ReedSmith

and US patents. Casale began a revamp of that plant in 2014 and completed the revamp in 2018. After again learning of Topsoe's prior art technology and seeing Topsoe's technology in an operating plant, Casale filed for the patents it now claims Topsoe infringes. Casale never disclosed this IFFCO plant prior art to the patent office during prosecution or during Casale's recent request for supplemental examination. In short, Casale filed patent applications that it knew covered this (and other) prior art while concealing that information from the patent office.

Beyond that, Casale's letters accusing Topsoe of infringement omits pertinent information:

(1) the validity of the EP patent has been challenged in opposition proceedings based upon a number of prior art references;

(2) Casale itself presented prior art to the USPTO in a supplemental examination (none of which included the Topsoe prior art of which Casale is well-aware);

(3) the USPTO determined that the prior art Casale did raise created a substantial question about that patent's validity; and

(4) the USPTO has ordered a reexamination of Casale's patent.

Casale's patents may not survive these proceedings. Regardless, based on the prior art identified thus far, the validity of Casale's patents is questionable at best, and unenforceable regardless.

In light of these facts, Casale's infringement assertions, which Topsoe disputes, are particularly troubling. They appear designed to stifle competition. As such, we are concerned that Casale may have had communications with customers making allegations similar to those made in your letters that the SynCOR™ process "cannot be used commercially without a written consent of Casale SA" or implying to any extent that Topsoe's SynCOR™ process may infringe any of Casale's patents. To address these concerns, we demand a prompt response advising whether Casale, or its representatives, have had such communications with customers; and, if so, the name of each customer, date of each communication, whether the communication was oral or written, the name of the individual(s) who received such communication, and copies of each written communication.

Please respond to the issues raised above, and provide the information requested, within two weeks. If Casale still seeks amicable resolution, please also respond with Casale's availability for a teleconference including the name and title of each individual who will attend on behalf of Casale.

Very truly yours,

Robert R. Riddle

RRR:dd

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Date
14.06.2022

Reference	Application No./Patent No.
AMC121WEP	18702977.2 - 1108 / 3583067
Applicant/Proprietor	
Casale SA	

Communication of a notice of opposition

You are hereby informed of a notice of opposition to the European patent specified above (see attached copy in the enclosure). All annexes to the notice(s) of opposition / letter as well as the consolidated list of all opposition citations are available for inspection via the European Patent Register at **www.epo.org/register**. Should you wish to receive these documents in paper format, they will be supplied to you free of charge if specifically requested on receipt of this communication (see OJ EPO 2022, A28).

If oral proceedings are to take place, parties are advised to check the electronic file via European Patent Register in advance of the hearing to ensure they are in possession of all relevant documents.

An invitation to file observations and to file amendments, where appropriate, to the description, claims and drawings (R. 79(1) EPC) will be issued separately.

The period within which such observations may be filed will not be fixed until the following conditions are met:

(a) the opposition period has expired;

(b) the notice of opposition has been examined for certain formal requirements (R. 77 EPC).

For the Opposition Division

Europäisches Patentamt • European Patent Office • Office européen des brevets •

✓ Enclosure: Notice of opposition O1: Linde AG
O2: thyssenkrupp Industrial Solutions AG

Evidence used

The opposition is based on the following citations, published before the filing date of the patent in suit (Article 54(2) EPC):

A1: Dr. Klaus Noelker and Dr. Joachim Johanning, *Autothermal reforming: a flexible syngas route with future potential*, 2010, veröffentlicht als Preprint eines Vortrags

A2: US 8,137,422 B2

A3: EP 2 817 260 B1

A4: Ryota Shimura, *Urea Product Expansion by Newly Developed CO2 Recovery Process from Primary Reformer Flue Gas*, AIChE TECHNICAL MANUAL 2006, Vol. 47, S. 237-246

A5: P. Heussinger, *Hydrogen, 3. Purification*, Ullmann's Encyclopedia of Industrial Chemistry, 2011

Grounds of opposition

1. Claim 1 (independent)

Article 100(a) EPC – Lack of novelty in view of A1

Document A1 discloses a

1.1) Process for synthesis of ammonia from natural gas *(p. 6 ff: AMMONIA PLANTS BASED ON AUTO THERMAL REFORMING; Figure 2, Options 2 and 3)*,

comprising:

1.2) conversion of a charge of desulphurized natural gas and steam *(Table 3; page 12: Description of Uhde's ATR test facility)* with oxygen-enriched air or with oxygen, into a synthesis gas containing hydrogen, CO and CO2, in a conversion section *(Figure 2, options 2 and 3)*;

1.3) a treatment of said synthesis gas comprising at least a shift reaction of the carbon monoxide into CO2 *(Fig. 2, options 2 and 3 each disclose a CO conversion)* and subsequent separation of CO2 from the gas *(Fig. 2, options 2 and 3: CO2 removal)*, thus obtaining a CO2-depleted synthesis gas and a CO2-rich gaseous flow containing the CO2 separated from the gas;

Topsoe, Inc. – EX1003
Page 670 of 1210

optionally, a step for methanation of the synthesis gas *(Figure 2, option 2)* and/or addition of nitrogen to the synthesis gas *(Figure 2, option 3)*,

characterized by:

1.4) 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 and

1.5) 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 streams having the same composition,

1.6) wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia, optionally after further purification.

In the last paragraph of A1 it is disclosed:

"A complete separation of the entire CO2 could also be realized in the ATR-based plant ... provided the fired heater would be fed with syngas instead of natural gas."

A1 thus proposes using synthesis gas as a fuel instead of natural gas in a furnace within the meaning of the opposed patent (par. [0014]). Since this measure leads to a complete CO2 capture, that is an ammonia production from natural gas without CO2 release into the atmosphere, the synthesis gas can only be CO2-depleted synthesis gas. A1 therefore also shows feature 1.4) of claim 1.

As ammonia synthesis would be impossible without synthesis gas, it is clear to the person skilled in the art that not all, but only a first part of the CO2-depleted syngas can be used as fuel, while a second part is intended for the synthesis of ammonia. A1 thus also implicitly discloses features 1.5) and 1.6) of claim 1.

Document A1 therefore discloses all the features of claim 1, whose subject matter consequently is not new (Article 54 EPC).

Article 100(a) EPC – Lack of inventive step in view of A2 and A3 or A4

Even if claim 1 were found surprisingly new, it is still not valid as it is not based on an inventive step.

The document A2 discloses a

1.1) Process for synthesis of ammonia from natural gas *(Fig. 2: natural gas 10 is converted to ammonia 31)*,

Topsoe, Inc. – EX1003
Page 671 of 1210

comprising:

1.2) a 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 *(Natural gas 10 is mixed with steam and converted into synthesis gas through partial oxidation or autothermal reforming in a O2-fired reactor 11 (Par. [0048]))*;

1.3) a treatment of said synthesis gas comprising at least a shift reaction of the carbon monoxide into CO2 *(the* synthesis *gas 14 is subject to a shift reaction in MTS reactor 15 (par. [0050]))* 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 *(from the shifted synthesis gas 16, a pure CO2 is separated in the CO2 separation unit 23, wherein a CO2-depleted synthesis gas 16' is obtained (Par. [0054]))*.

1.4) In addition, A2 also discloses feature 1.6), since the CO2-depleted synthesis gas 16' is intended as a process gas after further purification for the synthesis of ammonia *(the synthesis gas 16' is further cleaned in the PSA unit 17 and after the admixture of nitrogen 19 it is fed as stream 18 to the ammonia synthesis 30 for conversion into ammonia 31 (par [0051], [0053]))*.

Claim 1 thus differs from citation A2 by features 1.4) and 1.5).

This difference has the effect that the CO2 emission in the synthesis of ammonia from natural gas is greatly reduced.

This effect solves the objective technical problem of how ammonia can be synthesized from natural gas with greatly reduced CO2 emission.

A solution to the problem can be found in A3, which deals with the generation of a CO2-depleted synthesis gas from natural gas with reduced CO2 emission *(Abstract; Col. 3, lines 39-43; Fig. 2, 14)*.

The process disclosed in A3 includes:

1.2) a conversion of a charge of desulfurized natural gas and steam *(Col. 3, lines 39-43; Fig. 2, 14)* with oxygen-enriched air or with oxygen in a synthesis gas containing hydrogen, CO and C02, in a conversion section *(Fig. 2 shows next to the steam reformer 100 also a reactor 20 designated as "oxygen secondary reformer" (Col. 5, lines 57-59), which is supplied with an oxygen-rich gas 26 to form a reformate stream 22 comprising hydrogen and carbon monoxide (Col. 7, lines 4-17))*;

Topsoe, Inc. – EX1003
Page 672 of 1210

1.3) a treatment of the synthesis gas that includes at least one shift reaction of the carbon monoxide in CO2 (*the reformate stream 32 cooled in the heat exchanger 30 is treated in the shift reactor 40)* and a subsequent separation of CO2 from the gas whereby a CO2-depleted synthesis gas and a CO2-rich gas stream, containing the CO2 separated from the gas, is obtained *(the process stream 42 obtained in the shift reactor 40 is subjected to gas scrubbing in the gas scrubber 60, wherein stream 62 with a reduced content of CO2 and a detergent stream 66 loaded with CO2 are produced (col. 4, lines 13-22). The stream 62 is then decomposed in the separating device 70 into the hydrogen-containing product gas 72, which is largely carbon-free and depleted in C02 compared to the process stream 42, and a by-product 76 containing methane and CO),*

1.4) a 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 (*a portion of the hydrogen product 72 is used to form fuel 74 for the steam reformer 700 (col. 5, lines 27-33) and is therefore to be regarded as a fuel fraction*) and

1.5) 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 streams having the same composition (*the part of the hydrogen-containing product gas 72 used to form the fuel 74 is a "divided portion" (Col. 5,* lines *39-41), which has the same chemical composition as the hydrogen-containing product gas 72 (Col. 5, lines 12-14)).*

A solution for the objective technical problem can also be found in A4, which deals with the synthesis of ammonia from natural gas with reduced CO2 emissions (introduction). It can be seen from the examples in the Figures 1 and 4 that the reduction in CO2 emissions is achieved by using synthesis gas to fire the reformer used to generate synthesis gas.

A person skilled in the art who, before the priority date of the patent in suit, had attempted to solve the problem starting from A2 would have consulted A3 and A4 and recognized the advantages of these teachings. He would have transferred it to the method according to A2 without any practical difficulties and arrived without exercising an inventive step at the subject-matter of claim 1 which therefore lacks an inventive step (56 EPC).

2. Claim 2 (depending on claim 1)

Article 100 (a) EPC – Lack of novelty using A1

The citation A1 does not explicitly disclose the features of claim 2, according to which

2.1) the fuel fraction is between 1% and 40% of the total amount of CO2-depleted syngas,

Topsoe, Inc. – EX1003
Page 673 of 1210

2.2) preferably between 10% and 30%.

However, the phrase *"A complete separation of the entire CO2 could also be realized in the ATR-base plant... provided the fired heater would be fed with syngas instead of natural gas"* in the last paragraph of A1 implicitly discloses that between 1% and 99% of the syngas is separated as fuel fraction. Since the ranges specified in claim 2 are within the implicitly disclosed range and the patent in suit contains no information about the special effects associated with these ranges; they cannot be referred to as selection invention to be considered new.

The subject-matter of claim 2 is therefore not new compared to A1 (Article 54 EPC).

Article 100 (a) EPC – Lack of inventive step in view of A1 or A2 and A3

The Table 4 of A3 contains values for the amounts of CO2-depleted synthesis gas used as fuel in a process according to Fig. 2. These values are valid for a delivery rate of CO2-depleted synthesis gas or hydrogen product of 100,000 Nm/h. From this the shares of the fuel fraction in the total quantity of the CO2-depleted syngas are calculated as 19%, 24%, 29% and 32%, so A3 also shows the features of claim 2, which therefore lacks an inventive step in view of A1 or A2 in combination with A3.

3. <u>Claim 3 (dependent on one of claims 1 or 2)</u>

Article 100 (a) EPC – Lack of inventive step in view of A1 or A2 and A3 as well as knowledge of the skilled person

In addition to the admixture of nitrogen 19 downstream of the CO2 separation unit 23 or the PSA-unit 17, reference A2 discloses methanation of the CO2-depleted synthesis gases downstream of the CO2 separation unit 23 or the PSA unit 17 *(section [0027], [0056], [0059])*. A1 also shows a methanation step *(Fig. 2, option 2, methanation unit)* and a nitrogen addition step *(Fig. 2, option 2, liquid nitrogen wash)*. However, neither a combination of A2 and A3 nor the A1 shows that

3.1) the fuel fraction is separated upstream of the methanation step

3.2) or upstream of the nitrogen addition step.

Claim 3 thus differs from a combination of A2 and A3 by either feature 3.1) or 3.2).

Topsoe, Inc. – EX1003
Page 674 of 1210

These differences have the effect that a reduced amount of CO2-depleted syngas must be treated in the methanation step or in the nitrogen addition step.

This solves the problem of reducing the effort for methanation or nitrogen addition.

A person skilled in the art concerned with this task would have recognized that regarding the CO2 emissions it makes no difference whether CO2 or CO are supplied to at least one furnace with the fuel fraction or with methane formed from these substances during methanation. For economic considerations, he would use the fuel fraction upstream of the methanation step branched off from the CO2-depleted synthesis gas, since then the apparatuses needed for the methanation step are made smaller and can be operated at lower cost.

A person skilled in the art knows that the more nitrogen includes a fuel fraction, the lower is the calorific value. Since the fuel fraction is a cost factor, he will try to reach the target reduction of CO2 emissions, with the smallest possible amount of fuel. Therefore, due to routine considerations, he would have avoided diluting the CO2-depleted syngas with nitrogen before the diversion of the fuel fraction and had branched off the fuel fraction upstream of the nitrogen addition.

The skilled person would therefore be arrived without exercising an inventive step at the subject of claim 3 which consequently lacks inventive step in view of A1 or A2 and A3 and knowledge of the skilled person (56 EPC).

4. **Claim 4 (dependent on one of claims 1 to 3)**

Article 100 (a) EPC – Lack of inventive step in view of A1 or A2 and A3 as well as knowledge of the skilled person

The feature of claim 4, according to which

4.1) the CO2-depleted synthesis gas (12) contains no more than 1000 vol.ppm CO2,

is not disclosed in A1, A2 or A3.

Claim 4 thus differs from citation A1 or a combination of A2 and A3 by feature 4.1).

Topsoe, Inc. – EX1003
Page 675 of 1210

When burning a fuel fraction obtained according to claim 4, a release of only very small amounts of CO2 into the atmosphere is achieved, so that the effect of the difference can be seen in that the CO2 emission is minimized.

This effect solves the objective technical task of minimizing CO2 emissions.

