the fumes of the primary reformer, and option (3) is a plant according to FIG. 1, *e.g.*, a plant having conversion section including an autothermal reformer downstream from a pre-reformer and without a primary reformer therebetween.

Patent Owner respectfully notes that the consumption of the plant of option (3), which includes the conversion section of claim 1, is much less than the consumption of option (2). Patent Owner further notes that the total duty of the furnaces according to option (3) is only 75% of option (1). Patent Owner respectfully submits that the reduced fuel consumption and the reduced total duty of the plant of option (3) depends from the specifically claimed *front-end* (where conversion of the charge of desulpherized natural gas and steam is performed) that is suitable for producing also the gas fraction used as fuel in the furnace(s). Accordingly, the conversion section of claim 1 provides improvements over the cited references and conventional systems.

Patent Owner further notes that Licht does not disclose "wherein said fuel fraction is fed as fuel to at least one furnace," as recited in currently amended independent claim 1. As a primary reformer is absent from currently amended independent claim 1 and the alleged fuel fraction of Licht appears to be fed to a primary reformer, Licht does not disclose feeding the fuel fraction to at least one furnace that does not include a primary reformer.

Accordingly, Patent Owner respectfully requests withdrawal of this rejection and reconsideration of currently amended independent claim 1. Dependent claims 2-4, 8-11, 17, and 20 are patentable over the cited reference by virtue of their own separately claimed subject matter and also for depending from patentable independent claim 1.

With specific respect to dependent claim 10, Patent Owner respectfully submits that this claim has been amended to recite "wherein said fuel fraction of the synthesis gas feeds one or more of the following apparatuses: a steam production and/or superheating furnace; or one or more furnaces for pre-heating the charge of the autothermal reformer or natural-gas desulphurization section," thereby removing "one or more burners of a primary steam reformer" from the claim. Patent Owner respectfully submits that the fuel fraction of the alleged synthesis gas of Licht does not appear to feed "a steam production and/or superheating furnace; or one or more furnaces for pre-heating the charge of the autothermal reformer or natural-gas desulphurization section." To the contrary, Licht states "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." Licht, therefore, does not disclose "wherein said fuel fraction of the synthesis gas feeds one or more of the following apparatuses: a steam production and/or superheating furnace; or one or more furnaces for pre-heating the charge of the autothermal reformer or natural-gas desulphurization section."

Patent Owner further notes that EP '260, while referencing a fuel gas ***produced*** by the PSA unit, does not teach or suggest use of the actually synthesis gas as fuel. Accordingly, claim 10 is allowable over both Licht and EP '260.

II. REJECTION UNDER 35 U.S.C. § 103

a. REJECTION I

Claims 5 and 6 stand rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over U.S. Patent No. 8,137,422 to Licht et al. ("Licht '422") as applied to claims 1-4, 8, 11, 17, and 20 in view of U.S. Patent Publication No. 2004/0234426 to Reddy et al. ("Reddy"). Dependent claims 5 and 6 are patentable over the cited references by virtue of their own separately claimed subject matter and also for depending from patentable independent claim 1.

b. REJECTION II

Claims 7, 12 and 14-16 stand rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over Licht '422 as applied to claims 1-4, 8, 11, 17, and 20 in view of Non-Patent Literature titled "Ammonia: Principles and Industrial Practice" ("Ammonia"). Dependent claims 7, 12, and 14-16 are patentable over the cited references by virtue of their own separately claimed subject matter and also for depending from patentable independent claim 1.

c. REJECTION III

Claims 1, 11, 14, 15, 16, and 19 stand rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over Foreign Patent No. EP2817260 ("EP '260") in view of Licht '422.

The PTO has not established a *prima facie* case of obviousness against currently amended independent claim 1 because the PTO has not demonstrated, at a minimum, that the cited references teach or suggest *each* and *every* limitation of claim 1. For example, at a minimum, the PTO has not demonstrated that the cited references teach or suggest "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 including an autothermal reformer downstream from a pre-reformer and without a primary reformer therebetween***," as recited in currently amended independent claim 1. (Emphasis added).

As provided above, Licht does not disclose "a conversion section including an autothermal reformer downstream from a pre-reformer and without a primary reformer therebetween." Patent Owner further submits that an express feature of EP '260 is the ***absence*** of a pre-former in the disclosed systems. For example, paragraph [0031] of EP '260 recites that "[a] remarkable advantage of the invention is the opportunity to use a low SC ration ***without the need of a pre-reformer***." Accordingly, the PTO has not demonstrated that the combination of EP '260 and Licht teaches or suggests "a conversion section including an autothermal reformer downstream from a pre-reformer and without a primary reformer therebetween." Patent Owner further submits that one of ordinary skill in the art would have no motivation to modify the system of EP '260 to include a pre-reformer, and EP '260 expressly teaches away from the inclusion of a pre-reformer.

Patent Owner further notes "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" is also absent from EP '260. In fact, EP'260 makes use of a fuel gas *produced* by the PSA unit, that is a tail gas and not a stream separated from the CO2-depleted synthesis gas.

Accordingly, Patent Owner respectfully requests withdrawal of this rejection and reconsideration of currently amended independent claim 1. Dependent claims 11, 14, 15, 16, and 19 are patentable over the cited reference by virtue of their own separately claimed subject matter and also for depending from patentable independent claim 1.

d. REJECTION IV

Claims 21 and 23 stand rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over the Admitted Prior Art in view of Licht '422.

The PTO has not established a *prima facie* case of obviousness against currently amended independent claim 21 because the PTO has not demonstrated, at a minimum, that the cited references teach or suggest *each* and *every* limitation of claim 21. For example, at a minimum, the PTO has not demonstrated that the cited references teach or suggest "separating a part of the synthesis gas, ***directly*** downstream of decarbonation, for use as fuel fraction, and allocating a remaining process fraction of the synthesis gas for ammonia conversion in a synthesis section, ***wherein the part of the synthesis gas separated for use as the fuel fraction is upstream from the synthesis section***," as recited in currently amended independent claim 21.

Patent Owner respectfully submits the Admitted Prior Art and Licht do not teach or suggest the part of the synthesis gas separated for use as the fuel fraction is upstream from the synthesis section. To the contrary, Licht merely references that secondary reforming reactors are "used widely for the production of ammonia" (*Licht*, col. 7, ln. 17-19). Thus, Licht provides no teaching of the location of separation of the synthesis gas for use as the fuel fraction.

Patent Owner further submits that EP '260 does not cure this deficiency of Licht. While EP '260 references a "fuel gas 22," Patent Owner respectfully submits that the referenced fuel gas of EP '260 is a tail gas having a different quality and pressure than a fuel fraction which is a portion of the CO2-depleted synthesis gas.

Different quality means different composition: a CO2-depleted synthesis gas is more noble and valuable because it is made of a hydrogen-rich stream with respect to a PSA tail gas that is a composition made of waste components such as carbon monoxide and methane. Due to its high content in hydrogen, the CO2-depleted synthesis gas has a much higher heating value than the tail (waste) gas produced by the PSA unit of EP'260. Moreover, its composition is more constant in time with respect to the composition of a tail gas and allows a better control of the burner and of the heat generated in the furnace. The tail gas of EP'260 having a variable composition makes it more difficult to adjust the settings of the burner that needs to provide a

constant amount of heat to the furnace. A CO2-depleted synthesis gas being rich in hydrogen brings also an environmental advantage with respect to the use of a tail gas comprising carbon. Such tail gas, when combusted in the furnace, generate carbon dioxide (see col. 2, ll. 6-12 of the patent specification). In contrast, combustion of a hydrogen-rich stream produces water.

The difference in pressure results in the synthesis gas of the claimed fuel fraction being a more dense gas with a flow rate that is much easier to control than a PSA tail gas because the transportation of the fuel fraction entails only the use of control valves to ensure a sufficient pressure to reach the combustion burner (without the need to use fans or compressors to perform this transport). Moreover, even assuming, *arguendo*, the fuel gas 22 of EP '260 is considered the fuel fraction by the PTO, Patent Owner respectfully submits that this fuel gas 22 does not appear to be separated directly downstream from the decarbonation, but is instead produced by the pressure swing absorption unit. *See* EP '260, paragraph [0052].