The skilled person dealing with this task would have been aware that the CO2 emission decreases with the carbon content of the fuel fraction. He would therefore have tried to remove carbon as completely as possible from the hydrogen-rich shifted synthesis gas by using methods known to him. Such a method is known from the document A5.

Document A5 deals, among others, with the separation of CO2 from hydrogen-rich gases. On page 327 it is stated that it is possible to reduce the CO2 concentration of such gas to less than 50 ppm with methanol scrubbing known to a skilled worker since many decades.

To solve the problem, the skilled person had therefore used a methanol wash and had arrived without exercising an inventive step at the subject-matter of claim 4, which consequently lacks inventive activity in view of A1 or A2 and A3 as well as knowledge of the skilled person (56 EPC).

5. Claim 5 (dependent on one of claims 1 to 4)

Article 100 (a) EPC – Lack of inventive step in view of A1 or A2 and A3 as well as knowledge of the skilled person

Claim 5 requires that

5.1) the enriched air contains at least 50% oxygen,

5.2) preferably at least 90% oxygen.

In the table on page 19 of A1 values for the nitrogen content of the oxidizing agent used for synthesis gas production are given. In case A (enriched air) these are 42% and in case B (pure oxygen) 5%. It follows that the enriched air used as an oxidizing agent contains 58% or 95% oxygen.

Topsoe, Inc. – EX1003
Page 676 of 1210

Values for the oxygen content of the oxidant introduced in the secondary reformer can also be obtained from A3 *(col. 7, lines 38-43)*, which are between 98% and 100%.

Claim 5 is therefore either not new, if dependent on claim 1 (Article 54 EPC), or not inventive (56 EPC).

6. Claim 6 (dependent on one of claims 1 to 5)

Article 100 (a) EPC – Lack of inventive step in view of A1 or A2 and A3 as well as knowledge of the skilled person

Claim 6 states that

6.1) the 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 *(A3, Abstract, Fig. 1, 2 and 3)*; one or more furnaces for pre-heating the charge of an autothermal reformer *(A1, last paragraph)* or partial oxidation reactor or natural-gas desulphurization section.

The heating of steam generating furnaces, superheating furnaces, furnaces for preheating the charge of a partial oxidation reactor or a natural gas desulfurization section with a gaseous fuel has been state of the art for many decades and is known to the person skilled in the art, which is why he would also use the fuel fraction of the synthesis gas for heating such furnaces without exercising an inventive step, especially because he recognizes that this measure can also reduce the CO2 emissions of the process.

The claim 6 is therefore either not new (Article 54 EPC) or not inventive (Article 56 EPC).

7. Claim 7 (dependent on one of claims 1 to 6)

Article 100 (a) EPC – Lack of inventive step in view of A2 and A3 as well as knowledge of the skilled person

Claim 7 states that

Topsoe, Inc. – EX1003
Page 677 of 1210

7.1) a purge gas of the ammonia synthesis process, containing hydrogen and methane, is treated so as to recover the hydrogen contained in it, 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.

In paragraphs [0056]-[0058] of A2 it is stated that a flushing gas 27 containing methane must be discharged from the ammonia synthesis circuit in order to control inert substances. The flushing gas 27 is broken down in the PSA 17, hydrogen and nitrogen being produced for recycling into the ammonia synthesis gas 18, as well as a methane-containing fuel 22 (Par. [0052]).

A3 describes the separation of a methane-containing by-product 76 from the CO2 depleted stream 62. At least a part 78 of the by-product 76 is recycled in the natural gas feed 10 and subjected to conversion to synthesis gas (col. 4, lines 36-39, col. 4, line 56-col. 5, line 6). The document A3 further describes (col. 5, lines 27-33) that optionally a part 77 of the methane-containing by-product 76 can be used to fire the reformer 100.

The skilled person would therefore recognize that a gas containing methane could either be burned or used for synthesis gas production. He would implement this teaching and arrive without exercise of an inventive step at the subject-matter of claim 7, which consequently lacks inventive step considering A2 and A3 as well as the knowledge of the skilled person (Article 56 EPC).

8. Claim 8 (dependent on one of claims 1 to 7)

Article 100 (a) EPC – Lack of inventive step in view of A1 or A2 and A3 as well as knowledge of the skilled person

The feature of claim 8, according to which

8.1) a part of the 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, preferably all of it, is used as fuel; any remaining part of said first stream is fed to the synthesis of ammonia together with the second stream,

is not disclosed in A1, A2 or A3.

Claim 8 thus differs from citation A1 or a combination of A2 and A3 by feature 8.1).

Topsoe, Inc. – EX1003
Page 678 of 1210

As an effect of this difference, the patent in suit states (Par. [0069]-[0070]) that the calorific value of the fuel fraction increases, the volume flow of combustion gases is reduced and nitrogen for the ammonia synthesis is obtained. It solves the tasks to achieve these effects.

A person skilled in the art knows that a fuel fraction has a lower calorific value the more nitrogen it contains. Since the fuel fraction is a cost factor, he would have tried to achieve the desired reduction in CO2 emissions with as little fuel as possible. As a result of routine considerations, he would have separated nitrogen from the portion of the CO2-depleted syngas intended for fuel fraction production to obtain nitrogen-depleted syngas as the fuel fraction. Since ammonia synthesis gas contains hydrogen and nitrogen, without exercising an inventive step it would have a non-fuel portion of the fuel fraction consisting largely of hydrogen supplied together with the separated nitrogen of the ammonia synthesis.

The skilled person would therefore be arrived without exercising an inventive step at the subject matter of claim 8, which consequently lacks inventive step in view of A1 or A2 and A3 and knowledge of the skilled person.

9. <u>Claim 9 (dependent on one of claims 1 to 8)</u>

Article 100 (a) EPC – Lack of inventive step in view of A1 or A2 and A3 as well as knowledge of the skilled person

The feature of claim 9, according to which the process includes

9.1) a step of expansion, with production of mechanical work, of the CO2-depleted syngas (12), optionally after heating it,

is not disclosed in A1, A2 or A3.

Claim 9 thus differs from citation A1 or a combination of A2 and A3 by feature 9.1).

This difference has the effect that the pressure difference between the CO2 depleted synthesis gas and place of combustion of its fuel fraction is used to increase the efficiency of the process.

This solves the problem of using the pressure of the fuel fraction to improve process efficiency.

Topsoe, Inc. – EX1003
Page 679 of 1210

Using the pressure of a gas, especially a hydrogen-rich gas, to expand the gas while performing mechanical work, for example in a turbine, belongs to knowledge of the skilled person. Also part of this knowledge is that the work can be increased if the gas is warmed up prior to expansion.

The skilled person would therefore be arrived without exercising an inventive step at the subject matter of claim 9, which consequently lacks inventive step in view of A1 or A2 and A3 and knowledge of the skilled person.

10.Claim 10 (dependent on one of claims 1 to 9)

Article 100 (a) EPC – Lack of inventive step in view of A2, A3 and A1 as well as knowledge of the skilled person

The feature of claim 10, according to which

10.1) the overall steam/carbon ratio in the conversion step is greater than 2.0, preferably greater than 2.4 and more preferably greater than 2.7,

has according to the patent in suit, the effect that the conversion of methane and CO to CO2 during the shift is increased.

This difference solves the problem of how methane and CO can be converted more effectively in the shift.

A skilled person knows that methane and CO can be converted more effectively by shift, if more steam is fed to the shift reactor. Therefore, he will perform the shift with a steam portion as high as possible. To this end, he can feed steam to the shift reactor independently or together with the synthesis gas. From A2 (paragraph [0005]), he knows that synthesis gas with an overall steam/carbon ratio between 2.7 and 3.0 can be generated through primary and secondary reforming.

A1 (p. 18) also shows the feature of claim 10. A1 states that the ATR can be operated with a steam/carbon ratio of 3.0 when oxygen-enriched air is used as oxidant, and with 2.0, when operating with pure oxygen.

Topsoe, Inc. – EX1003
Page 680 of 1210

The person skilled in the art, through a simple combination of the teachings from A2 and A3 and possibly A1 as well as knowledge of the field, would arrive at the feature of claim 10, which is therefore not inventive (56 EPC).

11. Claim 11 (dependent on one of claims 1 to 10)

Article 100 (a) EPC – Lack of inventive step in view of A1 or A2 and A3 as well as knowledge of the skilled person

Claim 11 requires that

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

11.2) an amount of natural gas is provided as additional fuel *(trim fuel)*, wherein said additional fuel accounts for not more than 15% of the total combustion heat.

Neither A3 nor A1 explicitly discloses the features of claim 11. However, in A3 (col.5, lines 27-45) it is disclosed that fuel gas 74 is only optionally replaced by part of the by-product 77 or by the "trim fuel" 18. The reformer 100 is the only fuel gas consumer, so that implicitly also feature 11.1) is disclosed by A3.

In the last paragraph of A1 it is stated:

> *"A complete separation of the entire CO2 could also be realized in the AIR-based plant ... provided the fired heater would be fed with syngas instead of natural gas."*

Since otherwise complete CO2 separation would not be achievable, the "fired heater" is the only fuel consumer in the conversion step, so that synthesis gas fuel fraction forms the total fuel of the furnaces used in the conversion section and A1 also implicitly discloses feature 11.1).

According to the patent in suit, feature 11.2) has the effect that the performance of the fuel fraction heated consumer can be controlled quickly.

This solves the problem of how to adapt, that is to trim, the fuel supply to consumers with quickly fluctuating operating conditions.

Topsoe, Inc. – EX1003
Page 681 of 1210

To solve this problem, the person skilled in the art would have searched a combustible gas that was available quickly and easily and would have used natural gas as trim gas either solely on the basis of his expertise or through the suggestion of A3 (col. 5, lines 27-42). Since, on the one hand, natural gas is cheaper than fuel fraction obtained from the CO2-depleted synthesis gas and on the other hand also the CO2 emissions can cause costs (CO2 tax), the skilled person for economic reasons would have used as little natural gas as possible as an additional fuel and would have arrived to the feature 11.2) without inventive step.

The skilled person would have arrived through a mere combination of the teachings from A2 and A3 and possibly A1 as well as knowledge in the art to the features of claim 11, which is therefore not based on inventive step (Article 56 EPC).

12. Claim 12 (dependent on one of claims 1 to 11)

Article 100 (a) EPC – Lack of inventive step in view of A1 or A2 and A3 as well as knowledge of the skilled person

Claim 12 requires that

12.1) 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.

Feature 12.1 solves the same problem as feature 11.2) (patent in suit, par. [0084]), namely to quickly adjust, which means to trim, the fuel supply to consumers to fluctuating operating conditions.

The production of a product in excess, in order to always be able to cover the temporally fluctuating needs of a consumer, with the amount of product not consumed by the consumer being supplied to an alternative utilization or discarded, is conventional and known to the person skilled in the art. He therefore had solved the task according to feature 12.1) without being inventive.

The person skilled in the art would have arrived, simply by combining the teachings from A2 and A3 and possibly A1, as well as knowledge of the field, at the features of claim 12, which is therefore not based on an inventive step (Article 56 EPC).

13. Claim 13 (dependent on one of claims 1 to 12)

Topsoe, Inc. – EX1003
Page 682 of 1210

Article 100 (a) EPC – Lack of inventive step in view of A1 or A2 and A3 as well as knowledge of the skilled person

Claim 13 requires that

13.1) the conversion of the natural gas charge into synthesis gas comprises a step of autothermal reforming, optionally with pre-reforming, or a step of partial oxidation; wherein said step of autothermal reforming or partial oxidation is performed with a steam/carbon ratio not greater than 2 *(A2, Par. [0018] and [0023]*.

Claim 13 is therefore not based on an inventive step in view of A2 and A3 and possibly also technical knowledge of the field (Article 56 EPC).

14. Claim 14 (dependent on one of claims 1 to 13)

Article 100 (a) EPC – Lack of inventive step in view of A1 or A2 and A3 as well as knowledge of the skilled person

Claim 14 provides that

14.1) the conversion of the natural gas into synthesis gas comprises: primary reforming of the natural gas in the presence of steam and secondary reforming performed with said oxygen flow or enriched air (A3, Abstract, Fig. 2).

Claim 14 is therefore not based on an inventive step in view of A2 and A3 and possibly also in view of the knowledge of the field (Article 56 EPC).

15. Conclusion

Overall, the subject matter of the patent in suit is not patentable, since all claims 1 to 14 lack either the novelty or inventive step necessary for the grant of the patent. The request for revocation of the patent is therefore justified. If the opposition division does not agree with the above statements, an alternative request is made for oral proceedings to be scheduled.

Linde GmbH

Topsoe, Inc. – EX1003
Page 683 of 1210

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Die nachstehend aufgeführten Unterlagen werden zu folgender Anmeldung nachgereicht:

Anmeldenummer und/oder EP-Veröffentlichungsnummer	EP18702977.2 - EP3583067
Zeichen des Anmelders oder Vertreters	E21C004

	Beschreibung der Unterlage	Ursprünglicher Dateiname	Vergebener Dateiname
1	Anderes Dokument	Einspruch.pdf	OTHER-1.pdf
2	Sonstige Beweismittel	A1.pdf	Other-evidence-1.pdf
3	Sonstige Beweismittel	A2.pdf	Other-evidence-2.pdf
4	Sonstige Beweismittel	A3.pdf	Other-evidence-3.pdf
5	Sonstige Beweismittel	A5.pdf	Other-evidence-4.pdf
6	Sonstige Beweismittel	A4.pdf	Other-evidence-5.pdf

	Gebühren	Angewandter Faktor	Gebühren-verzeichnis	Zu zahlender Betrag
15-1	010 Einspruchsgebühr	1	840.00	840.00
	Insgesamt:		**EUR**	**840.00**

	Zahlung	
1	Zahlungsart:	Abbuchung vom laufenden Konto
	Währung:	EUR
	Hiermit wird das Europäische Patentamt ermächtigt, die auf der Seite "Gebühren" angegebenen Gebühren und Auslagen vom nachstehenden laufenden Konto beim EPA abzubuchen.	
	Nummer des laufenden Kontos:	28000028
	Kontoinhaber:	Linde GmbH
2	Rückerstattung/Rückzahlung	
	Etwaige Rückzahlungen auf laufendes Konto beim EPA:	28000028
	Kontoinhaber:	Linde GmbH

Topsoe, Inc. – EX1003
Page 684 of 1210

Unterschriften

Ort:	
Datum:	08.Juni 2022
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in Eigenschaft als:	Representative
Funktion des bzw. der Unterzeichneten:	Patent Counsel

Topsoe, Inc. – EX1003
Page 685 of 1210

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	E21C004	Dr. Werner Fischer	+49.89.7446-2950	+49.89.7446-2992	08.06.2022

Europäisches Patent EP 3 583 067 B1 (Anmeldenr.: 18702977.2)
Titel: VERFAHREN ZUR SYNTHESE VON AMMONIAK MIT GERINGEN EMISSIONEN VON CO2 IN DIE ATMOSPHÄRE
Patentinhaber: Casale S.A., Schweiz
Bekanntmachung des Hinweises auf die Patenterteilung: 08.09.2021

Namens der Linde AG, Klosterhofstr. 1, 80331 München, Deutschland, wird gegen das oben genannte Patent in vollem Umfang

E I N S P R U C H

eingelegt.

Es wird beantragt, das europäische Patent in vollem Umfang zu widerrufen.

Die Einspruchsgebühr in Höhe von Euro 840,-- soll vom laufenden Konto Nr. 2800 0028 der Einsprechenden beim Europäischen Patentamt abgebucht werden. Der Abbuchungsauftrag ist als Anlage beigefügt.

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Sitz der Gesellschaft: Pullach, Registergericht: München, HRB 256407
Aufsichtsrat: Christoph Hammerl (Vorsitzender)
Geschäftsführung: Sean Durbin, Jürgen Nowicki, Matthias von Plotho

Verwendete Schriften:

Der Einspruch stützt sich auf die folgenden, vor dem Anmeldetag des Streitpatents veröffentlichten Entgegenhaltungen (Artikel 54 (2) EPÜ):

A1: Dr Klaus Noelker and Dr Joachim Johanning, *Autothermal reforming: a flexible syngas route with future potential*, 2010, veröffentlicht als Preprint eines Vortrags

A2: US 8,137,422 B2

A3: EP 2 817 260 B1

A4: Ryota Shimura, *Urea Product Expansion by Newly Developed CO2 Recovery Process from Primary Reformer Flue Gas*, AIChE TECHNICAL MANULA 2006, Vol. 47, S. 237-246

A5: P. Heussinger, *Hyrogen, 3. Purification*, Ullmann's Encyclopedia of Industrial Chemistry, 2011

Einspruchsgründe:

1. Anspruch 1 (unabhängig):

Artikel 100 (a) EPÜ – Mangelnde Neuheit unter Verwendung von A1

Die Entgegenhaltung A1 offenbart ein

1.1) Verfahren zur Synthese von Ammoniak aus Erdgas *(S. 6 ff: AMMONIA PLANTS BASED ON AUTOTHERMAL REFORMING; Figure 2, Options 2 und 3)*,

umfassend:

1.2) eine Umwandlung einer Charge von entschwefeltem Erdgas und Dampf *(Table 3; Page 12: Description of Uhde's ATR test facility)* mit sauerstoffangereicherter Luft oder mit Sauerstoff in ein Synthesegas, das Wasserstoff, CO und CO2 enthält, in einem Umwandlungsabschnitt *(Figure 2, Options 2 und 3)*;

1.3) eine Behandlung des Synthesegases die mindestens eine Shift-Reaktion des Kohlenmonoxids in CO2 *(Figure 2, Options 2 und 3 weisen jeweils eine CO conversion auf)* und eine anschließende Abtrennung von CO2 aus dem Gas *(Figure 2, Options 2 und 3: CO_2 removal)* umfasst, wodurch ein CO2-abgereichertes Synthesegas und ein CO2-reicher Gasstrom, der das aus dem Gas abgetrennte CO2 enthält, erhalten wird; optional einen Schritt zur Methanisierung *(Figure 2, Option 2)* des Synthesegases und/oder Zugabe von Stickstoff zu dem Synthesegas *(Figure 2, Option 3)*,

gekennzeichnet durch:

1.4) eine Abtrennung eines Teils des CO2-abgereicherten Synthesegases als Brennstofffraktion, wobei die Brennstofffraktion als Brennstoff mindestens einem Ofen zugeführt wird und

1.5) wobei die Abtrennung der Brennstofffraktion die Aufspaltung des CO2-abgereicherten Synthesegases in mindestens einen ersten Strom und einen zweiten Strom umfasst, wobei die Ströme die gleiche Zusammensetzung aufweisen,

1.6) wobei der erste Strom die Brennstofffraktion bildet und der zweite Strom Prozessgas ist, das für die Synthese von Ammoniak, optional nach weiterer Reinigung, vorgesehen ist.

Im letzten Absatz der A1 wird ausgeführt:
"A complete separation of the entire CO2 could also be realized in the ATR-based plant ... provided the fired heater would be fed with syngas instead of natural gas."

Die A1 schlägt somit vor, in einem Ofen im Sinne des angegriffenen Patents (Abs. [0014]) satt Erdgas Synthesegas als Brennstoff einzusetzen. Da diese Maßnahme zu einer vollständigen CO2-Abtrennung, d.h. einer Ammoniakerzeugung aus Erdgas ohne CO2-Freisetzung in die Atmosphäre dienen soll, kann es sich bei dem Synthesegas nur um CO2-abgereichertes Synthesegas handeln. Die A1 zeigt daher auch das Merkmal 1.4) des Anspruchs 1.

Weil ohne Synthesegas eine Ammoniaksynthese unmöglich wäre, ist für den Fachmann klar, dass nicht das gesamte, sondern nur ein erster Teil des CO2-abgereicherten Synthesegases als Brennstoff eingesetzt werden kann, während ein zweiter Teil für die Synthese von Ammoniak vorgesehen ist. Die A1 offenbart somit implizit auch die Merkmale 1.5) und 1.6) des Anspruchs 1.

Das Dokument A1 offenbart daher sämtliche Merkmale des Anspruchs 1, dessen Gegenstand folglich nicht neu ist (Artikel 54 EPÜ).

Artikel 100 (a) EPÜ – Mangelnde erfinderische Tätigkeit unter Verwendung von A2 und A3 bzw. A4

Auch wenn der Anspruch 1 überaschenderweise für neu befunden werden sollte, ist er dennoch nicht rechtsbeständig, da er nicht auf einer erfinderischen Tätigkeit beruht.

Die Entgegenhaltung A2 offenbart ein

1.1) Verfahren zur Synthese von Ammoniak aus Erdgas *(Fig. 2: Erdgas 10 wird zu Ammoniak 31 umgesetzt),*

umfassend:

1.2) eine Umwandlung einer Charge von entschwefeltem Erdgas und mit sauerstoffangereicherter Luft oder mit Sauerstoff in ein Synthesegas, das Wasserstoff, CO und CO2 enthält, in einem Umwandlungsabschnitt *(Erdgas 10 wird mit Dampf gemischt und in einem O2-befeuerten Reaktor 11 durch Partielle Oxidation oder Autothermalreformierung zu einem Synthesegas umgesetzt (Abs. [0048]));*

1.3) eine Behandlung des Synthesegases die mindestens eine Shift-Reaktion des Kohlenmonoxids in CO2 *(das Synthesegas 14 wird im MTS-Reaktor 15 einer Shiftreaktion unterzogen (Abs. [0050]))* und eine anschließende Abtrennung von CO2 aus dem *Gas umfasst, wodurch ein* CO2-abgereichertes Synthesegas und ein CO2-reicher Gasstrom, der das aus dem Gas abgetrennte CO2 enthält, erhalten wird *(von dem geshifteten Synthesegas 16 wird in der CO2-Abtrenneinheit 23 reines CO2 abgetrennt, wobei ein CO2-abgereichertes Synthesegas 16' erhalten wird (Abs. [0054])).*

Darüber hinaus offenbart die A2 auch das Merkmal 1.6), da das CO2-abgereicherte Synthesegas 16' als Prozessgas nach weiterer Reinigung für die Synthese von Ammoniak vorgesehen ist *(das Synthesegas 16' wird in der PSA-Einheit 17 weiter gereinigt und nach Zumischung von Stickstoff 19 als Strom 18 der Ammoniaksynthese 30 zur Umsetzung in Ammoniak 31 zugeführt (Abs. [0051], [0053])).*

Der Anspruch 1 unterscheidet sich somit von der Entgegenhaltung A2 durch die Merkmale 1.4) und 1.5).

Dieser Unterschied hat den Effekt, dass die CO2-Emission bei der Synthese von Ammoniak aus Erdgas stark reduziert ist.

Dieser Effekt löst die objektive technische Aufgabe, wie Ammoniak aus Erdgas mit stark verringerter CO2-Emission synthetisiert werden kann.

Eine Lösung für die gestellte Aufgabe kann der A3 entnommen werden, die sich mit der Erzeugung eines CO2-abgereicherten Synthesegases aus Erdgas mit verringerter CO2-Emission befasst *(Abstract; Sp. 3, Z. 39-43; Fig. 2, 14)*.

Das in der A3 offenbarte Verfahren umfasst:

1.2) eine Umwandlung einer Charge von entschwefeltem Erdgas und Dampf *(Sp. 3, Z. 39-43; Fig. 2, 14)* mit sauerstoffangereicherter Luft oder mit Sauerstoff in ein Synthesegas, das Wasserstoff, CO und CO2 enthält, in einem Umwandlungsabschnitt *(Fig. 2 zeigt neben dem Dampfreformer 100 auch einen als „oxygen secondary reformer" bezeichneten Reaktor 20 (Sp. 5, Z. 57-59), dem ein sauerstoffreiches Gas 26 zugeführt wird, um einen Wasserstoff und Kohlenmonoxid umfassenden Reformatstrom 22 zu erhalten (Sp. 7, Z. 4-17))*;

1.3) eine Behandlung des Synthesegases die mindestens eine Shift-Reaktion des Kohlenmonoxids in CO2 *(der im Wärmetauscher 30 abgekühlte Reformatstrom 32 wird im Shift-Reaktor 40 behandelt)* und eine anschließende Abtrennung von CO2 aus dem Gas umfasst, wodurch ein CO2-abgereichertes Synthesegas und ein CO2-reicher Gasstrom, der das aus dem Gas abgetrennte CO2 enthält, erhalten wird *(der im Shift-Reaktor 40 erhaltene*

Prozessstrom 42 wird im Gas Scrubber 60 einer Gaswäsche unterzogen, wobei ein im CO2-Gehalt reduzierter Strom 62 und ein mit CO2 beladener Waschmittelstrom 66 entstehen (Sp. 4, Z. 13-22). Der Strom 62 wird anschließend in der Trenneinrichtung 70 in das wasserstoffhaltige Produktgas 72, das weitgehend kohlenstofffrei und im Vergleich zum Prozessstrom 42 an CO2 abgereichert ist, sowie ein Methan und CO enthaltendes Nebenprodukt 76 zerlegt),

1.4) eine Abtrennung eines Teils des CO2-abgereicherten Synthesegases als Brennstofffraktion, wobei die Brennstofffraktion als Brennstoff mindestens einem Ofen zugeführt wird *(ein Teil des Wasserstoffprodukts 72 wird zur Bildung von Brennstoff 74 für den Dampfreformer 100 eingesetzt (Sp. 5, Z. 27-33) und ist daher als Brennstofffraktion anzusprechen)* und

1.5) wobei die Abtrennung der Brennstofffraktion die Aufspaltung des CO2-abgereicherten Synthesegases in mindestens einen ersten Strom und einen zweiten Strom umfasst, wobei die Ströme die gleiche Zusammensetzung aufweisen *(bei dem zur Bildung des Brennstoffs 74 eingesetzten Teil des wasserstoffhaltigen Produktgases 72 handelt es sich um eine „divided portion" (Sp. 5, Z. 39-41), die die gleich chemische Zusammensetzung aufweist, wie das wasserstoffhaltige Produktgas 72 (Sp. 5, Z. 12-14))*

Eine Lösung für die objektiv gestellte technische Aufgabe kann auch der A4 entnommen werden, die sich mit der Synthese von Ammoniak aus Erdgas mit reduzierter CO2-Emission befasst (Einleitung). Den Beispielen der Figuren 1 und 4 ist zu entnehmen, dass die Reduzierung der CO2-Emission durch die Verwendung von Synthesegas zur Befeuerung des zur Synthesegaserzeugung eingesetzten Reformers erreicht wird.

Ein Fachmann, der vor dem Prioritätstag des Streitpatents versucht hätte, die gestellte Aufgabe ausgehend von A2 zu lösen, würde A3 und A4 konsultiert und die Vorteile dieser Lehren erkannt

haben. Er hätte sie ohne praktische Schwierigkeiten auf das Verfahren gemäß A2 übertragen und wäre ohne Ausübung einer erfinderischen Tätigkeit zum Gegenstand des Anspruchs 1 gelangt, dem es daher an erfinderischer Tätigkeit mangelt (56 EPÜ).

2. Anspruch 2 (abhängig von Anspruch 1):

Artikel 100 (a) EPÜ – Mangelnde Neuheit unter Verwendung von A1

Die Entgegenhaltung A1 offenbart nicht explizit die Merkmale des Anspruchs 2, wonach die

2.1) die Brennstofffraktion zwischen 1% und 40% der Gesamtmenge des CO2-abgereicherten Syngases,

2.2) vorzugsweise zwischen 10% und 30%, umfasst.

Die Formulierung *"A complete separation of the entire CO2 could also be realized in the ATR-based plant ... provided the fired heater would be fed with syngas instead of natural gas."* im letzten Absatz der A1 offenbart aber implizit, dass zwischen 1% und 99% des Syngases als Brennstofffraktion abgetrennt werden. Da die in Anspruch 2 angegebenen Bereiche innerhalb des implizit offenbarten Bereichs liegen und das Streitpatent keine Angaben darüber enthält, das besondere Effekte mit diesen Bereichen verbunden sind, können sie auch nicht im Sinne einer Auswahlerfindung als neu angesehen werden.

Der Gegenstand des Anspruchs 2 ist folglich nicht neu gegenüber A1(Artikel 54 EPÜ).

Artikel 100 (a) EPÜ – Mangelnde erfinderische Tätigkeit unter Verwendung von A1 bzw. A2 und A3

Die Tabelle 4 der A3 enthält Werte für die in einem Verfahren gemäß Fig. 2 als Brennstoff eingesetzten Mengen an CO2-abgereichertem Synthesegas. Diese Werte gelten jeweils für eine Abgabemenge von CO2-abgereichertem Synthesegas bzw. Wasserstoffprodukt von 100.000Nm/h. Hieraus errechnen sich die Anteile der Brennstofffraktion an der Gesamtmenge des CO2-abgereicherte Synthesegases zu 19%, 24%, 29% und 32%, so dass die A3 auch die Merkmale des Anspruchs 2 zeigt, dem es daher in Anbetracht von A1 bzw. A2 und A3 an erfinderischer Tätigkeit mangelt (56 EPÜ).