Accordingly, Patent Owner respectfully requests withdrawal of this rejection and reconsideration of currently amended independent claim 21. Dependent claim 23 is patentable over the cited reference by virtue of its own separately claimed subject matter and also for depending from patentable independent claim 21.

e. REJECTION V

Claim 22 stands rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over the admitted prior are in view of Licht '422 as applied to claims 21 and 23 above, and further in view of EP '260. Dependent claim 22 is patentable over the cited references by virtue of their own separately claimed subject matter and also for depending from patentable independent claim 21.

III. NEW CLAIMS 24-26

a. NEW INDEPENDENT CLAIM 24 AND DEPENDENT CLAIM 25

New independent claim 24 is added herein. Patent Owner respectfully submits the PTO has not demonstrated that the cited references teach or suggest "purification of the CO2-depleted synthesis gas with a dryer and a liquid nitrogen wash after the shift reaction; addition of nitrogen to the CO2-depleted synthesis gas after the shift reaction," as recited in new claim 24.

With respect to Licht, this reference does not appear to disclose "purification of the CO2-depleted synthesis gas with a dryer and a liquid nitrogen wash," does not appear to disclose that this purification is "after the shift reaction," and does not appear to disclose "addition of nitrogen to the CO2-depleted synthesis gas after the shift reaction." Mere reference in Licht to a

secondary reactor being "used widely for the production of ammonia" does not disclose the specific step of "addition of nitrogen to the ***CO2-depleted synthesis gas after the shift reaction***." (Emphasis added).

With respect to EP '260, this reference appears to describe that "prior art layouts" include "an ASU unit to furnish oxygen, a high-temperature shift, then CO2 removal, drying and nitrogen wash to remove inerts" (*EP '260*, paragraph [0015]). EP '260, however, appears to describe that the fuel gas 22 is ***produced*** by the PSA unit. *See* paragraph [0052]. This fuel gas is also referred to as the tail gas of the of PSA unit. *See* EP '260, paragraph [0034]. As the tail gas is ***produced*** by the PSA unit, EP '260 provides no teaching or suggestion of a removal **(1)** downstream of the PSA, **(2)** of a portion of the CO2-depleted synthesis gas as ***fuel fraction*** and even less **(3)** in relation to a system that includes a dryer and a liquid nitrogen wash. As provided above, while EP '260 references a "fuel gas 22," Patent Owner respectfully submits that the referenced fuel gas of EP '260 is a tail gas having a different quality and pressure than a fuel fraction which is a portion of the CO2-depleted synthesis gas.

Different quality means different composition: a CO2-depleted synthesis gas is more noble and valuable because it is made of a hydrogen-rich stream with respect to a PSA tail gas that is a composition made of waste components such as carbon monoxide and methane. Due to its high content in hydrogen, the CO2-depleted synthesis gas has a much higher heating value than the tail (waste) gas produced by the PSA unit of EP'260. Moreover, its composition is more constant in time with respect to the composition of a tail gas and allows a better control of the burner and of the heat generated in the furnace. The tail gas of EP'260 having a variable composition makes it more difficult to adjust the settings of the burner that needs to provide a constant amount of heat to the furnace. A CO2-depleted synthesis gas being rich in hydrogen brings also an environmental advantage with respect to the use of a tail gas comprising carbon. Such tail gas, when combusted in the furnace, generate carbon dioxide (see **col. 2, ll. 6-12** of the patent specification). In contrast, combustion of a hydrogen-rich stream produces water.

The in pressure difference results in the synthesis gas of the claimed fuel fraction being a more dense gas with a flow rate that is much easier to control than a PSA tail gas because transportation of the fuel fraction entails only the use of control valves to ensure a sufficient pressure to reach a combustion burner (without the need to use fans or compressors to perform this transport).

Dependent claim 25 is patentable over the cited reference by virtue of their own separately claimed subject matter and also for depending from patentable independent claim 24. Furthermore, claim 25 recites that "the part of the CO2-depleted synthesis gas that is separated as the fuel fraction is separated ***before the purification of the CO2-depleted synthesis gas*** with the dryer and the liquid nitrogen wash after the shift reaction." (Emphasis added). Reference in EP '260 to prior art layouts that include drying and a nitrogen wash and reference to PSA tail gas does not disclose the specifics of separation of the synthesis gas as the fuel fraction before the purification of the CO2-depleted synthesis gas with the dryer and the liquid nitrogen wash after the shift reaction. Patent Owner respectfully submits that the claimed purification is simpler and less costly due smaller amounts of gas to be purified, lower energy consumption, and no recycling of nitrogen (which has a lower calorific value) to the furnace. Furthermore, there is a lower consumption of nitrogen in the liquid nitrogen wash. Patent Owner also notes that passing through the liquid nitrogen makes the fuel gas colder, and more fuel would be needed to feed the furnace. For example, if the fuel is cold, its enthalpy is lower. Therefore, if the purpose of combustion of such fuel is to transfer a fixed amount of heat to the furnace, it is necessary to burn more fuel with respect to a hot or pre-heated fuel.

Accordingly, new claims 24 and 25 are allowable over the cited references.

b. NEW INDEPENDENT CLAIM 26

New independent claim 26 is added herein. Patent Owner respectfully submits that the PTO has not demonstrated that the cited references teach or suggest a process for synthesis of ammonia wherein the conversion section is "without a primary reformer" and "the fuel fraction of the synthesis gas feeds one or more of a steam production and/or superheating furnace or one or more furnaces for pre-heating the charge of an autothermal reformer or natural-gas desulphurization section."

With respect to Licht and as provided above, a primary reformer appears to be required for the system of Licht to operate as intended. Moreover, the alleged synthesis gas of Licht appears to feed the primary reformer, rather than the claimed "one or more of a steam production and/or superheating furnace or one or more furnaces for pre-heating the charge of an autothermal reformer or natural-gas desulphurization section." Accordingly, Licht does not teach or suggest a process for synthesis of ammonia wherein the conversion section is "without a primary reformer" and "the fuel fraction of the synthesis gas feeds one or more of a steam production

and/or superheating furnace or one or more furnaces for pre-heating the charge of an autothermal reformer or natural-gas desulphurization section."

With respect to EP '260, this reference appears to describe that "a fuel gas 22" is produced by the PSA unit. *EP '260*, paragraph [0052]. This fuel gas is also referred to as the tail gas of the of PSA unit. *See* EP '260, paragraph [0034]. As the fuel gas is ***produced*** by the PSA unit, EP '260 provides no teaching or suggestion of a removal of fuel fraction of ***synthesis gas*** in relation to a system that feeds one or more of a steam production and/or superheating furnace or one or more furnaces for pre-heating the charge of an autothermal reformer or natural-gas desulphurization section. As provided above, while EP '260 references a "fuel gas 22," Patent Owner respectfully submits that the referenced fuel gas of EP '260 is a tail gas having a different quality and pressure than a fuel fraction which is a portion of the CO2-depleted synthesis gas.

Different quality means different composition: a CO2-depleted synthesis gas is more noble and valuable because it is made of a hydrogen-rich stream with respect to a PSA tail gas that is a composition made of waste components such as carbon monoxide and methane. Due to its high content in hydrogen, the CO2-depleted synthesis gas has a much higher heating value than the tail (waste) gas produced by the PSA unit of EP'260. Moreover, its composition is more constant in time with respect to the composition of a tail gas and allows a better control of the burner and of the heat generated in the furnace. The tail gas of EP'260 having a variable composition makes it more difficult to adjust the settings of the burner that needs to provide a constant amount of heat to the furnace. A CO2-depleted synthesis gas being rich in hydrogen brings also an environmental advantage with respect to the use of a tail gas comprising carbon. Such tail gas, when combusted in the furnace, generate carbon dioxide (see col. 2, ll. 6-12 of the patent specification). In contrast, combustion of a hydrogen-rich stream produces water.

The difference in pressure results in the synthesis gas of the claimed fuel fraction being a more dense gas with a flow rate that is much easier to control than a PSA tail gas because the transportation of the fuel fraction entails only the use of control valves to ensure a sufficient pressure to reach a combustion burner (without the need to use fans or compressors to perform this transport).