3. Anspruch 3 (abhängig von einem der Ansprüche 1 oder 2)

Artikel 100 (a) EPÜ – Mangelnde erfinderische Tätigkeit unter Verwendung von A1 bzw. A2 und A3 sowie fachmännischem Können

Neben der Zumischung von Stickstoff 19 stromabwärts der CO2-Abtrenneinheit 23 bzw. der PSA-Einheit 17, offenbart die Entgegenhaltung A2 eine Methanisierung des CO2-abgereicherten Synthesegase stromabwärts der CO2-Abtrenneinheit 23 bzw. der PSA-Einheit 17 *(Abs. [0027], [0056], [0059])*. Auch die A1 zeigt einen Methanisierungsschritt *(Fig. 2, Option 2, methanation unit)* sowie einen Nitrogen-Additionsschritt *(Fig. 2, Option 2, liq. nitrogen wash)*. Allerdings zeigt weder eine Kombination von A2 und A3 noch die A1, dass

3.1) die Brennstofffraktion stromaufwärts des Methanisierungsschritts

3.2) oder stromaufwärts des Nitrogen-Additionsschritts abgetrennt wird.

Der Anspruch 3 unterscheidet sich somit von einer Kombination aus A2 und A3 entweder durch das Merkmal 3.1) oder 3.2).

Diese Unterschiede haben den Effekt, dass im Methanisierungsschritt oder im Nitrogen-Additionsschritt eine verringerte Menge an CO2-abgereichertem Synthesegas behandelt werden muss.

Dies löst die Aufgabe, den Aufwand für die Methanisierung oder die Nitrogen-Addition zu reduzieren.

Ein mit dieser Aufgabe befasster Fachmann würde erkannt haben, dass es bezüglich der CO2-Emissionen keinen Unterschied macht, ob dem mindestens einen Ofen mit der Brennstofffraktion CO2 bzw. CO oder aus diesen Stoffen bei der Methanisierung gebildetes Methan zugeführt wird. Aus wirtschaftlichen Überlegungen würde er daher die Brennstofffraktion stromaufwärts des Methanisierungsschritts von dem CO2-abgereicherten Synthesegas abgezweigt haben, da dann die für den Methanisierungsschritt benötigten Apparate zu geringeren Kosten kleiner ausgeführt und betrieben werden können.

Der Fachmann weiß, dass eine Brennstofffraktion einen umso geringeren Heizwert besitzt, je mehr Stickstoff sie umfasst. Da die Brennstofffraktion einen Kostenfaktor darstellt, wird er versuchen, die angestrebte Reduzierung der CO2-Emission, mit einer möglichst geringen Brennstoffmenge zu erreichen. Aufgrund von Routineüberlegungen hätte er es daher vermieden, das CO2-abgereicherete Synthesegas vor der Abzweigung der Brennstofffraktion mit Stickstoff zu verdünnen und hätte die Brennstofffraktion stromaufwärts der Nitrogen-Addition abgezweigt.

Der Fachmann wäre daher ohne Ausübung einer erfinderischen Tätigkeit zum Gegenstand des Anspruchs 3 gelangt, dem es folglich in Anbetracht von A1 bzw. A2 und A3 sowie fachmännischem Können an erfinderischer Tätigkeit mangelt (56 EPÜ).

4. Anspruch 4 (abhängig von einem der Ansprüche 1 bis 3)

Artikel 100 (a) EPÜ – Mangelnde erfinderische Tätigkeit unter Verwendung von A1 bzw. A2 und A3 sowie fachmännischem Können

Das Merkmal des Anspruchs 4, wonach

4.1) das CO2-abgereicherte Synthesegas (12) nicht mehr als 1000 Vol.ppm CO2 enthält,

ist weder in A1, A2 oder A3 offenbart.

Der Anspruch 4 unterscheidet sich somit von der Entgegenhaltung A1 bzw. einer Kombination von A2 und A3 durch das Merkmal 4.1).

Bei der Verbrennung einer gemäß Anspruch 4 erhaltenen Brennstofffraktion gelangen nur sehr geringe CO2-Mengen in die Atmosphäre, so dass der Effekt des Unterschieds darin gesehen werden kann, dass die CO2-Emission minimiert wird.

Dieser Effekt löst die objektive technische Aufgabe, die CO2-Emission zu minimieren.

Dem mit dieser Aufgabe befassten Fachmann wäre bewusst gewesen, dass die CO2-Emiossion mit dem Kohlenstoffgehalt der Brennstofffraktion abnimmt. Er hätte daher versucht, den Kohlenstoff aus dem wasserstoffreichen geshifteten Synthesegas durch den Einsatz ihm bekannter Verfahren möglichst vollständig abzutrennen. Ein solches Verfahren aus dem Dokument A5 bekannt.

Das Dokument A5 befasst sich u.a. mit der Abtrennung von CO2 aus wasserstoffreichen Gasen. Auf Seit 327 wird angegeben, dass es möglich ist, mit der dem Fachmann seit vielen Jahrzehnten vertrauten Methanol-Wäsche die CO2-Konzentration eines derartigen Gases auf weniger als 50 ppm zu verringern.

Zur Lösung der gestellten Aufgabe hätte der Fachmann daher eine Methanol-Wäsche eingesetzt und wäre ohne Ausübung einer erfinderischen Tätigkeit zum Gegenstand des Anspruchs 4 gelangt, dem es folglich in Anbetracht von A1 bzw. A2 und A3 sowie fachmännischem Können an erfinderischer Tätigkeit mangelt (56 EPÜ).

5. Anspruch 5 (abhängig von einem der Ansprüche 1 bis 4)

Artikel 100 (a) EPÜ – Mangelnde erfinderische Tätigkeit unter Verwendung von A1 bzw. A2 und A3 sowie fachmännischem Können

Der Anspruch 5 fordert, dass

5.1) die angereicherte Luft mindestens 50% Sauerstoff,

5.2) vorzugsweise mindestens 90% Sauerstoff, enthält.

In der Tabelle auf Seite 19 der A1 werden Werte für den Stickstoffgehalt des bei der Synthesegaserzeugung eingesetzt Oxidationsmittels angegeben. Im Falle A (enriched air) sind dies 42% und im Fall B (pure oxygen) 5%. Daraus folgt, dass die als Oxidationsmittel eingesetzte angereicherte Luft 58% bzw. 95% Sauerstoff enthält.

Auch aus der A3 können Werte für den Sauerstoffgehalt des im Sekundärreformer eingesetzten Oxydationsmittel entnommen werden *(Sp. 7, Z. 38-43)*, die zwischen 98% und 100% liegen.

Der Anspruch 5 ist daher entweder nicht neu, wenn rückbezogen auf Anspruch 1 (Artikel 54 EPÜ), oder nicht erfinderisch (56 EPÜ).

6. Anspruch 6 (abhängig von einem der Ansprüche 1 bis 5)

Artikel 100 (a) EPÜ – Mangelnde erfinderische Tätigkeit unter Verwendung von A1 bzw. A2 und A3 sowie fachmännischem Können

Der Anspruch 6 gibt an, dass

6.1) die Brennstofffraktion des Synthesegases eine oder mehrere der folgenden Vorrichtungen speist: einen Dampferzeugungs- und/oder Überhitzungsofen; einen oder mehrere Brenner eines Primärdampfreformers *(A3, Abstract, Fig. 1, 2 und 3)*; einen oder mehrere Öfen zum Vorheizen der Charge eines autothermischen Reformers *(A1, letzter Absatz)* oder eines Partialoxidationsreaktors oder eines Erdgasentschwefelungsabschnitts.

Die Beheizung von Dampferzeugungsöfen, Überhitzungsöfen, Öfen zum Vorheizen der Charge eines Partialoxidationsreaktors oder eines Erdgasentschwefelungsabschnitts mit einem gasförmigen Brennstoff ist seit vielen Jahrzehnten Stand der Technik und dem Fachmann bekannt, weshalb er ohne Ausübung einer erfinderischen Tätigkeit die Brennstofffraktion des Synthesegases auch zur Beheizung derartiger Öfen einsetzten würde, zumal er erkennt, dass auch durch diese Maßnahme die CO2-Emission des Verfahrens reduziert werden kann.

Der Anspruch 6 ist daher entweder nicht neu (Artikel 54 EPÜ) oder nicht erfinderisch (Artikel und 56 EPÜ).

7. Anspruch 7 (abhängig von einem der Ansprüche 1 bis 6)

Artikel 100 (a) EPÜ – Mangelnde erfinderische Tätigkeit unter Verwendung von A2 und A3 sowie fachmännischem Können

Der Anspruch 7 gibt an, dass

7.1) ein Spülgas des Ammoniaksyntheseverfahrens, das Wasserstoff und Methan enthält, so behandelt wird, dass der darin enthaltene Wasserstoff zurückgewonnen wird, wobei ein wasserstoffreiches Gas und ein Methan enthaltendes Endgas erhalten wird, wobei mindestens ein Teil des Endgases als Prozessgas wiederverwertet wird und dem Schritt der Umwandlung des Erdgases in Synthesegas unterzogen wird.

In den Absätzen [0056]-[0058] der A2 wird angegeben, dass zur Kontrolle von inerten Stoffen ein methanhaltiges Spülgas 27 aus dem Ammoniak-Synthesekreis ausgeschleust werden muss. Das Spülgas 27 wird in der PSA 17 zerlegt, wobei Wasserstoff und Stickstoff zur Rückführung in das Ammoniak-Synthesegas 18 sowie ein methanhaltiger Brennstoff 22 (Abs. [0052]) anfallen.

Die A3 beschreibt die Abtrennung eines methanhaltigen Nebenprodukts 76 aus dem CO2-abgereicherten Strom 62. Zumindest ein Teil 78 des Nebenprodukts 76 wird in den Erdgas-Einsatz 10 zurückgeführt und der Umwandlung in Synthesegas unterzogen (Sp. 4, Z. 36-39, Sp. 4, Z. 56 – Sp. 5, Z. 6). Die A3 beschreibt weiter (Sp. 5, Z. 27-33), dass optional ein Teil 77 des methanhaltigen Nebenprodukts 76 zur Befeuerung des Reformers 100 eingesetzt werden kann.

Der Fachmann hätte daher erkannt, dass ein methanhaltiges Gas entweder verbrannt oder als Einsatz für die Synthesegaserzeugung genutzt werden kann. Er hätte diese Lehre umgesetzt und wäre ohne Ausübung einer erfinderischen Tätigkeit zum Gegenstand des Anspruchs 7 gelangt, dem es folglich in Anbetracht von A2 und A3 sowie fachmännischem Können an erfinderischer Tätigkeit mangelt (Artikel 56 EPÜ).

8. Anspruch 8 (abhängig von einem der Ansprüche 1 bis 7)

Artikel 100 (a) EPÜ – Mangelnde erfinderische Tätigkeit unter Verwendung von A1 bzw. A2 und A3 sowie fachmännischem Können

Das Merkmal des Anspruchs 8, wonach

8.1) ein Teil des CO2-abgereicherten Syngases in einer Einheit zur Abtrennung von Stickstoff behandelt wird, wobei ein erster Strom von stickstoffabgereichertem Syngas und ein zweiter, mit Stickstoff angereicherter Strom erhalten wird; wobei mindestens ein Teil des ersten Stroms, vorzugsweise alles davon, als Brennstoff verwendet wird; wobei jeder verbleibende Teil des ersten Stroms zusammen mit dem zweiten Strom der Ammoniaksynthese zugeführt wird,

ist weder in A1, A2 oder A3 offenbart.

Der Anspruch 8 unterscheidet sich somit von der Entgegenhaltung A1 bzw. einer Kombination von A2 und A3 durch das Merkmal 8.1).

Als Effekte dieses Unterschieds gibt das Streitpatent an (Abs. [0069]-[0070]), dass der Heizwert der Brennstofffraktion erhöht, der Volumenstrom der Verbrennungsgase reduziert und Stickstoff für die Ammoniaksynthese gewonnen wird. Er löst die Aufgaben, diese Effekte zu erreichen.

Der Fachmann weiß, dass eine Brennstofffraktion einen umso geringeren Heizwert besitzt, je mehr Stickstoff sie umfasst. Da die Brennstofffraktion einen Kostenfaktor darstellt, hätte er versucht, die angestrebte Reduzierung der CO2-Emission, mit einer möglichst geringen Brennstoffmenge zu erreichen. Aufgrund von Routineüberlegungen hätte er Stickstoff von dem für die Erzeugung der Brennstofffraktion vorgesehenen Teil des CO2-abgereichereten Synthesegas abgetrennt, um stickstoffabgereichertes Synthesegas als Brennstofffraktion zu erhalten. Da Ammoniaksynthesegas Wasserstoff und Stickstoff enthält, hätte er ohne Ausübung einer erfinderischen Tätigkeit einen nicht als Brennstoff benötigten Teil der weitgehend aus Wasserstoff bestehenden Brennstofffraktion zusammen mit dem abgetrennten Stickstoff der Ammoniaksynthese zugeführt.

Der Fachmann wäre daher ohne Ausübung einer erfinderischen Tätigkeit zum Gegenstand des Anspruchs 8 gelangt, dem es folglich in Anbetracht von A1 bzw. A2 und A3 sowie fachmännischem Können an erfinderischer Tätigkeit mangelt (56 EPÜ).

9. <u>Anspruch 9 (abhängig von einem der Ansprüche 1 bis 8)</u>

Artikel 100 (a) EPÜ – Mangelnde erfinderische Tätigkeit unter Verwendung von A1 bzw. A2 und A3 sowie fachmännischem Können

Das Merkmal des Anspruchs 9, wonach das Verfahren

9.1) auch einen Schritt der Expansion unter Erzeugung mechanischer Arbeit des CO2-abgereicherten Syngases (12), optional nach dessen Erwärmung, umfasst,

ist weder in A1, A2 oder A3 offenbart.

Der Anspruch 9 unterscheidet sich somit von der Entgegenhaltung A1 bzw. einer Kombination von A2 und A3 durch das Merkmal 9.1).

Dieser Unterschied hat den Effekt, dass der Druckunterschied zwischen des CO2-abgrecherten Synthesegases und seinem Verbrennungsort der Brennstofffraktion zur Effizienzsteigerung des Verfahrens genutzt wird.

Dies löst die Aufgabe, den Druck der Brennstofffraktion zur Verbesserung der Verfahrenseffizienz zu nutzen.

Den Druck eines Gases, insbesondere eines wasserstoffreichen Gases, dadurch zu nutzen, dass das Gas unter Verrichtung mechanischer Arbeit beispielsweise in einer Turbine entspannt wird, gehört zum fachmännischen Wissen. Ebenso gehört zu diesem Wissen, dass die verrichtete Arbeit erhöht werden kann, wenn das Gas vor der Expansion angewärmt wird.

Der Fachmann wäre daher ohne Ausübung einer erfinderischen Tätigkeit zum Gegenstand des Anspruchs 8 gelangt, dem es folglich in Anbetracht von A1 bzw. A2 und A3 sowie fachmännischem Können an erfinderischer Tätigkeit mangelt (56 EPÜ).

10. Anspruch 10 (abhängig von einem der Ansprüche 1 bis 9)

Artikel 100 (a) EPÜ – Mangelnde erfinderische Tätigkeit unter Verwendung von A2, A3 und A1sowie fachmännischem Können

Das Merkmal des Anspruchs 10, wonach

10.1) das Gesamt-Dampf/Kohlenstoff-Verhältnis im Umwandlungsschritt größer als 2,0, vorzugsweise größer als 2,4 und besonders bevorzugt größer als 2,7 ist,

hat gemäß dem Streitpatent den Effekt, die Umwandlung von Methan du CO zu CO2 während der Shift zu erhöhen.

Dieser Unterschied löst die Aufgabe, wie Methan und CO in der Shift effektiver umgesetzt werden können.

Der Fachmann weiß, dass Methan und CO umso effektiver durch Shift umgesetzt werden können, je mehr Dampf dem Shift-Reaktor zugeführt wird. Er wird daher die Shift mit einem möglichst hohen Dampfanteil durchführen. Hierzu kann er dem Shift-Reaktor Dampf unabhängig oder zusammen mit dem Synthesegas zuführen. Aus der A2 (Abs. [0005]) weiß er, dass Synthesegas durch Primär- und Sekundärreformierung mit einem Gesamt-Dampf/Kohlenstoff-Verhältnis zwischen 2,7 und 3,0 erzeugt werden kann.

Darüber zeigt auch die A1 (S. 18) das Merkmal des Anspruchs 10. Die A1 gibt an, dass das der ATR mit einem Dampf/Kohlenstoff-Verhältnis von 3,0 betrieben werden kann, wenn als Oxidationsmittel sauerstoffangereicherte Luft eingesetzt wird, und mit 2,0, wenn der Betrieb mit reinem Sauerstoff durchgeführt wird.

Der Fachmann wäre somit durch eine bloße Kombination der Lehren aus A2 und A3 und ggf. A1sowie fachmännischem Können zum Merkmal des Anspruchs 10 gelangt, der daher nicht erfinderisch ist (56 EPÜ).

11. Anspruch 11 (abhängig von einem der Ansprüche 1 bis 10)

Artikel 100 (a) EPÜ – Mangelnde erfinderische Tätigkeit unter Verwendung von A1 bzw. A2 und A3 sowie fachmännischem Können

Anspruch 11 schlägt vor, dass

11.1) die Synthesegas-Brennstofffraktion den gesamten Brennstoff der im Umwandlungsabschnitt verwendeten Öfen bildet, oder

11.2) eine Menge an Erdgas als Zusatzbrennstoff *(trim fuel)* bereitgestellt wird, wobei dieser Zusatzbrennstoff nicht mehr als 15% der gesamten Verbrennungswärme ausmacht.

Weder A3 noch A1 offenbart explizit die Merkmale des Anspruchs 11. Allerdings wird in der A3 (Sp.5, Z. 27-45) ausgeführt, dass Brenngas 74 lediglich optional durch einen Teil des Nebenprodukts 77 oder des „trim fuels"18 ergänzt wird. Der Reformer 100 ist der einzige Brenngasverbraucher, so dass implizit auch das Merkmal 11.1) durch die A3 offenbart wird.

Im letzten Absatz der A1 wird angegeben:
"A complete separation of the entire CO2 could also be realized in the ATR-based plant ... provided the fired heater would be fed with syngas instead of natural gas."

Da ansonsten keine vollständige CO2-Abtrennung erreichbar wäre, stellt der „fired heater" den einzigen Brennstoff-Verbraucher im Umwandlungsschritt dar, so dass Synthesegas-Brennstofffraktion den gesamten Brennstoff der im Umwandlungsabschnitt verwendeten Öfen bildet und die A1 das Merkmal 11.1) ebenfalls implizit offenbart.

Das Merkmal 11.2) hat gemäß Streitpatent den Effekt, dass die Leistung der mit der Brennstofffraktion beheizten Verbraucher schnell geregelt werden kann.

Dies löst die Aufgabe, die Brennstoffzufuhr zu den Verbrauchern schnell an schwankende Betriebsbedingungen anzupassen, d.h. zu trimmen.

Zur Lösung dieser Aufgabe hätte der Fachmann ein rasch und unkompliziert verfügbares Brenngas gesucht und hätte entweder allein aufgrund seines Fachwissens oder durch Anregung der A3 (Sp. 5, Z. 27-42) Erdgas als Trimm-Gas eingesetzt. Da einerseits Erdgas billiger ist als die aus dem CO2-abgereicherten Synthesegas gewonnene Brennstofffraktion und andererseits auch die CO2-Emissionen Kosten verursachen können (CO2-Abgabe), hätten der Fachmann aus wirtschaftlichen Gründen so wenig Erdgas wie möglich als Zusatzbrennstoff eingesetzt und wäre zu dem im Merkmal 11.2) angegebenen Wert gelangt, ohne erfinderisch tätig werden zu müssen.

Der Fachmann wäre somit durch eine bloße Kombination der Lehren aus A2 und A3 und ggf. A1sowie fachmännischem Können zu den Merkmalen des Anspruchs 11 gelangt, der daher nicht auf einer erfinderischen Tätigkeit beruht (Artikel 56 EPÜ).

12. Anspruch 12 (abhängig von einem der Ansprüche 1 bis 11)

Artikel 100 (a) EPÜ – Mangelnde erfinderische Tätigkeit unter Verwendung von A1 bzw. A2 und A3 sowie fachmännischem Können

Anspruch 12 schlägt vor, dass

12.1) die Brennstofffraktion im Überschuss in Bezug auf den für den Umwandlungsabschnitt erforderlichen Brennstoff erzeugt wird, wobei die Menge der Brennstofffraktion, die über die erforderliche hinausgeht, aus dem Verfahren exportiert wird, und eine Regelung des Umwandlungsabschnitts durch Modulieren der Menge der zum Umwandlungsabschnitt gerichteten Brennstofffraktion und der aus dem Prozess exportierten Menge erfolgt.

Das Merkmal 12.1 löst dieselbe Aufgabe wie das Merkmal 11.2) (Streitpatent, Abs. [0084]) nämlich, die Brennstoffzufuhr zu den Verbrauchern schnell an schwankende Betriebsbedingungen anzupassen, d.h. zu trimmen.

Die Erzeugung eines Produkts im Überschuss, um den zeitlich schwankenden Bedarf eines Verbrauchers stets decken zu können, wobei die vom Verbraucher nicht abgenommene Produktmenge einer alternativen Verwertung zugeführt oder verworfen wird, ist konventionell und dem Fachmann bekannt. Er hätte daher die gestellte Aufgabe entsprechend dem Merkmal 12.1) gelöst, ohne erfinderisch tätig zu werden.

Der Fachmann wäre somit durch eine bloße Kombination der Lehren aus A2 und A3 und ggf. A1sowie fachmännischem Können zu den Merkmalen des Anspruchs 12 gelangt, der daher nicht auf einer erfinderischen Tätigkeit beruht (Artikel 56 EPÜ).

13. Anspruch 13 (abhängig von einem der Ansprüche 1 bis 12)

Artikel 100 (a) EPÜ – Mangelnde erfinderische Tätigkeit unter Verwendung von A1 bzw. A2 und A3 sowie fachmännischem Können

Anspruch 13 fordert, dass

13.1) die Umwandlung der Erdgas-Charge in Synthesegas einen Schritt des autothermen Reformierens, optional mit Vorreformierung, oder einen Schritt der partiellen Oxidation umfasst; wobei der Schritt des autothermen Reformierens oder der partiellen Oxidation mit einem Dampf/Kohlenstoff- Verhältnis von nicht mehr als 2 durchgeführt wird *(A2, Abs. [0018] und [0023])*.

Der Anspruch 13 beruht daher in Anbetracht von A2 und A3 sowie ggf. auch fachmännischem Können nicht auf einer erfinderischen Tätigkeit (Artikel 56 EPÜ).

14. Anspruch 14 (abhängig von einem der Ansprüche 1 bis 13)

Artikel 100 (a) EPÜ – Mangelnde erfinderische Tätigkeit unter Verwendung von A1 bzw. A2 und A3 sowie fachmännischem Können

Anspruch 14 sieht vor, dass

14.1) die Umwandlung des Erdgases in Synthesegas umfasst: primäres Reformieren des Erdgases in Gegenwart von Dampf und sekundäres Reformieren, das mit dem Sauerstoffstrom oder angereicherter Luft durchgeführt wird (A3, Abstract, Fig. 2).

Der Anspruch 14 beruht daher in Anbetracht von A2 und A3 sowie ggf. auch fachmännischem Können nicht auf einer erfinderischen Tätigkeit (Artikel 56 EPÜ).

15. Schlussfolgerung

Insgesamt ist der Gegenstand des Streitpatents nicht patentfähig, da es sämtlichen Ansprüchen 1 bis 14 entweder an der für die Patenterteilung notwendigen Neuheit oder erfinderischen Tätigkeit mangelt. Der gestellte Antrag auf Widerruf des Patentes ist damit gerechtfertigt.

Sollte sich die Einspruchsabteilung den obigen Ausführungen nicht anschließen, wird hilfsweise die Anberaumung einer mündlichen Verhandlung beantragt.

Linde GmbH

Dr. Werner Fischer
AV 521190

Anlagen: Entgegenhaltungen A1 bis A5
Abbuchungsauftrag

Europäisches Patentamt
European Patent Office
Office européen des brevets

Notice of opposition to a European patent

I. Patent opposed

Patent No.	EP3583067
Application No.	EP18702977.2
Date of mention of the grant in the European Patent Bulletin (Art. 97(3), Art. 99(1) EPC)	08 September 2021
Title of the invention	PROCESS FOR THE SYNTHESIS OF AMMONIA WITH LOW EMISSIONS OF CO2 IN ATMOSPHERE

II. Proprietor of the patent

first named in the patent specification	Casale SA
Opponent's or representative's reference	S06318-E

III. Opponent

Name	thyssenkrupp Industrial Solutions AG
Address:	ThyssenKrupp Allee 1 45143 Essen Germany
State of residence or of principal place of business	Germany
Multiple opponents (see additional sheet)	☐

IV. Authorisation

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Additional representative(s) on additional sheet/see authorisation	☐	

Topsoe, Inc. – EX1003
Page 709 of 1210

Authorisation(s)

is/are enclosed ☐

has/have been registered under No. ☐

V. **Opposition is filed against**

the patent as a whole ☒

claim(s) No(s).

VI. **Grounds for opposition:**

Opposition is based on the following grounds:

(a) the subject-matter of the European patent opposed is not patentable (Art. 100(a) EPC) because:

- it is not new (Art. 52(1); Art. 54 EPC) ☒
- it does not involve an inventive step (Art. 52(1); Art. 56 EPC) ☒
- patentability is excluded on other grounds, namely articles ☐

(b) the patent opposed does not disclose the invention in a manner sufficiently clear and complete for it to be carried out by a person skilled in the art (Art. 100(b) EPC; see Art. 83 EPC). ☐

(c) the subject-matter of the patent opposed extends beyond the content of the application/of the earlier application as filed (Art. 100(c) EPC, see Art. 123(2) EPC). ☐

VII. **Facts (Rule 76(2)(c) EPC)**

presented in support of the opposition are submitted herewith on an attached document ☒

VIII. **Other requests:**

IX. Evidence presented

D1	Patent document	US2004/0234426 (A1) , 25.11.2004 original file name: D1 - US20040234426A1.pdf attached as: Published-Evidence-1.pdf
D2	Patent document	EP1648817 (B1) , 25.10.2006 original file name: D2 - EP1648817(B1).pdf attached as: Published-Evidence-2.pdf
D3	Patent document	EP2266922 (A1) , 22.12.2010 original file name: D3 - EP2266922A1.pdf attached as: Published-Evidence-3.pdf
D4	Non-patent literature - book	Appl, Dr. Max, "Ammonia Principles and Industrial Practice" Germany: WILEY-VCH Verlag GmbH, 1999 ISBN: 3-527-29593-3 original file name: D4 - Max_Appl_Ammonia_principles_1999.pdf attached as: Published-Evidence-4.pdf
D5	Patent document	DE102015210803 (A1) , 15.12.2016 original file name: D5 - Poschlad_DE102015210803A1.pdf attached as: Published-Evidence-5.pdf
D6	Patent document	DE102014209635 (A1) , 26.11.2015 original file name: D6 - Poschlad_DE102014209635A1.pdf attached as: Published-Evidence-6.pdf

X. **Payment**

Method of payment	Debit from deposit account

The European Patent Office is hereby authorised, to debit from the deposit account with the EPO any fees and costs indicated in the fees section below.

Currency:	EUR
Deposit account number:	28001082
Account holder:	Gulde & Partner Patent- und Rechtsanwaltskanzlei mbB

Refunds

Any refunds should be made to EPO deposit account:	28001082
Account holder:	Gulde & Partner Patent- und Rechtsanwaltskanzlei mbB

Fees

	Factor applied	Fee schedule	Amount to be paid
010 Opposition fee	1	840.00	840.00
Total:		EUR	840.00

	A Forms	Details:	System file name:
A-1	Form for notice of opposition		ep-oppo.pdf

	B Attached document files	Original file name:	System file name:
B-1	1. Facts and arguments	S06318-E - Opposition.pdf	OPPO.pdf

	C Attached evidence files	Original file name:	System file name:
C-1	1. Patent document	D1 - US20040234426A1.pdf	Published-Evidence-1.pdf
C-2	2. Patent document	D2 - EP1648817(B1).pdf	Published-Evidence-2.pdf
C-3	3. Patent document	D3 - EP2266922A1.pdf	Published-Evidence-3.pdf
C-4	4. Patent document	D5 - Poschlad_DE102015210803A1.pdf	Published-Evidence-5.pdf
C-5	5. Patent document	D6 - Poschlad_DE102014209635A1.pdf	Published-Evidence-6.pdf
C-6	1. Non-patent literature - book	D4 - Max_Appl_Ammonia_principles_1999.pdf	Published-Evidence-4.pdf

Topsoe, Inc. – EX1003
Page 712 of 1210

Signature of opponent or representative

Place	Berlin
Date:	08 June 2022
Signed by:	Jan Neigenfink 8125
Association:	Gulde & Partner Patent- und Rechtsanwaltskanzlei mbB
Representative name:	Dr. Jan Neigenfink
Capacity:	(Representative)

Topsoe, Inc. – EX1003
Page 713 of 1210

GULDE & PARTNER
PATENT- UND RECHTSANWALTSKANZLEI mbB

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European Patent Office

80298 Munich

Date	June 8, 2022 SAL/NG/ajs
Gulde Ref.	S06318-E
Country	Europe
File No.	EP18702977.2 / EP3583067
Applicant	Casale SA
Title	Opposition procedure against EP 3 583 067 B1 of Casale SA

Notice of Opposition

In the name and on behalf of

thyssenkrupp Industrial Solutions AG
ThyssenKrupp Allee 1
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we hereby file notice of opposition pursuant to Art. 99(1) EPC concerning the European patent

EP 3 358 067 B1 (EP 18702977.2)

Proprietor:

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Dr. Simon Lang, Dipl.-Phys. [ABC]
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REQUESTS

- It is requested to revoke the patent EP 3 358 067 B1 ("the disputed patent") pursuant to Art. 101 (2) EPC in its entirety. The request to revoke the patent EP 3 358 067 B1 is based on Art. 100 (a) EPC.