D. ALLOWABLE SUBJECT MATTER

The Examiner's allowance of claims 13 and 18 is appreciated.

Patent Owner submits the following comments concerning the Examiner's statements of reasons for the indication of allowable subject matter in the Office Action. Patent Owner respectfully submits that the claimed invention(s) as set forth in each of the independent claims and the dependent claims must be read as a whole, and not as a single feature or subcombination of features which represent less than the entirety of the claimed invention as a whole. While a particular feature or subcombination of features referred to by the Examiner in the Statement of Reasons for Allowance may represent a basis for distinguishing the claimed invention(s) over the cited art, Patent Owner further submits that this may not necessarily be the *sole* ground for distinguishing the claimed invention(s) over the cited art of record. Accordingly, the Examiner's statement should, in Patent Owner's view, not be read as constituting or meaning that the claimed invention(s) can or should be reduced to a single "feature" of the claimed invention(s) or to a subcombination of features that is less than the entire claimed invention(s) as a whole, nor that the single feature referenced by the Examiner or subcombination of features referenced by the Examiner in the Statement of Reasons for Allowance is the only or sole grounds for distinguishing the invention(s) over the cited art of record, or that Patent Owner necessarily agrees with any characterization of the cited art set forth in the Statement of Reasons for Allowance.

E. CONCLUSION

In view of the foregoing, Patent Owner respectfully submits that the other rejections to the claims are now moot and do not, therefore, need to be addressed individually at this time. It will be appreciated, however, that this should not be construed as Patent Owner acquiescing to any of the purported teachings or assertions made in the last action regarding the cited art or the pending application, including any official notice. Instead, Patent Owner reserves the right to challenge any of the purported teachings or assertions made in the last action at any appropriate time in the future, should the need arise. Furthermore, to the extent that the Examiner has relied on any Official Notice, explicitly or implicitly, Patent Owner specifically requests that the Examiner provide references supporting the teachings officially noticed, as well as provide the required motivation or suggestion to combine references with the other art of record.

For at least the foregoing reasons, Patent Owner respectfully submits that the pending claims are neither anticipated by nor made obvious by the applied art. In the event that the Examiner finds any remaining impediment to allowance of this application that may be clarified through a telephone interview, the Examiner is requested to contact the undersigned attorney.

The Commissioner is hereby authorized to charge payment of any of the following fees that may be applicable to this communication, or credit any overpayment, to Deposit Account No. 50-6181: (1) any filing fees required under 37 CFR § 1.16; (2) any patent application and reexamination processing fees under 37 CFR § 1.17; and/or (3) any post issuance fees under 37 CFR § 1.20. In addition, if any additional extension of time is required, which has not otherwise been requested, please consider this a petition therefor and charge any additional fees that may be required to Deposit Account No. 50-6181.

Dated this 2nd day of November, 2023.

Respectfully submitted,

/Marcus S. Simon, Reg.# 50258/
MARCUS S. SIMON
Registration No. 50,258
Attorney for Patent Owner
Dorsey & Whitney LLP
Customer No. 116407
Telephone No. 801.933.7360

MSS: JR: sm

VIA *e*FILE

PATENT APPLICATION
Docket No. 283386WOUS01_495230-44

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re patent of	CASALE SA	)
Control/Serial No.:	96/000,424	)
Patent No.	11,286,168	) Art Unit 3991
Issued:	March 29, 2022	)
Confirmation No.:	9950	)
For:	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE	)
Examiner:	Jerry Johnson	)
Customer No.:	116407	)

GENERAL AUTHORIZATION TO CHARGE FEES

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Sir:

With respect to the above-identified application, the Commissioner is authorized to charge any fees under 37 C.F.R. §§ 1.16 and 1.17 and any provision for this reexamination proceeding which may be required and to treat any concurrent or future reply requiring a petition for an extension of time under 37 C.F.R. § 1.136(a)(3) for its timely submission as incorporating a petition therefor for the appropriate length of time and to charge any fees which may be required during the course of prosecution, or credit any overpayment, to Deposit Account No. 50-6181.

Dated this 2nd day of November, 2023.

Respectfully submitted,

/Marcus S. Simon, Reg.# 50258/
MARCUS S. SIMON
Registration No. 50,258
Attorney for Applicant
Dorsey & Whitney LLP
Customer No. 116407
Telephone: 801.933.7360

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
Approved for use through 11/30/2020. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT
(Not for submission under 37 CFR 1.99)

Application Number	96000424
Filing Date	2018-01-31
First Named Inventor	Francesco Baratto
Art Unit	3991
Examiner Name	Jerry D. Johnson
Attorney Docket Number	283386WOUS01_495230-44

U.S.PATENTS Remove

Examiner Initial*	Cite No	Patent Number	Kind Code[1]	Issue Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1	3479298	A	1969-11-18	SZE, et al.	

If you wish to add additional U.S. Patent citation information please click the Add button. Add

U.S.PATENT APPLICATION PUBLICATIONS Remove

Examiner Initial*	Cite No	Publication Number	Kind Code[1]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear
	1					

If you wish to add additional U.S. Published Application citation information please click the Add button. Add

FOREIGN PATENT DOCUMENTS Remove

Examiner Initial*	Cite No	Foreign Document Number[3]	Country Code[2] i	Kind Code[4]	Publication Date	Name of Patentee or Applicant of cited Document	Pages,Columns,Lines where Relevant Passages or Relevant Figures Appear	T[5]
	1							

If you wish to add additional Foreign Patent Document citation information please click the Add button Add

NON-PATENT LITERATURE DOCUMENTS Remove

Examiner Initials*	Cite No	Include name of the author (in CAPITAL LETTERS), title of the article (when appropriate), title of the item (book, magazine, journal, serial, symposium, catalog, etc), date, pages(s), volume-issue number(s), publisher, city and/or country where published.	T[5]

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	96000424
	Filing Date	2018-01-31
	First Named Inventor	Francesco Baratto
	Art Unit	3991
	Examiner Name	Jerry D. Johnson
	Attorney Docket Number	283386WOUS01_495230-44

	1	Notice of Opposition for European Patent Application No. 18702977.2 mailed June 14, 2022	
	2	Response letter from Topsoe counsel dated June 13, 2023	
	3	"Fertiliser Policy for Sustainable Agriculture", The Fertiliser Associate of India Annual Seminar 2009, December 3-5, 2009, 10 pages	

If you wish to add additional non-patent literature document citation information please click the Add button Add

EXAMINER SIGNATURE

Examiner Signature		Date Considered	

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609. Draw line through a citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

[1] See Kind Codes of USPTO Patent Documents at www.USPTO.GOV or MPEP 901.04. [2] Enter office that issued the document, by the two-letter code (WIPO Standard ST.3). [3] For Japanese patent documents, the indication of the year of the reign of the Emperor must precede the serial number of the patent document. [4] Kind of document by the appropriate symbols as indicated on the document under WIPO Standard ST.16 if possible. [5] Applicant is to place a check mark here if English language translation is attached.

INFORMATION DISCLOSURE STATEMENT BY APPLICANT (Not for submission under 37 CFR 1.99)		
	Application Number	96000424
	Filing Date	2018-01-31
	First Named Inventor	Francesco Baratto
	Art Unit	3991
	Examiner Name	Jerry D. Johnson
	Attorney Docket Number	283386WOUS01_495230-44

CERTIFICATION STATEMENT

Please see 37 CFR 1.97 and 1.98 to make the appropriate selection(s):

That each item of information contained in the information disclosure statement was first cited in any communication from a foreign patent office in a counterpart foreign application not more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(1).

OR

☐ That no item of information contained in the information disclosure statement was cited in a communication from a foreign patent office in a counterpart foreign application, and, to the knowledge of the person signing the certification after making reasonable inquiry, no item of information contained in the information disclosure statement was known to any individual designated in 37 CFR 1.56(c) more than three months prior to the filing of the information disclosure statement. See 37 CFR 1.97(e)(2).

See attached certification statement.

The fee set forth in 37 CFR 1.17 (p) has been submitted herewith.

✓ A certification statement is not submitted herewith.

SIGNATURE

A signature of the applicant or representative is required in accordance with CFR 1.33, 10.18. Please see CFR 1.4(d) for the form of the signature.