- As an auxiliary measure, oral proceedings pursuant to Art. 116 (1) EPC are requested.

WRITTEN REASONED STATEMENT PURSUANT TO RULE 76(1), (2) EPC

Bibliographic data of EP 3 358 067 B1 (EP 18702977.2)

Filing date:	31.01.2018
Priority date:	15.02.2017
	06.10.2017
Publication date:	25.12.2019
Grant date:	08.09.2021

GROUND FOR OPPOSITION PURSUANT TO ART. 100 (A) EPC

Granted claims 1 to 14 do not fulfill the requirements of Art. 52(1) EPC together with Art. 54(1), (2) EPC and Art. 56 EPC. Opponent cites the following documents:

Table 1: cited documents

Number	Document	Publication date
D1	US 2004/ 0234426 A1	25.11.2004
D2	EP 1 648 817 B1	26.04.2006
D3	EP 2 266 922 A1	29.12.2010
D4	Max Appl Ammonia Principles and Industrial Practice, 1999, Wiley-VCH, ISBN 3-527-29593-3;	1999
D5	DE 10 2015 210 803 A1	15.12.2016
D6	DE 10 2014 209 635 A1	26.11.2015

The earliest priority date of the disputed patent is 15.02.2017. Therefore, D1 to D6 form state of the art pursuant to Art. 54(2) EPC.

1. GRANTED CLAIM 1

1.1 LACK OF NOVELTY IN VIEW OF D1

The subject matter of claim 1 lacks novelty in view of D1. The features of claim 1 in comparison to the disclosure of D1 are shown in table 2.

Table 2: claim 1 in comparison to the disclosure of D1

Feature	EP 3 358 067 B1	D1 (US 2004 / 0234426 A1)
a)	Process for synthesis of ammonia from natural gas, comprising:	**claims** (i.e. claim 1, claim 8).
b)	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;	**claim 8**
c)	a treatment of said synthesis gas comprising 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.
d)	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],** "A subsequent acid gas removal unit (here: carbon dioxide removal unit) 650 removes significant quantities of carbon dioxide, ..."
e)	optionally, a step for methanation of the synthesis gas and/or addition of nitrogen to the synthesis gas,	**paragraph [0039]**, "...and a methanator 660 downstream of the acid gas removal unit converts residual carbon monoxide and carbon dioxide to methane."

f)	separation of a part of said CO2-depleted synthesis gas as fuel fraction	**paragraph [0014]**, "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."
g)	wherein said fuel fraction (14) is fed as fuel to at least one furnace	**paragraph [0018]**, "at least one of the purge gas and the fuel gas are combusted in the primary reformer."
h)	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 streams having the same composition	**paragraph [0040]**, "A **first portion** of methanator effluent 662A is fed to the PSA 685 that separates the methanator effluent 662A into a hydrogen rich stream 662A and a waste stream 662A", predominantly comprising methane, hydrogen, and nitrogen. A **second portion** of methanator effluent 662B is fed directly to the syngas compressor 680, that also compresses hydrogen rich stream 662A to form a compressed syngas having a molar ratio of hydrogen to nitrogen of about 3.0."
i)	wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia,	**paragraph [0040]**, "The waste gas is preferably combined with the purge gas from the synloop 690 to combined waste gas stream 672 and fed into the burner of primary reformer 610, while the synthesis loop 690 produces ammonia product 692."

j)	optionally after further purification.	**see g),** methanation as optional further purification

D1 has already been cited in the examination proceedings. It was out of question that D1 discloses features a) to g) and i) to j). D1 also discloses feature h). In the examination proceedings it was argued that the split of the CO2-depleted synthesis gas does not lead to two streams having the same composition, because the fuel gas is allegedly a purge stream resulting as a by-product from a transformation process of a CO2 depleted synthesis gas into a purified synthesis gas.

However, figure 6 of D1 discloses that the CO2 depleted syngas is split after methanation 660 into two stream 662A and 662B that do, in fact, have the same composition.

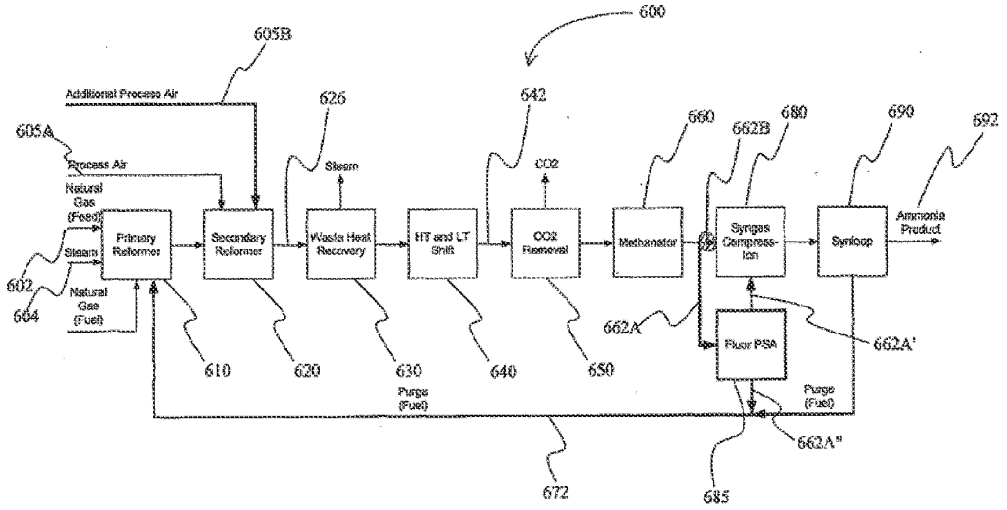


Figure 6

figure 1 - Figure 6 of D1

Paragraph [0040] also states:

> *"**A first portion of methanator effluent 662A** is fed to the PSA 685 that separates the methanator effluent 662Ainto a hydrogen rich stream 662A and a waste stream 662A",*

> *predominantly comprising methane, hydrogen, and nitrogen.* ***A second portion of methanator effluent 662B*** *is fed directly to the syngas compressor 680, that also compresses hydrogen rich stream 662A to form a compressed syngas having a molar ratio of hydrogen to nitrogen of about 3.0."*

Claim 1 does not restrict any further treatment of the fuel fraction before it is fed to a furnace.

Therefore, granted claim 1 is not novel in view to D1 pursuant to Art. 54(1), (2) EPC.

1.2 Lack of Inventive Step based on D2

Claim 1 is not based on an inventive step based on reference D2.

D2 discloses a process for the production of hydrogen, that can of course be used for the production of ammonia (**feature a)**). For example, in paragraph [0014] it is stated that the disclosed process steps have proven themselves also for the production of ammonia. Furthermore, claim 1 of D2 reads:

> 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 by means of steam, and catalytic conversion of the resulting carbon monoxide to carbon dioxide and hydrogen takes place in a downstream conversion stage (**feature c)**) by means of steam,
> wherein the carbon dioxide is removed from the converted gas stream (8) by means of a gas scrubber (7) (**feature d)**), and the scrubbed hydrogen-rich gas stream (10) is then separated in a pressure swing adsorption system (**feature j)**) (11) into a product gas stream (12) consisting of hydrogen and a waste gas stream (13), and
> wherein the waste gas stream (13), together with hydrogen (14) which is branched off from the gas stream (10) behind the gas scrubber (7), is passed to the reformer (4) as a combustion gas that is largely free of carbon, and burned there (**features f), g), h), i)**)

As for features f), g), h), and i) it is shown in Fig. 1 of D2, that a CO2-depleted gas stream is split into a product gas stream that is being purified and then used as process gas, whereas stream 14 with the same composition is sent to a reformer as fuel gas.

Fig.1

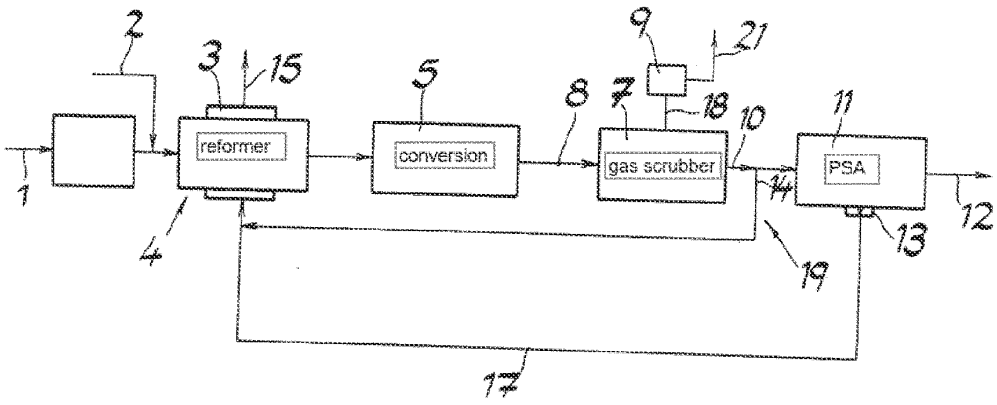


figure 2 - Figure 1 of D2

Claim 1 does not restrict the fuel gas fraction to be the only fuel gas to be sent to a furnace. On the contrary the term "fuel fraction" indicates, that this fuel gas is a fraction of the fuel gas that is actually directed to the respective furnace as it is also shown in every embodiment in figures 1 to 4.

Since D2 does not directly aim for the production of ammonia but rather the preparation of syngas that can later be used for the synthesis of ammonia (which is what claim 1 of the disputed patent also discloses), the subject matter of granted claim 1 differs from D2 by the explicit formulation of feature b) (and optional feature e),

> 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.

This feature results in the technical effect, that the hydrogen to nitrogen molar ratio for the syngas can be maintained at a ratio of about 3 to 1 for the further synthesis of ammonia.

The objective technical problem is to improve the production process of hydrogen to form a syngas that is suitable for the production of ammonia.

This process step is well known, so that a person skilled in the art would include, for example, a secondary reformer for the production of syngas solely based on the basic knowledge of the person skilled in the art.

Secondary reforming is, for example, also shown in D1 (i.e. [0020]), which is an example for ammonia production. Also, D4 discloses the typical conditions for the production of ammonia (4.1.1).

As an alternative for steam reforming with a primary and a secondary reformer, it is also known to utilize an autothermal reformer. This alternative is for example shown in D5 (i.e. [0003]) and D6 (i.e. [0006]). The person skilled in the art is able to choose from these alternatives based on the process conditions that they have to work with.

When a primary and secondary reformer is used, oxygen enriched air will be used in the secondary reformer (feature b) first alternative).

In an autothermal reformer oxygen is used for the reforming process (feature b) second alternative). One advantage of the autothermal reformer is that nitrogen can be added later in the process which can have an advantageous effect on the dimensions of certain apparatuses of the front end of an ammonia plant.

Therefore, feature b.), is not based on an inventive step pursuant to Art. 56 EPC based on D2 with the knowledge of the person skilled in the art or at least in combination with one of the references D1, D4, D5 or D6.

As for optional feature e) a methanation is a commonly used method for purification (see i.e., D1, Fig. 6 or D4, 4.1) next to a PSA. The person skilled in the art would easily be able to choose a methanation for the process instead of a PSA (feature e) first alternative).

When an autothermal reformer is used, the person skilled in the art would automatically include the addition of nitrogen, as elaborated above (feature e) second alternative).

Therefore, optional feature e) is not based on an inventive step pursuant to Art. 56 EPC based on D2 with the knowledge of the person skilled in the art or at least in combination with one of the references D1, D4, D5 or D6.

1.3 Lack of Inventive Step based on D3

Claim 1 is not based on an inventive step based on reference D3.

D3 discloses, analogous to reference D2, a process for the production of hydrogen, that can of course be used for the production of ammonia (**feature a)**). For example, in paragraph [0055] it is stated that secondary reforming as further step in the production of ammonia and methanol is used. Furthermore, claim 1 of D2 reads:

> A process for producing a hydrogen-containing product gas (72), comprising:
> (a) introducing a process stream (10) comprising steam and at least one hydrocarbon selected from the group consisting of methane, ethane, propane, butane, pentane, and hexane into a plurality of catalyst-containing reformer tubes (104) in a reformer furnace (100) and reacting the process stream inside the plurality of catalyst-containing reformer tubes (104) at a first temperature ranging from 700°C to 1000°C and a first pressure ranging from 0.2 to 5 MPa (2 to 50 atmospheres) to form a reformate stream (12) comprising hydrogen, carbon monoxide, methane and steam and withdrawing the reformate stream (12) from the plurality of catalyst-containing reformer tubes (104);
> (b) reacting the reformate stream (12, 32) in the presence of a shift catalyst (44) at a second temperature ranging from 190°C to 500°C and a second pressure ranging from 0.2 to 5 MPa (2 to 50 atmospheres) to form a second process stream (42) comprising carbon dioxide, hydrogen, carbon monoxide and methane (**feature c)**);

(c) scrubbing the second process stream (42) with a wash stream (64) to form a carbon dioxide-depleted stream (62) and a carbon dioxide-loaded wash stream (66) (**feature d**));
(d) separating the carbon dioxide-depleted stream (62) to form the hydrogen-containing product gas (72) and a by-product gas (76) comprising methane and carbon monoxide;
(e) introducing a portion of the by-product gas (76) into the process stream (10, 14) at a location upstream of the plurality of catalyst-containing reformer tubes (104) and/or into the reformate stream (12) at a location upstream of a reforming catalyst (24) in a secondary reforming reactor (20); and
(f) combusting a fuel gas (74) comprising a portion of the hydrogen-containing product gas (72), optionally a portion (77) of the by-product gas (76), and optionally a supplementary fuel (18) in the reformer furnace (100) (**features f), g), h), i)**) external to the plurality of catalyst-containing reformer tubes (104) to supply energy for reacting the process stream inside the plurality of catalyst-containing reformer tubes (104), and withdrawing a flue gas (110) from the reformer furnace (100).

Before the product gas is passed on it can be additionally purified via a PSA 70, as described in paragraph [0033] (**feature j**)).

As for features f), g), h), and i) it is shown in Fig. 1 of D3, that a CO2-depleted gas stream is split into a product gas stream and a fuel gas stream 74 with the same composition. The fuel gas stream is sent to a reformer.

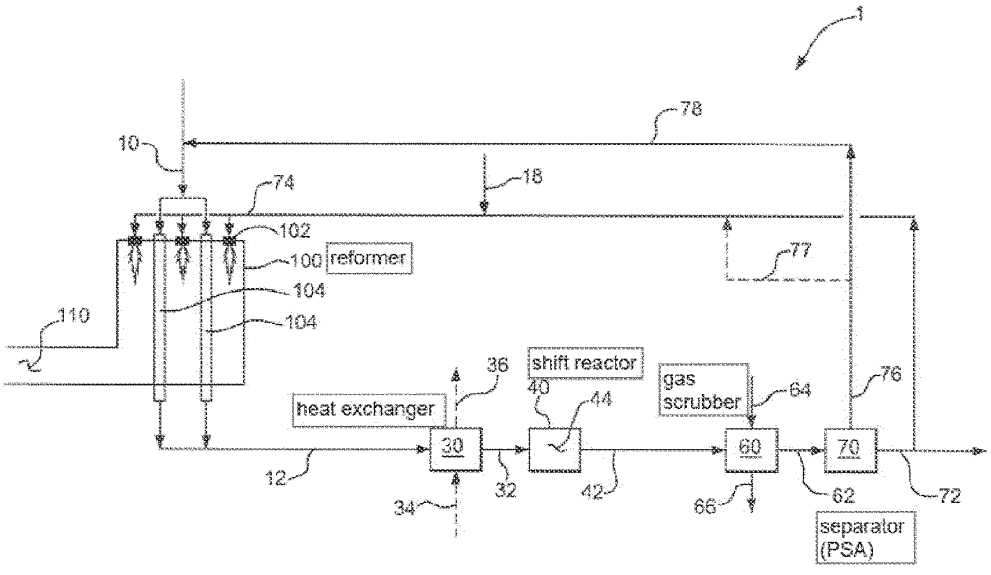


FIG. 1

figure 3 - Figure 1 of D3

Analogously to what has been elaborated according to reference D2, D3 also does not directly aim for the production of ammonia but rather the preparation of syngas that can later be used for the synthesis of ammonia (which is what claim 1 of the disputed patent also discloses), the subject matter of granted claim 1 differs from D3 by the explicit formulation of feature b) (and optional feature e),

> 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.

This feature results in the technical effect, that the hydrogen to nitrogen molar ratio for the syngas can be maintained at a ratio of about 3 to 1 for the further synthesis of ammonia.

The objective technical problem is to improve the production process of hydrogen to form a syngas that is suitable for the production of ammonia.

This process step is well known, so that a person skilled in the art would include, for example, a secondary reformer for the production of syngas solely based on the basic knowledge of the person skilled in the art.

Secondary reforming is for example also shown in D1 (i.e. [0020]), which is an example for ammonia production. Also, D4 discloses the typical conditions for the production of ammonia (4.1.1).

As an alternative for steam reforming with a primary and a secondary reformer it is also known to utilize an autothermal reformer. This alternative is for example shown in D5 (i.e. [0003]) and D6 (i.e. [0006]). The person skilled in the art is able to choose from these alternatives based on the process conditions that they have to work with.

When a primary and secondary reformer is used, oxygen enriched air will be used in the secondary reformer (feature b) first alternative).

In an autothermal reformer oxygen is used for the reforming process (feature b) second alternative). One advantage of the autothermal reformer is that nitrogen can be added later in the process which can have an advantageous effect on the dimensions of certain apparatuses of the front end of an ammonia plant.

Therefore, feature b.), is not based on an inventive step pursuant to Art. 56 EPC based on D3 with the knowledge of the person skilled in the art or at least in combination with one of the references D1, D4, D5 or D6.

As for optional feature e) a methanation is a commonly used method for purification (see i.e., D1, Fig. 6 or D4, 4.1) next to a PSA. The person skilled in the art would easily be able to choose a methanation for the process instead of a PSA (feature e) first alternative).

When an autothermal reformer is used, the person skilled in the art would automatically include the addition of nitrogen, as elaborated above (feature e) second alternative).

Therefore, optional feature e) is not based on an inventive step pursuant to Art. 56 EPC based on D3 with the knowledge of the person skilled in the art or at least in combination with one of the references D1, D4, D5 or D6.

2. GRANTED CLAIM 2

Granted claim 2 adds the features:

> wherein said fuel fraction is comprised between 1 % and 40% of the total amount of said CO2-depleted syngas, preferably between 10% and 30%.

The features of claim 2 are part of the general knowledge of the person skilled in the art. D4, for example, discloses typical energy consumptions of ammonia plants. The aim of the granted patent is to reduce the external natural gas needed as fuel gas, by splitting the CO2 depleted syngas into a product gas stream and a fuel gas stream. Table 39 on page 186 of D4 discloses an Energy analysis of a low energy ammonia plant.

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	1.91
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	0.08	0.46
Total losses	11.51	10.89	10.55
NH_3 product	20.98	17.12	20.14
Efficiency, %	64.69	58.40	65.60

figure 4 - Table 39 of D4

In the first lines the natural gas consumption for the reformer feed as well as for the reformer fuel is shown. In the examples the ratio for the fuel needed for the reformer to the total natural gas consumption is well in the scope between 10 % to 30 %.

The person skilled in the art would obviously attempt to reduce the needed natural gas as fuel to a minimum and would therefore replace the natural gas needed as fuel with the fraction of the CO2 depleted gas stream.

Therefore, dependent claim 2 is not based on an inventive step pursuant to Art. 56 EPC in view of D1, D2 or D3 in combination with the basic knowledge and/or reference D4.

3. GRANTED CLAIM 3

Granted claim 3 adds the features:

> wherein said fuel fraction is separated upstream of the methanation step or upstream of the nitrogen addition step.

D2 discloses that the fuel fraction is separated upstream of the PSA. As described above (2.1.1 b)) a methanation can easily be used instead of a PSA since their initial goal of these purification steps is the same. The person skilled in the art is able to decide when a methanation is advantageous over a PSA. Furthermore, a methanation is disclosed by D1.

Therefore, dependent claim 3 is not based on an inventive step pursuant to Art. 56 EPC in view of D2 in combination with the basic knowledge of the person skilled in the art or D1.

According to the nitrogen addition step, it is obvious for the person skilled in the art to add nitrogen after the fuel fraction is separated from the process gas stream. Nitrogen reduces the heating value of the fuel fraction. In order to have an efficient fuel fraction, it is desired to wait for the addition of nitrogen until the stream is split into the process gas stream and the fuel fraction.

Therefore, the second alternative of dependent claim 3 is not based on an inventive step pursuant to Art. 56 EPC in view of D1, D2 or D3 in combination with the basic knowledge of the person skilled in the art.

4. GRANTED CLAIM 4

Granted claim 4 adds the features:

> wherein said CO2-depleted syngas contains no more than 1000 ppm by volume of CO2.

D4 discloses typical values of CO2 rates before and after CO2 depletion in an ammonia process on page 130 (table 33). The CO2 amount in lean gas is 0,1 % which corresponds to 1000 ppm.

Therefore, dependent claim 4 is not based on an inventive step pursuant to Art. 56 EPC in view of D1, D2 or D3 in combination with D4.

5. GRANTED CLAIM 5

Granted claim 5 adds the features:

> wherein said enriched air contains at least 50% of oxygen, preferably at least 90% oxygen.

D1 discloses in paragraph [0026]:

> *"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,"*

Therefore, dependent claim 5 is not novel in view to D1 pursuant to Art. 54(1), (2) EPC.

6. GRANTED CLAIM 6

Granted claim 6 adds the features:

> wherein said fuel fraction (14) 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;
> one or more furnaces for pre-heating the charge of an autothermal reformer or partial oxidation reactor or natural-gas desulphurization section.

D1 discloses in paragraph [0018] that the fuel gas is combusted in the primary reformer. It is obvious for the person skilled in the art to use the fuel gas where fuel gas is needed. Additionally, the person skilled in the art would, of course, use the fuel gas in the apparatuses claimed in claim 6.

Therefore, dependent claim 6 is not novel in view to D1 pursuant to Art. 54(1), (2) EPC and is not based on an inventive step pursuant to Art. 56 EPC in view of D1 in combination with the basic knowledge of the person skilled in the art.

7. GRANTED CLAIM 7

Granted claim 7 adds the features:

> wherein: a purge gas of the ammonia synthesis process, containing hydrogen and methane, is treated so as to recover the hydrogen contained in it, 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.

A hydrogen recovery section is well known in ammonia plants. D4 discloses hydrogen recovery in the process for production of ammonia on pages 166 to 169.

Therefore, dependent claim 7 is not based on an inventive step pursuant to Art. 56 EPC in view of D1, D2 or D3 and the basic knowledge of the person skilled in the art respectively D4.

8. GRANTED CLAIM 8

Granted claim 8 adds the features:

> 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, preferably all of it, is used as fuel; any remaining part of said first stream is fed to the synthesis of ammonia together with the second stream.

Nitrogen wash is well known in ammonia plants. D4 discloses, for example, liquid nitrogen wash on page 137 (4.3.2.5).

Therefore, dependent claim 8 is not based on an inventive step pursuant to Art. 56 EPC in view of D1, D2 or D3 and the basic knowledge of the person skilled in the art respectively D4.

9. GRANTED CLAIM 9

Granted claim 9 adds the features:

> also comprising a step of expansion, with production of mechanical work, of the CO2-depleted syngas, optionally after heating it.

When, for example, the separated fuel fraction has a greater pressure than the possible pressure at which the furnace can be operated, it is not only obvious, but mandatory to reduce the pressure and expand the CO2 depleted syngas. It is well known to use the energy, that can be generated from the expansion process, for example in a turbine to generate mechanical work.

Therefore, dependent claim 9 is not based on an inventive step pursuant to Art. 56 EPC in view of D1, D2 or D3 in combination with the basic knowledge of the person skilled in the art.

10. GRANTED CLAIM 10

Granted claim 10 adds the features:

> wherein the overall steam/carbon ratio in the conversion step is greater than 2.0, preferably greater than 2.4 and more preferably greater than 2.7.

D4 discloses on page 71 in the last paragraph:

> *"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."*

Therefore, dependent claim 10 is not based on an inventive step pursuant to Art. 56 EPC in view of D1, D2 or D3 in combination with the basic knowledge of the person skilled in the art respectively D4.

11. GRANTED CLAIM 11

Granted claim 11 adds the features:

> 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.

Feature f) of claim 1 of D3 discloses:

> *"combusting a fuel gas (74) comprising a portion of the hydrogen-containing product gas (72), optionally a portion (77) of the by-product gas (76), and optionally a supplementary fuel (18) in the reformer furnace (100) external to the plurality of catalyst-containing reformer tubes (104) to supply energy for reacting the process stream inside the plurality of catalyst-containing reformer tubes (104), and withdrawing a flue gas (110) from the reformer furnace (100)."*

By-product gas and supplementary fuel are only optional. Therefore, the fuel gas fraction 74 can form all the fuel. Optionally, additional natural gas 18 can be used as trim fuel.

Therefore, dependent claim 11 is not based on an inventive step pursuant to Art. 56 EPC in view of D3 in combination with one of the references D1, D4, D5 or D6.

12. GRANTED CLAIM 12

Granted claim 12 adds the features:

> 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.

If the circumstances allow it to produce excess fuel that can be used in other units, which otherwise would be provided with fuel that produces an overall higher amount of CO2 emissions, it is obvious for the person skilled in the art to produce excess fuel in order to reduce CO2 emissions.

Therefore, dependent claim 12 is not based on an inventive step pursuant to Art. 56 EPC in view of D1, D2 or D3 in combination with the basic knowledge of the person skilled in the art.

13. GRANTED CLAIM 13

Granted claim 13 adds the features:

> the conversion of the natural gas charge into synthesis gas comprises a step of autothermal reforming, optionally with pre-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.

As described in 2.1.1 b) the use of an autothermal reformer is not based on an inventive step. Furthermore, D5 discloses, for example, in paragraph [0020] that the steam/carbon ratio of an autothermal reformer can preferably be at a ratio not greater than 2.

Therefore, dependent claim 13 is not based on an inventive step pursuant to Art. 56 EPC in view of D1, D2 or D3 in combination with D5.

14. GRANTED CLAIM 14

Granted claim 14 adds the features:

> wherein the conversion of the natural gas into synthesis gas comprises: primary reforming of the natural gas in the presence of steam and secondary reforming performed with said oxygen flow or enriched air.

D1 discloses in paragraph [0018] that a primary and a secondary reformer are being used for the conversion of natural gas.

Furthermore, as described above, the general process for the production of ammonia is well known.

Therefore, dependent claim 14 is not is not novel in view to D1 pursuant to Art. 54(1), (2) EPC. Dependent claim 14 is also not based on an inventive step pursuant to Art. 56 EPC in view of D2 or D3 in combination with the basic knowledge of the person skilled in the art, respectively D4.

SUMMARY

Granted claims 1, 5, 6 and 14 lack novelty in view of the explicit and implicit disclosure of D1.
In addition, granted claims 1 to 14 are not based on an inventive step.

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European Patent Attorney

Dr. Jan Neigenfink
European Patent Attorney • Partner

Enclosures
D1 – D6

Nov. 18, 1969 M. C. SZE ET AL 3,479,298

PRODUCTION OF HYDROGEN

Filed Aug. 4, 1964

INVENTOR
M.C. Sze &
D.B. Stewart
BY
Fulwider, Mason & Engelman

United States Patent Office 3,479,298 Patented Nov. 18, 1969

3,479,298

PRODUCTION OF HYDROGEN

Morgan C. Sze, Garden City, N.Y., and Donald B. Stewart, Towaco, N.J., assignors to The Lummus Company, New York, N.Y., a corporation of Delaware

Filed Aug. 4, 1964, Ser. No. 387,292
Int. Cl. C01b 1/16
U.S. Cl. 252—373 8 Claims

ABSTRACT OF THE DISCLOSURE

Process for producing a hydrogen-containing gas from a light hydrocarbon, such as natural gas, wherein a natural gas-steam mixture (mole ratio of steam to natural gas of 3.0–3.8:1) is reacted in a primary reformer, maintained at a pressure above 400 p.s.i.g. and a temperature above 1450° F., to partially convert the natural gas. The effluent from the primary reformer is mixed with a mixture of steam and a free oxygen-containing gas, preheated to a temperature of 1000°–1500° F., in a secondary reformer to produce a hydrogen rich effluent, containing less than 0.5% natural gas.

This invention relates to the reforming of hydrocarbons, and more particularly to the steam reforming of a hydrocarbon to produce a gas rich in hydrogen, which is suitable for further treatment to form ammonia, methanol, etc.