Signature	/Marcus S. Simon, Reg.# 50258/	Date (YYYY-MM-DD)	2023-11-02
Name/Print	Marcus S Simon	Registration Number	50258

This collection of information is required by 37 CFR 1.97 and 1.98. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1 hour to complete, including gathering, preparing and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. **SEND TO: Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.**

Privacy Act Statement

The Privacy Act of 1974 (P.L. 93-579) requires that you be given certain information in connection with your submission of the attached form related to a patent application or patent. Accordingly, pursuant to the requirements of the Act, please be advised that: (1) the general authority for the collection of this information is 35 U.S.C. 2(b)(2); (2) furnishing of the information solicited is voluntary; and (3) the principal purpose for which the information is used by the U.S. Patent and Trademark Office is to process and/or examine your submission related to a patent application or patent. If you do not furnish the requested information, the U.S. Patent and Trademark Office may not be able to process and/or examine your submission, which may result in termination of proceedings or abandonment of the application or expiration of the patent.

The information provided by you in this form will be subject to the following routine uses:

1. The information on this form will be treated confidentially to the extent allowed under the Freedom of Information Act (5 U.S.C. 552) and the Privacy Act (5 U.S.C. 552a). Records from this system of records may be disclosed to the Department of Justice to determine whether the Freedom of Information Act requires disclosure of these record s.

2. A record from this system of records may be disclosed, as a routine use, in the course of presenting evidence to a court, magistrate, or administrative tribunal, including disclosures to opposing counsel in the course of settlement negotiations.

3. A record in this system of records may be disclosed, as a routine use, to a Member of Congress submitting a request involving an individual, to whom the record pertains, when the individual has requested assistance from the Member with respect to the subject matter of the record.

4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

FAI

ENSURING FOOD SECURITY

THE FERTILISER ASSOCIATION OF INDIA

Annual Seminar 2009

"FERTILISER POLICY FOR SUSTAINABLE AGRICULTURE"

3-5 December, 2009
Hyderabad



PREPRINTS OF SEMINAR PAPERS

Topsoe, Inc. – EX1003
Page 656 of 1210

Energy Efficiency and CO_2 Reduction Potential in Ammonia Plants Based on Lean Gas

SVEND ERIK NIELSEN
and
HANS CHRISTIAN FERDINANDSEN
Haldor Topsøe A/S
Lyngby, Denmark

In today's market energy efficiency is very important to plants struggling with high cost of natural gas. Furthermore, the world faces climate challenges, and the emission of greenhouse gases attracts attention. In view of this, there is an increasing interest in improving energy efficiency of plants using expensive natural gas.

This paper specifically deals with the latest generation technology for production of ammonia when the natural gas is lean, and sufficient CO_2 needs to be produced for converting all ammonia into urea. Various schemes for optimising the ammonia process in order to minimise the energy consumption as well as the emission of CO_2 are discussed in detail.

Introduction

Various ammonia process schemes for energy efficient production will be presented. The focus will be on keeping the combined feed and fuel consumption low. Furthermore schemes for lean natural gas feedstock enabling to balance the carbon dioxide with ammonia production to ensure all ammonia can be converted into urea, will be presented.

Energy Efficient Ammonia Production

The typical process flow diagram for a large capacity and energy efficient ammonia plant based on Topsøe technology is shown in **Figure 1**.

The Topsøe ammonia process design is tailor-made to suit the specific objectives set by clients and local conditions – the flexibility in design ensures that the most optimal solution can be found, which may be to achieve the lowest Inside Battery Limit (ISBL) specific energy consumption for the ammonia plant or the best integration with the entire complex to achieve the overall lowest energy consumption for urea production.

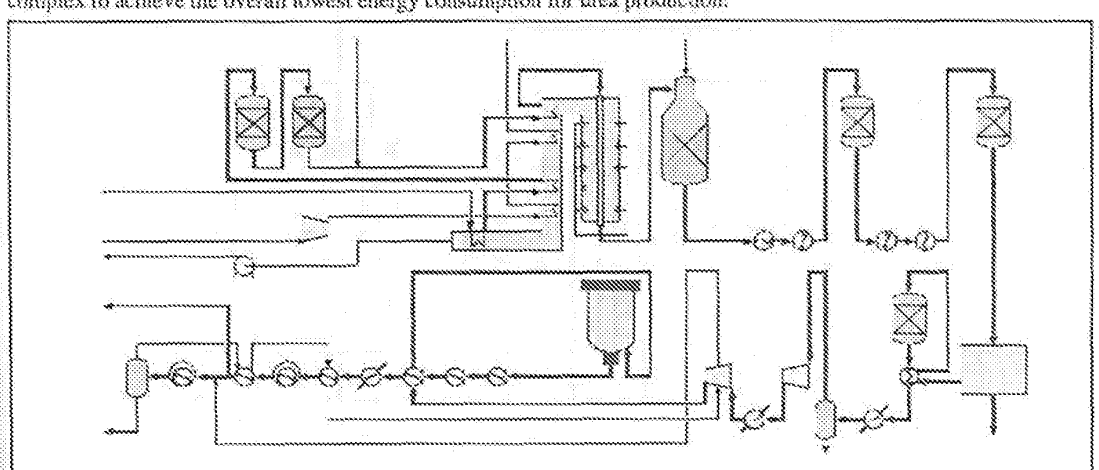


Figure 1 – Process flow diagram for Topsøe ammonia plant

In order to make an optimal design, it is imperative to understand the specifics of the project – for example, in a grassroots project or in a project where virtually no off-site facilities (availability of steam and/or power capacities) are available, the lowest specific energy consumption could be achieved by adopting an ammonia plant configuration which maximises MP steam production and export. Such design would incorporate a gas turbine (GT) for running one of the major process compressors (commonly the process air compressor) with the exhaust gases from GT either routed to the tubular reformer as pre-heated combustion air (CA) or to an HRSG (heat recovery steam generator). Either of these GT schemes will result in a high export of MP steam which would then be used to meet the requirements of the urea plant (process and driving the CO_2 compressor) and reduce the load on the auxiliary boilers in the off-sites.

However, if for example, the project is a brownfield project with certain margins/spare capacities in the GT generators and/or HRSG's, or where the steam can be generated in a cheaper way in the off-sites, the ideal solution will be to use the existing facilities to the extent possible and save CAPEX in the ammonia plant by reducing the generation and export of steam. In such cases, it will be beneficial for the complex to go for an ammonia plant with a somewhat smaller steam export, and thereby a higher specific energy consumption. On the other hand this will assure a better utilisation of the existing auxiliary boiler, and therefore also a higher energy efficiency of the off-sites/utility sections, instead of running the auxiliary boilers at minimum load due to the high steam production in the ammonia plant. This will normally result in a better overall energy efficiency for the entire complex. Finally, also in cases where cheap fuel is available for the off-sites boilers, it can be beneficial to reduce the steam production in the ammonia plant.

As mentioned above, the flexibility in the Topsøe design allows for wide variations in the process configuration and in operating conditions in the various process sections to arrive at a total steam production that covers steam requirement in urea (partially or completely).

In the following, one way of reducing the steam generation/export from the ammonia plant will be described. Reduced steam production can be achieved by an alternative process scheme which includes a gas heated heat exchange reformer. This reformer denominated HTER-p (Haldor Topsøe exchange reformer – parallel) is installed in parallel with the primary reformer and the secondary reformer. The HTER-p is fed independently with desulphurised natural gas mixed with process steam. This allows adjustment of steam to carbon ratio separately of the primary reformer feed in order to achieve the desired conversion. The heat for the reforming reaction in the HTER-p is supplied by the gas coming from the secondary reformer. The reforming section of the process scheme with HTER-p is shown in **Figure 2**.

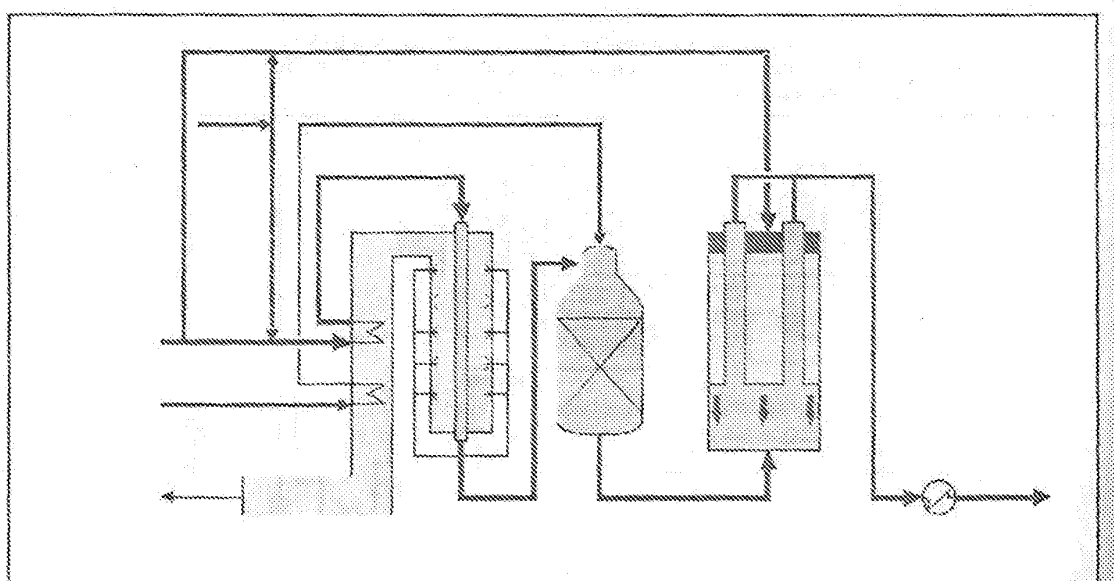


Figure 2 – HTER-p

Topsoe, Inc. – EX1003
Page 658 of 1210

In the following, emphasis will be put on how to achieve balanced carbon dioxide production from lean natural gas feedstock, since the issue on steam export and carbon dioxide production to a certain extent go hand in hand.

Schemes for Balancing Carbon Dioxide and Ammonia for Urea Production Using Lean Natural Gas Feedstock

Production of ammonia from lean natural gas will result in disproportionate amounts of ammonia and carbon dioxide for urea production due to the low content of carbon in the feedstock. The amount of carbon dioxide produced will therefore be insufficient to ensure that all ammonia can be converted to urea. As such, it is of great interest to consider how best to achieve a stoichiometric balance of carbon dioxide and ammonia for urea production when the feedstock is lean natural gas with low carbon content.

In the following four different schemes, often used in the industry, will be described and compared, which all provides a balanced production of carbon dioxide and ammonia for urea production:

- Scheme with cryogenic synthesis gas purification
- Scheme with excess synthesis gas production
- Scheme with CDR (carbon dioxide recovery) unit
- Scheme with/without HRU (hydrogen recovery unit)

Scheme with Cryogenic Synthesis Gas Purification

The scheme using cryogenic purification as final clean up is based on primary and secondary reforming, using excess air in the secondary reformer, followed by two-step shift system, carbon dioxide removal, methanation and cryogenic purification. Apart from the high process air flow, the scheme is characterised by a high methane leakage from the reforming section. In order to satisfy the required carbon dioxide production the flow of feedstock is adjusted to match the desired production. The synthesis gas is finally purified in a cryogenic "cold box", where the synthesis gas is adjusted to get a hydrogen to nitrogen ratio of 3:1 as required in the ammonia synthesis. In the cryogenic unit excess methane and synthesis gas is removed and this excess gas is used as fuel in the primary reformer, similar to the scheme with excess synthesis gas production given below. However, due to the excess amount of process air and also the high methane leakage from the reforming unit, the feed flow is significantly higher in this scheme compared to the other schemes described. Consequently a relatively, large amount of unconverted feedstock passes through the front-end ending up in the cryogenic unit. The waste gas from the cryogenic purification, containing excess hydrogen and unconverted feedstock, may be used as fuel in the primary reformer, similar to the scheme producing excess synthesis gas.

Despite the fact that the reforming duty is smaller than for the other cases, all the rest of the front-end equipment, and in particular the process air compressor, are significantly larger in size compared to conventional ammonia plant configuration and this is essentially due to the high feed flow. On the other hand the loop is inert-free and somewhat smaller than a usual ammonia synthesis loop with inerts.

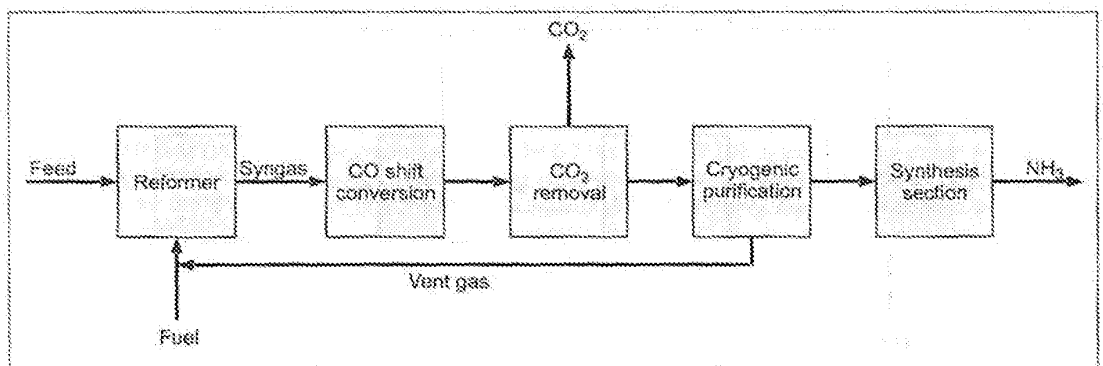


Figure 3 – Scheme with cryogenic synthesis gas purification

Topsoe, Inc. – EX1003
Page 659 of 1210

Scheme with Excess Synthesis Gas Production

In the conventional ammonia scheme based on primary and secondary reforming followed by two-step shift system, carbon dioxide removal and methanation, the feed flow is kept minimal by having a relatively low methane leakage from the reforming section and using exactly the amount of hydrocarbon feedstock needed for giving the desired carbon dioxide production. The stoichiometric amount of air is added to the secondary reformer needed for the ammonia synthesis. Plant control and operating conditions are completely identical to the normal scheme, without excess synthesis gas production having a hydrogen to nitrogen ratio of approx. 3:1. However, since the feed flow is dictated by the carbon dioxide production rather than the hydrogen and nitrogen production for the ammonia synthesis loop, an excess of synthesis gas is produced, and this excess synthesis gas is used as fuel in the primary reformer. Since no excess air is introduced in this scheme, all flows are minimised, and so is the front-end equipment size.

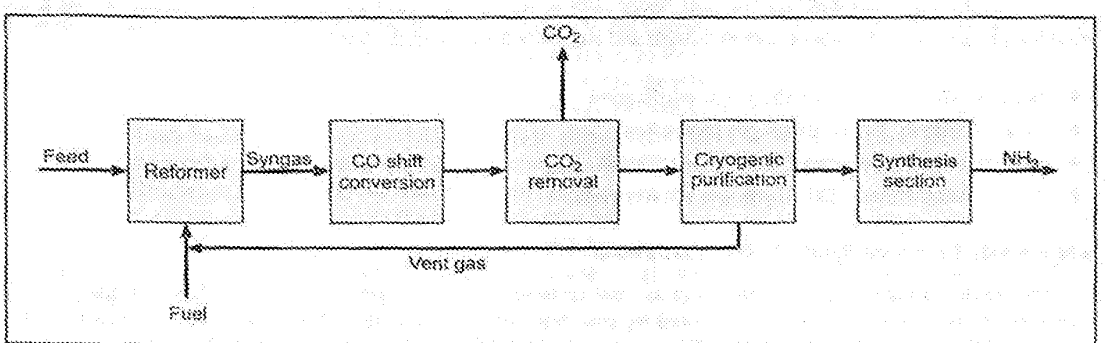


Figure 4 – Scheme with excess synthesis gas production

Scheme with CDR (Carbon Dioxide Removal) Unit

The process scheme is identical to the scheme described above, and the CDR unit can be considered as an add-on unit. As can be noted from the two schemes described above, they are both based on processing more feed gas through the front-end of the plant than needed for the ammonia synthesis, and thereby generating an excess of gas that need to be split from the synthesis gas and recycled back to the primary reformer as fuel.

Introducing a CDR unit is another way to produce the amount of carbon dioxide required for urea production. In this scheme, the feed gas flowing through the plant matches the requirement of hydrogen for the ammonia synthesis section, and the carbon dioxide production is matched by recovering carbon dioxide from the reformer flue gas. In this way the size of the front-end equipment is minimised, but a CDR unit is added as an extra unit to the normal front-end. The CDR unit is a unit similar to the normal carbon dioxide removal unit in the ammonia plant, having an absorber and a stripper, and operating close to atmospheric pressure. MHI (Mitsubishi Heavy Industries) has already supplied some CDR units for Indian ammonia plants, so the technology is well proven.

The energy input to the CDR will be LP steam for the stripper reboiler, power for the circulation pumps, and cooling water. The additional advantage of this unit is the reduction of the carbon footprint of the plant.

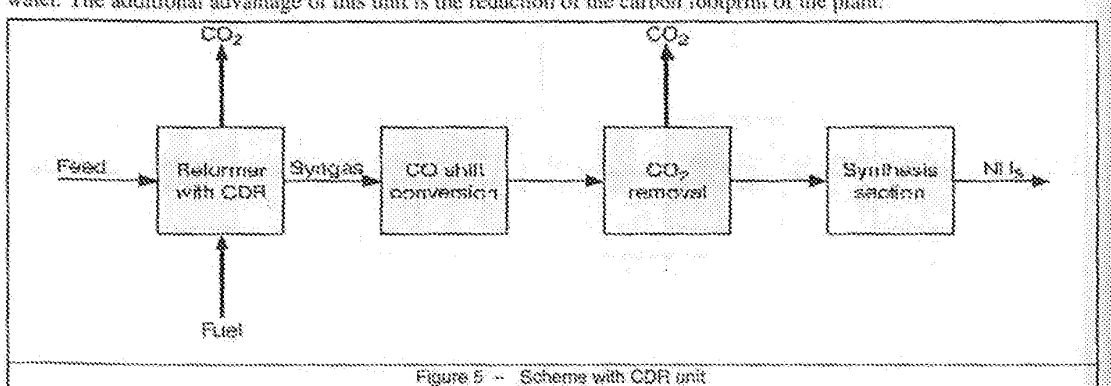


Figure 5 – Scheme with CDR unit

Topsoe, Inc. – EX1003
Page 660 of 1210

Scheme With/Without HRU (Hydrogen Recovery Unit)

A hydrogen recovery unit is installed in many ammonia plants as a mean for reducing the loss of hydrogen and thereby enhancing the ammonia production. The hydrogen recovery unit is normally beneficial when operating on rich natural gas or in cases where surplus ammonia production is an objective. However, when using lean natural gas for ammonia and subsequent urea production, omission of HRU is an alternative solution for achieving stoichiometric balance of ammonia and carbon dioxide for urea production.

When omitting HRU the off-gas coming from the ARU (ammonia recovery unit) will be send directly to the primary reformer as fuel. This scheme resembles the scheme with excess synthesis gas production described above. The main difference being that the gas returned as fuel is taken downstream the synthesis rather than upstream the synthesis.

The feed flow in this scheme is dictated by the carbon dioxide production as in the excess synthesis gas scheme. Consequently the front-end section of the plant will be identical for the two schemes. The flow through the synthesis section will be slightly higher, resulting in slightly larger loop equipment, but on the other hand the HRU cost is saved.

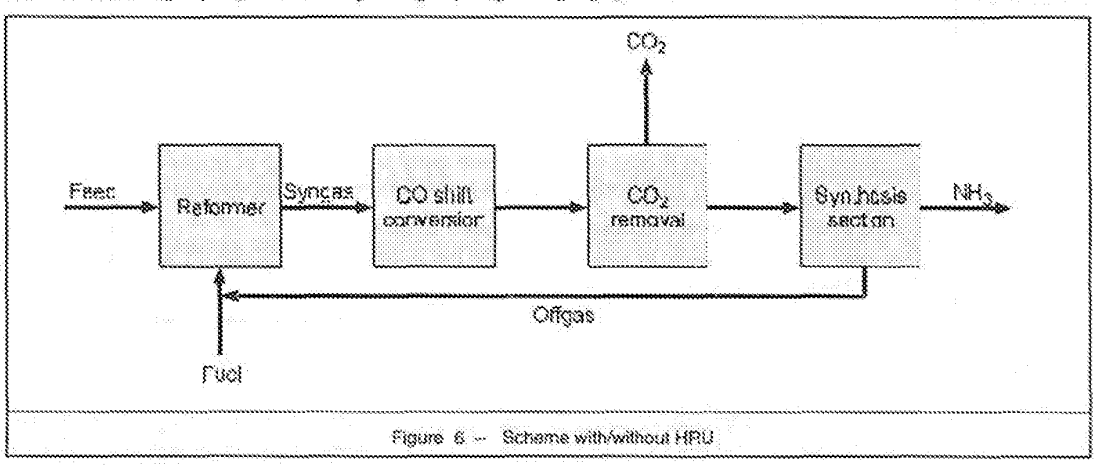


Figure 6 – Scheme with/without HRU

Reduced Steam Production and Minimum Carbon Footprint

The steam systems within ammonia plants have an important influence on the energy balance. The steam systems are used for energy transport within the ammonia plant most notably by carrying the energy generated in the process to the drivers for the rotating equipment installed in the ammonia plant. But the steam system is also an efficient way of exporting energy from the ammonia plant to adjacent facilities needing energy, e.g. a carbon dioxide compressor in a neighbouring urea plant.

As mentioned it is possible to vary the steam production in the ammonia plant to match exactly the requirement within the ammonia plant and of any other consumers in the complex. Further it is possible to carry the heat at various steam pressures. These levels being medium pressure (MP) or high pressure (HP) with values of around 40 bar g and 110 bar g, respectively. For the ammonia plant inside battery limits the lowest specific energy consumption is achieved by having MP steam export, if medium pressure steam is suitable for OSBL consumers. For an ammonia plant, with a capacity of 2,000 MTPD, the energy consumption will be 0.2-0.3 Gcal/MT NH_3 lower, if steam export for urea plant carbon dioxide compressor is as medium pressure steam rather than high pressure steam, leading to the lowest energy consumption for the ammonia plant ISBL, but not necessarily giving the lowest energy consumption for the entire complex.

In these days, there is a high focus on the Kyoto protocol, and thereby low carbon dioxide emissions (carbon footprint). To get a lower carbon footprint in an ammonia plant, one very interesting scheme is the scheme with the HTER-p. By introducing the HTER-p, the size of the primary reformer is reduced significantly. In addition, the cost of RG, WHB, SSH, steam drum and HP steam piping are also reduced. This results in reduced fuel consumption in the reformer, and thereby lower carbon dioxide emission. And if the HTER-p is combined with a CDR, the carbon footprint

of the plant is really minimised. Even though the CDR is an extra unit for the ammonia plant, it might be worthwhile to consider it along with the HTER-p because this is a way to minimise the natural gas consumption for the ammonia plant. With the high focus on carbon dioxide emissions, and the possibility to get carbon credits for the saved carbon dioxide, such a scheme might be worthwhile considering for future plants/revamps.

Case Studies : Comparison of Various Ammonia Production Schemes Using Lean Natural Gas Feedstock

The flexibility in the design of a Topsøe ammonia plant allows a great deal of tailoring as presented in the above. In the following the schemes described above will be compared using the following assumptions:

Capacity of ammonia, MTPD	2,000
Natural gas composition, mole%	
CH_4	97.59
C_2H_6	2.10
C_3H_8	0.05
C_4H_{10}	0.03
C_5H_{12}	0.03
CO_2	0.10
N_2	0.10
Natural gas LHV, kcal/Nm³	8,696
Steam export as MP steam (44 kg/cm² a, 385°C).	
Power calculated at 2,150 kcal/kWh.	
Cooling water pumps and fans included in electric power consumption.	
Only major compressors driven by steam turbines, the rest is motordriven.	
All ammonia product to urea.	

Case Study 1 : Base Case

Conventional front-end with primary and secondary reformer, process air compressor driven by gas turbine, two-step shift section, carbon dioxide removal and methanation followed by loop with two ammonia converters in series.

The feed flow has been adjusted to achieve an ammonia production capacity of 2,000 MTPD but with no consideration to the carbon dioxide production capacity.

CO_2 production, MTPD	2,362
MP steam export, tonnes/h	280
Natural gas consumption	
Feed, Gcal/MT NH_3	5.27
Fuel, Gcal/MT NH_3	2.80
Total natural gas consumption, Gcal/MT NH_3	8.07
Specific energy consumption	
Natural gas, Gcal/MT NH_3	8.07
Electric power, Gcal/MT NH_3	0.30
MP steam export, Gcal/MT NH_3	(2.27)
Net consumption, Gcal/MT NH_3	6.10

Case Study 2 : Cryogenic Purification Case

Front-end with primary reformer operating with lower than normal outlet temperature and thus higher methane slip, secondary reformer fed with excess process air, process air compressor driven by gas turbine, two-step shift section, carbon dioxide removal, methanation, driers and then cryogenic purification followed by inert free loop. The waste gas from the cryogenic purification is routed to the reformer as fuel.

The feed flow is adjusted to ensure enough carbon dioxide for complete conversion of ammonia into urea.

CO_2 production, MTPD	2,606
MP steam export, tonnes/h	193
Natural gas consumption	
Feed, Gcal/MT NH_3	6.34
Fuel, Gcal/MT NH_3	1.64
Total natural gas consumption, Gcal/MT NH_3	7.98
Specific energy consumption	
Natural gas, Gcal/MT NH_3	7.98
Electric power, Gcal/MT NH_3	0.26
MP steam export, Gcal/MT NH_3	(1.75)
Net consumption, Gcal/MT NH_3	**6.49**

The process feed flow is higher than in the base case partly due to the requirement for carbon dioxide production but also due to the higher slip of methane from the secondary reformer. The waste gas containing unconverted methane, inerts and some synthesis gas is used as fuel and consequently reduces the requirement for natural gas fuel. Overall this adds up to a natural consumption that is slightly lower compared to the base case.

The steam export in this scheme is lower than in the base case. It is due to lower temperature exit the secondary reformer which reduces the steam production and higher requirement for process steam.

This route ensures sufficient carbon dioxide for full conversion of ammonia into urea at an energy consumption that is 0.39 Gcal/MT NH_3 higher than the base case.

Case Study 3 : Excess Synthesis Gas Case

Conventional front-end with primary and secondary reformer, process air compressor driven by gas turbine, two-step shift section, carbon dioxide removal and methanation followed by loop with two ammonia converters in series. However, in this case excess synthesis gas is produced in order to get stoichiometric ratio of ammonia and carbon dioxide for subsequent urea production. The excess synthesis gas is taken upstream the synthesis gas compressor and used as fuel in the primary reformer.

CO_2 production, MTPD	2,606
MP steam export, tonnes/h	275
Natural gas consumption	
Feed, Gcal/MT NH_3	5.81
Fuel, Gcal/MT NH_3	2.54
Total natural gas consumption, Gcal/MT NH_3	8.35
Specific energy consumption	
Natural gas, Gcal/MT NH_3	8.35
Electric power, Gcal/MT NH_3	0.31
MP steam export, Gcal/MT NH_3	(2.50)
Net consumption, Gcal/MT NH_3	**6.16**

Compared to the base case, the natural gas consumption for reformer fuel is reduced as excess synthesis gas is routed to the primary reformer as fuel. On the other hand, this scheme requires additional natural gas for process feed, and the overall natural consumption increases compared to the base case.

The total natural gas consumption increases thereby increasing the energy consumption. On the contrary, excess synthesis gas production results in additional heat generation in the process. This additional heat converts into an increased steam production and thus a reduction of the incremental energy consumption.

Overall the route of increasing synthesis gas production by approx. 10% to make up for the carbon dioxide deficit results in an increase in energy consumption of 0.06 Gcal/MT NH_3. The corresponding CO_2 emission from the primary reformer is 969 MTPD for this scheme.

Case Study 4 : HTER-p With Excess Synthesis Gas Case

Front-end with HTER-p operating in parallel with primary reformer followed by secondary reformer, process air compressor driven by gas turbine, two step shift section, carbon dioxide removal and methanation followed by loop with two ammonia converters in series. Further in this case excess synthesis gas is produced in order to get stoichiometric ratio of ammonia and carbon dioxide for subsequent urea production. The excess synthesis gas is taken upstream the synthesis gas compressor and used as fuel in the primary reformer.

CO_2 production in ammonia plant, MTPD	2,606
MP steam export, tonnes/h	152
Natural gas consumption	
Feed, Gcal/MT NH_3	5.75
Fuel, Gcal/MT NH_3	1.67
Total natural gas consumption, Gcal/MT NH_3	7.42
Specific energy consumption	
Natural gas, Gcal/MT NH_3	7.42
Electric power, Gcal/MT NH_3	0.31
MP steam export, Gcal/MT NH_3	(1.38)
Net consumption, Gcal/MT NH_3	**6.35**

This scheme with HTER-p and excess synthesis gas production ensures sufficient production of carbon dioxide for full conversion of ammonia into urea. The natural gas feed consumption is comparable with the scheme producing excess synthesis gas but without HTER-p. This is obvious as it is governed by the requirement for carbon dioxide production. However the natural gas fuel consumption is reduced resulting in overall natural gas consumption that is 8 % less than in the base case and 11% less than in the scheme producing excess synthesis gas without HTER-p.

Case Study 5 : Carbon Dioxide Removal (CDR) from Flue Gas Case

Conventional front-end with primary and secondary reformer, process air compressor driven by gas turbine, two-step shift section, carbon dioxide removal and methanation followed by loop with two ammonia converters in series. The feed flow is as in the base case adjusted only to satisfy the need for ammonia production. However, a carbon dioxide removal (CDR) unit is installed to capture carbon dioxide from the flue gas to cover the carbon dioxide deficit for subsequent urea production.

CO_2 production in ammonia plant, MTPD	2,362
CO_2 captured from flue gas, MTPD	244
MP steam export, tonnes/h	237
Natural gas consumption	
Feed, Gcal/MT NH_3	6.27
Fuel, Gcal/MT NH_3	2.80
Total natural gas consumption, Gcal/MT NH_3	8.07
Specific energy consumption	
Natural gas, Gcal/MT NH_3	8.07
Electric power, Gcal/MT NH_3	0.31
MP steam export, Gcal/MT NH_3	(2.15)
Net consumption, Gcal/MT NH_3	**6.23**

Comparing the use of the CDR process with the base case means that the natural gas requirement is identical. The removal of carbon dioxide from the flue gas increases the energy requirement which is covered for by electric power consumption and reduced steam export.

The energy consumption thus increases by 0.13 Gcal/MT NH_3 if carbon dioxide is to be captured from the flue gas to cover the shortage of carbon dioxide for urea production compared to the base case.

Topsoe, Inc. – EX1003
Page 664 of 1210

Case Study 6 : Scheme Without HRU

Conventional front-end with primary and secondary reformer, process air compressor driven by gas turbine, two-step shift section, carbon dioxide removal and methanation followed by loop with two ammonia converters in series. However, in this scheme no hydrogen recovery unit is envisaged.

Compared to the excess synthesis gas case the natural gas consumption for reformer fuel is reduced slightly. On the other hand, steam export is also reduced resulting in an overall specific energy consumption compared to the excess synthesis gas case which is about 0.05 Gcal/MT NH_3 higher.

Case Study 7 : HTER-p With Carbon Dioxide Removal (CDR) from Flue Gas Case

Front-end with HTER-p operating in parallel with primary reformer followed by secondary reformer, process air compressor driven by gas turbine, two-step shift section, carbon dioxide removal and methanation followed by loop with two ammonia converters in series. However, a carbon dioxide removal (CDR) unit is installed to capture carbon dioxide from the flue gas to cover the carbon dioxide deficit for subsequent urea production.

CO_2 production in ammonia plant, MTPD	2,371
CO_2 captured from flue gas, MTPD	235
MP steam export, tonnes/h	123
Natural gas consumption	
Feed, Gcal/MT NH_3	5.32
Fuel, Gcal/MT NH_3	1.96
Total natural gas consumption, Gcal/MT NH_3	7.28
Specific energy consumption	
Natural gas, Gcal/MT NH_3	7.28
Electric power, Gcal/MT NH_3	0.27
MP steam export, Gcal/MT NH_3	(1.08)
Net consumption, Gcal/MT NH_3	6.47

This scheme with HTER-p and CDR results in an almost unchanged natural gas consumption for process feed but a significantly reduced natural gas consumption for fuel. Altogether the consumption of natural gas is reduced by nearly 10% in this scheme compared to the base case while additionally producing ammonia and carbon dioxide in stoichiometric ratio for urea production.

The reduced natural gas consumption is then reflected in reduced steam production and then reduced steam export. Due to crediting for steam export the net consumption in this case comes out with an increment of 0.37 Gcal/h compared to the base case despite having lower natural gas consumption and thereby being the scheme that has the lowest emission of carbon dioxide. Due to the CDR, the CO_2 emission from the primary reformer is only 501 MTPD or nearly 50 % lower than for the case with excess synthesis gas.

CONCLUSION

It is possible to produce ammonia in energy efficient manner when the natural gas is lean and sufficient carbon dioxide needs to be produced for converting all ammonia into urea.

Low specific energy consumption for ammonia plant can be achieved by having a high steam production in the ammonia plant and consequently also a high steam export.

However when considering the whole energy balance for a urea plant complex it may be advantageous to have a lower steam export from the ammonia plant, which will result in higher specific energy consumption for the ammonia production. This may provide better utilisation of the auxiliary boiler and therefore higher energy efficiency of the off-sites. The overall energy efficiency for the complex may thus be better than when having low specific energy consumption for the ammonia plant only.

Lean natural gas feedstock may require additional synthesis gas production in order to ensure sufficient carbon dioxide for full conversion of ammonia into urea. This will lead to higher emissions of carbon dioxide due to additional firing in the primary reformer. An alternative scheme is to use the Topsoe HTER-p combined with CDR as this will firstly reduce fuel consumption and secondly further remove some carbon dioxide from the flue gas. In fact this scheme may be very attractive when taking the carbon credits into consideration. ▩

Topsoe, Inc. – EX1003
Page 665 of 1210

ReedSmith
Driving progress
through partnership
Robert R. Riddle
Direct Phone: +1 713 469 3881
Email: rriddle@reedsmith.com

Reed Smith LLP
Suite 1700
811 Main Street
Houston, TX 77002-6110
+1 713 469 3800
Fax +1 713 469 3899
reedsmith.com

June 13, 2023

By E-Mail

Riccardo Biazzi
rbiazzi@zardi.ch
M. Zardi & Co. SA
Via G. B. Pioda 6 6900 Lugano CH

RE: Response to your letter dated June 1, 2023

Dear Mr. Biazzi,

You have sent correspondence on behalf of your client, Casale SA, accusing Topsoe of patent infringement absent written consent of Casale. Your correspondence, however, omits many important details. We find these omissions, as well as the assertion of patent infringement, to be made in bad faith, fraudulent, and anticompetitive. Given Casale's approach, the seriousness of Casale's allegations, Casale's initial offer to "resolve this matter amicably," and to mitigate any further harm to Topsoe that Casale's actions and allegations may be causing we suggest a teleconference between the parties' respective business principals and counsel to have a candid dialogue about the issues raised thus far. In advance, we provide additional information uncovered in our investigation, but note that our investigation is ongoing and that we reserve all legal and equitable rights against Casale.

Topsoe has worked to develop processes to reduce CO_2 emissions associated with ammonia production for more than two decades, and Topsoe's SynCOR™ process is a direct result of that work. Topsoe was using the features purportedly claimed by Casale long before Casale filed its patents (US 11,286,168 and EP 3583067). This information is publicly available and well-known to Casale.

While Casale points to a Topsoe Symposium paper from September 2022 to assert infringement, Casale neglects to mention its attendance at the Fertilizer Association of India (FAI) Annual Seminar in 2009 where Topsoe described an identical process. Specifically, Topsoe presented its process and published a companion paper, both titled "Energy efficiency and CO_2 reduction potential in ammonia plants based on lean gas." Both are prior art to Casale's patents, and both describe a process that includes the features Casale now attempts to claim as an invention, including for example, auto thermal reforming, high temperature and low temperature shift, CO_2 removal, and two fuel streams. The paper provides the following explanation and figures.

> Plant control and operating conditions are completely identical to the normal scheme, without excess synthesis gas production having a hydrogen to nitrogen ratio of approx. 3:1. However, since the feed flow is dictated by the carbon dioxide production rather than the hydrogen and nitrogen production for the ammonia synthesis loop, ***an excess of synthesis gas is produced, and this excess synthesis gas is used as fuel in the primary reformer.***

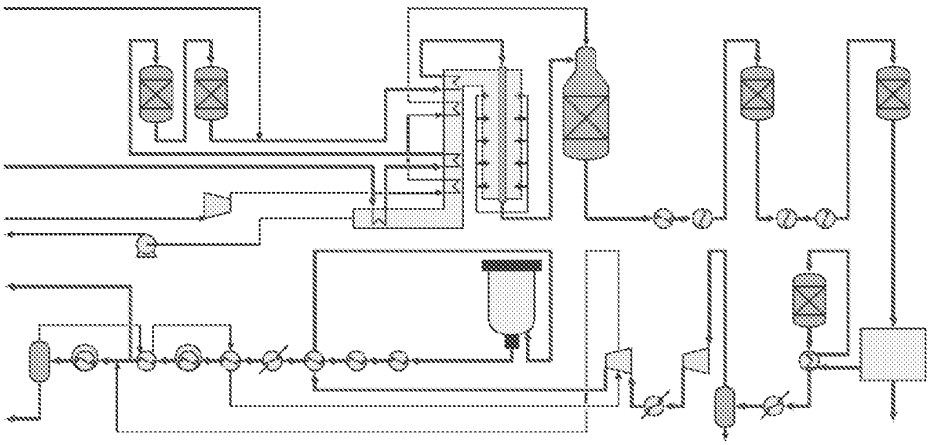


Figure 1: Process flow diagram for Topsøe ammonia plant

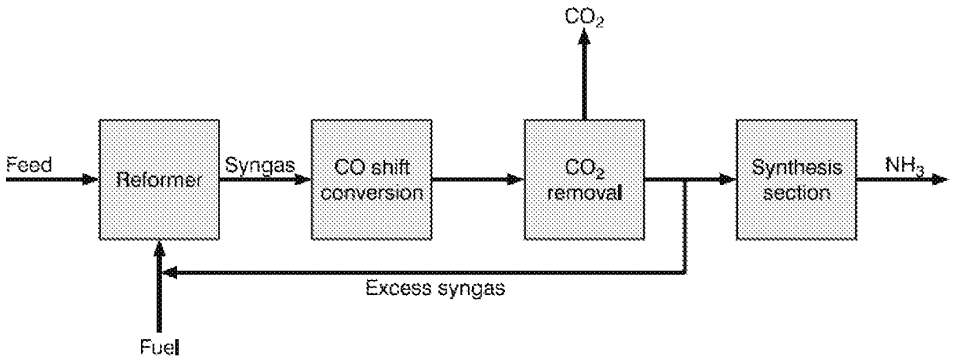


Figure 4: Scheme with excess synthesis gas production

Casale is a regular attendee and presenter at FAI meetings, attended the 2009 FAI meeting, and received preprints of the seminar papers, including the paper authored by Topsoe. Despite this, Casale did not disclose the Topsoe presentation or paper to the patent office. As such, Casale knowingly and intentionally committed fraud on the patent office by violating Casale's duty of candor pursuant to 37 C.F.R. § 1.56 rendering Casale's patent not only invalid, but also unenforceable.

Worse, Casale cannot excuse this fraud as a mere oversight. Our preliminary investigation reveals a pattern of fraudulent action by Casale. Apart from the 2009 Topsoe presentation and paper, Casale had direct access to Topsoe's technology implemented at IFFCO's Aonla Fertilizer plant prior to filing Casale's EP