Hydrocarbon feeds generally utilized include methane, ethane, propane, butanes and/or pentanes. In most prior art processes reforming was conducted at low pressures, i.e., 15 to 50 p.s.i.g., and at temperatures of from 1225 to 1450° F. Under such conditions steam was added to the feed to provide a steam to carbon ratio of from about 2:1 to 4:1 expressed as moles of steam to atoms of carbon. If the synthesis gas was to be used for the production of ammonia, air is introduced at some point in the process to provide a gas, which, after various treatments, contain approximately three moles of hydrogen for every mole of nitrogen.

Recent developments, particularly in the metallurgical and catalyst arts have permitted the operation of catalytic steam reformer units at increasingly higher pressures. At such higher pressures, in order to obtain the necessary methane decomposition at reasonable tubewall temperatures, it is necessary to operate the reformers at higher steam to carbon ratio, as for instance set forth in U.S. Patent No. 3,081,268 wherein ratios of from 4:1 to 8:1 are described. However, operating at such higher steam to carbon ratios increases the duty of the radiant heating section of the reformer, thus requiring more fuel to be fired. Additionally, at such higher pressures, methane decomposition, for instance, in the primary reformer is reduced thereby requiring the secondary reformer to perform an increasing amount of methane decomposition.

It is a primary object of our invention to provide an improved process for the reforming of hydrocarbons to form gaseous streams rich in hydrogen and carbon monoxide.

A further object of our invention is to provide an improved process for the steam reforming of hydrocarbons utilizing a process having lower fuel requirements.

Another object of our invention is to provide an improved process for the steam reforming of hydrocarbons at high pressures at steam and carbon ratios of from 3.0:1.0 to 3.8:1.0.

Still another object of our invention is to provide an improved process for the steam reforming of hydrocarbons at high pressures whereby the duty of the radiant heating section of the primary reformer is actually reduced by the lower steam to carbon ratios.

A still further object of our invention is to provide an improved process for the steam reforming of hydrocarbons at high pressures and lower steam to carbon ratios whereby the methane decomposition in the secondary decomposer is easily improved.

Yet another object of our invention is to provide an improved process for the steam reforming of hydrocarbons whereby wider flexibility of operation is achieved with greater range of feedstocks.

A further object of our invention is to provide an improved process for the steam reforming of hydrocarbons whereby deposition of carbon on the catalyst in the primary reformer is substantially eliminated when the hydrocarbon feed contains appreciable amounts of olefins.

Further objects of our invention will become apparent from the following description when taken in conjunction with the accompanying drawing illustrating a schematic flow diagram of our improved process.

In accordance with our invention, the hydrocarbon feed such as methane, ethane, propane or other light hydrocarbons are mixed with steam at a pressure of from 400 p.s.i.g. or greater, and preheated in the convection section of a primary reformer to a temperature of above about 800° F. The molal ratio of steam to atoms of carbons in the hydrocarbon feed stream is in the range of from 3.0 to 3.8. The preheated gas stream is then passed through the catalyst tubes in the reformer wherein the tubes are heated by the combustion of a fuel gas. The primary reformer effluent is withdrawn at an outlet temperature of about 1450° F. or higher. At this pressure and temperature, the primary reformer effluent is passed to a secondary reformer.

A mixture of steam and air, also preheated in the convection section of the primary reformer is introduced into the secondary reformer at a temperature in the range of 1000° to 1500° F. and mixed with the primary reformer effluent to complete the decomposition of the methane. The process gas leaving the secondary reformer is a raw ammonia synthesis gas containing hydrogen and carbon monoxide at approximately three times the nitrogen content, and with a methane content of 0.5 mole percent or lower. In the event that the hydrocarbon feed contains some olefins, some air is added to the steam admixed with the hydrocarbon feed to the primary reformer so that the oxygen content of the feed to the catalyst tubes is less than about 1.0 mole percent. By introducing air into the steam admixed with the hydrocarbon feed, deposition of carbon on the catalyst is essentially eliminated thereby permitting wider flexibility of operation with a greater range of feedstocks.

If a mixture of steam and oxygen is introduced into the secondary reformer, then the process gas leaving the secondary reformer is a gas suitable for further treatment to yield methanol or high purity hydrogen.

Referring now to the drawing, a hydrocarbon feed, in line **10**, such as methane, ethane, propane or other lighter hydrocarbons, is admixed with steam in line **11** and passed to a primary reformer, generally indicated as **13** including a convection section **14** and a radiant heating section **15**. Solely for the following description of the flow diagram, natural gas will be considered to be the feed to the process, however, this is in no way intended to limit the scope of the appended claims. The natural gas and steam at a pressure of about 400 p.s.i.g. to about 800 p.s.i.g. is preheated in the coil **16** positioned within the convection section **14** of reformer **13** and heated to a temperature of about 950° F. to about 1000° F. The molal ratio of steam to carbon atoms in the feed in line **12** is controlled so that such ratio is in the range of from 3.0 to 3.8.

As hereinabove mentioned, in the even that the hydrocarbon feed gas contains minor quantities of olefins, air

Topsoe, Inc. – EX1003
Page 737 of 1210

in line 17 is passed via line 18 under the control of valve 19, and admixed with the steam in line 11. Olefinic hydrocarbons exhibit a strong tendency to deposit carbonaceous matters on the catalyst contained in the tubes of the radiant section 15 of the primary reformer 13. By using small amounts of air or oxygen in the feed to the radiant heating section deposition of carbon in the catalyst is substantially eliminated.

The preheated natural gas and steam mixture is withdrawn from the coil 16 and passed through line 20 to the catalyst tubes in parallel, generally indicated as 21, vertically disposed within the radiant heat section 15 of the reformer 13. The catalyst tubes are heated by the combustion of a fuel in line 22 which is passed to burners, schematically illustrated as 23. In the radiant heating section 15 of the reformer 13, the preheated mixture of natural gas and steam is heated to a temperature whereby the mixture is withdrawn in line 24 from the radiant heating section 15 at a temperature of at least 1450° F. The upper temperature to which the gas mixture can be heated in the radiant heating section 21 is set by present metallurgical limitations. The gaseous effluent in line 24 is thereafter introduced into a secondary reformer, generally indicated as 25.

Air in line 17 is admixed with steam in line 26 and passed through line 27 to a coil 28 also positioned in the convection section 14 of the primary reformer 13. The mixture of steam and air is preheated in the convection section 15 to a temperature in the range of from 1000 to 1400° F. The preheated mixture is withdrawn through line 29 and admixed with the gaseous mixture in line 24 in the upper portion of the secondary reformer 25. At the temperature and pressure of the gaseous streams in lines 24 and 29, further decomposition of residual quantities of methane in line 24 is effected during passage through the catalyst bed 30 of the secondary reformer 25. A gaseous effluent is withdrawn from the secondary reformer 25 through line 31 and passed to subsequent processing units (not shown) for further treatment. The gaseous effluent in line 31 contains hydrogen and carbon monoxide at approximately three times the molar content of nitrogen in such gas stream. The gaseous stream in line 31 also contains less than about 0.5% methane.

By operating the primary reformer at pressures of above 400 p.s.i.g.; and at a steam to carbon ratio of from 3.0 to 3.8; and by using an air and steam mixture preheated in the primary reformer for introduction into the secondary reformer, the duty of the radiant heating section 15 of the primary reformer 13 is considerably reduced. As hereinbefore mentioned, at increasing pressures, methane decomposition is reduced in the primary reformer. Consequently, it is necessary to provide for a higher enthalpy of the feed streams to the secondary reformer to provide for the same overall methane decomposition as obtained in the reforming processes heretofore operated at lower pressures.

In known prior processes, all of the steam requirements were admixed with the hydrocarbon feed prior to passage through the catalyst tubes of the radiant heating section. With such processes, the total steam preheat duty was limited by the cracking temperature of the heaviest hydrocarbon constituent in the gas feed prior to contact of the hydrocarbon feed with the catalyst in the tubes of the radiant heating section. By preheating an air and steam mixture in the convection section of the primary reformer, the steam can be preheated to a much higher temperature. A more efficient use is made of the fuel fired in the radiant section of the primary reformer.

Further advantages of our process may be had by reference to the following examples illustrating inter alia, the net fuel savings obtained by reforming a hydrocarbon in accordance with our process. In all of the following examples, 100 moles of natural gas (100% CH_4) is introduced into the process. The temperature of the feed to the radiant heating section is set at 950° F. while the outlet temperature from the secondary reformer is maintained at 1700° F. The quantity of air which is passed through line 17 and admixed with the steam in line 26 to the subsequently introduced into the secondary reformer is maintained as to provide a ratio of hydrogen and carbon monoxide to nitrogen in the gaseous effluent withdrawn from the secondary reformer of about 3.0.

EXAMPLE I

Case No.	1	2	3
Pressure (p.s.i.g.)	400	400	400
Steam to primary reformer (moles)	630	370	370
Steam to secondary reformer (moles)	0	262	262
Total steam added (moles)	630	632	632
Air to secondary reformer (moles)	142.6	142.6	142.6
Temp. of air+steam to secondary (° F.)	1,000	1,000	1,200
Gas at outlet secondary reformer:			
CH_4 (moles)	0.83	0.83	0.83
CO (moles)	43.9	43.9	43.9
H_2 (moles)	292.8	292.9	292.9
CO_2 (moles)	55.2	55.3	55.3
N_2 (moles)	111.3	111.3	111.3
H_2O (moles)	536.9	537.9	537.9
Fired process duty in primary reformer (MM B.t.u./hr.) (radiant section)	9.180	8.580	8.355
Net fuel saving, percent		6.5	9.0

There was a net fuel saving of 9% with the operation according to case 3 as compared to the operation of case 1 where all of the steam is passed together with the feed through the primary reformer prior to introduction to the secondary reformer.

EXAMPLE II

Case No.	1	2	3
Pressure (p.s.i.g.)	400	400	400
Steam to primary reformer (moles)	1,099	370	370
Steam to secondary reformer (moles)	0	722	722
Total steam added (moles)	1,099	1,092	1,092
Air to secondary reformer (moles)	143.5	143.5	143.5
Temp. of air+steam to secondary (° F.)	1,000	1,000	1,200
Gas at outlet secondary reformer:			
CH_4 (moles)	0.18	0.18	0.18
CO (moles)	31.3	31.3	31.3
H_2 (moles)	307.7	307.7	307.7
CO_2 (moles)	68.6	68.6	68.6
N_2 (moles)	112.0	112.0	112.0
H_2O (moles)	983.4	983.9	983.9
Fired process duty in primary reformer (MM B.t.u./hr.) (radiant section)	12.398	10.712	10.493
Net fuel saving, percent		13.6	15.4

The above example illustrates the additional net fuel savings when introducing 60% more steam to the process as compared with Example I.

EXAMPLE III

Case No.	1	2	3
Pressure (p.s.i.g.)	600	600	600
Steam to primary reformer (moles)	630	370	370
Steam to secondary reformer (moles)	0	260	260
Total steam added (moles)	630	630	630
Air to secondary reformer (moles)	141.3	141.3	141.3
Temp. of air+steam to secondary (° F.)	1,000	1,000	1,200
Gas at outlet secondary reformer:			
CH_4 (moles)	1.77	1.78	1.78
CO (moles)	43.3	43.3	43.3
H_2 (moles)	290.3	290.2	290.2
CO_2 (moles)	55.0	54.9	54.9
N_2 (moles)	110.2	110.2	110.2
H_2O (moles)	537.6	536.3	536.3
Fired process duty in primary reformer (MM B.t.u./hr.) (Radiant section)	9.144	8.528	8.310
Net fuel saving, percent		6.7	9.1

Example III illustrates improved net fuel savings when operating at higher pressures but at the same quantity of steam as set forth in Example I.

As hereinbefore set forth, should it be desirable to produce a gas suitable for the synthesis of methanol, oxygen instead of air is to be admixed with the steam in line 26. Consequently, the term free-oxygen containing gas as used in the claims is to be interpreted as air, oxygen, or oxygen in admixture with inert gases.

It will be understood that the embodiments of the invention set forth above are illustrative only and that certain changes may be made by those skilled in the art within the scope of the invention as defined in the claims

Topsoe, Inc. – EX1003
Page 738 of 1210

We claim:

1. A process for the steam reforming of light hydrocarbons which comprises:

(a) admixing said hydrocarbon feed and steam at a pressure above about 400 p.s.i.g. to provide a feed stream having a molal ratio of steam to carbon atoms of from 3.0:1 to 3.8:1;

(b) heating said feed stream to a temperature above about 1450° F. in the presence of a reforming catalyst in a primary reforming zone to form a gaseous effluent including hydrogen;

(c) preheating a mixture of steam and a free oxygen-containing gas to a temperature of about 1000 to about 1500° F.;

(d) mixing the gaseous effluent of step (b) without further heating, with an amount of the mixture of step (c) to provide an effluent in step (f) containing no greater than about 0.5% of light hydrocarbons;

(e) passing the resulting mixture of step (d) through a secondary reforming zone; and

(f) withdrawing a gaseous effluent from said secondary reforming zone which is rich in hydrogen and contains no greater than about 0.5% of light hydrocarbons.

2. The process defined in claim 1 wherein air is admixed with the steam of step (a) to provide an oxygen content of the stream passing through the catalyst of less than 1.0 mole percent.

3. The process defined in claim 1 wherein the free oxygen-containing gas employed in step (c) is air and the air is present in the mixture in an amount to provide an effluent in step (f) containing about three moles of hydrogen and carbon monoxide per mole of nitrogen.

4. A process for reforming a light hydrocarbon which comprises:

(a) forming a feed mixture of said light hydrocarbon and steam at a pressure above about 400 p.s.i.g. and having a molal ratio of steam to carbon atoms of from 3.0:1 to 3.8:1;

(b) preheating said feed mixture in the convection zone of a primary reformer to a temperature above about 800° F.;

(c) heating said preheated feed mixture in a radiant heating zone of said primary reformer and in the presence of a reforming catalyst;

(d) withdrawing a gaseous effluent including hydrogen from said radiant heating zone at a temperature above about 1450° F.

(e) preheating a mixture of a free-oxygen containing gas and steam in said convection section of said primary reformer to a temperature between about 1000° F. and about 1500° F.;

(f) mixing in a secondary reforming zone the effluent of step (d), without further heating thereof, with an amount of the mixture of step (e) to provide a secondary reforming zone effluent containing no greater than about 0.5% of light hydrocarbons; and

(g) withdrawing a hydrogen-enriched gas from said secondary reforming zone containing no greater than about 0.5% of light hydrocarbons.

5. The process defined in claim 4 wherein the free-oxygen containing gas is air.

6. The process defined in claim 4 wherein the free-oxygen containing gas is oxygen.

7. The process defined in claim 4 wherein air is admixed with the steam of step (a) to provide an oxygen content of the stream passing through the catalyst of less than 1.0 mole percent.

8. The process defined in claim 4 wherein said hydrocarbon feed is natural gas.

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3,278,452	10/1966	Vorum	48—197 X

JOSEPH SCOVRONEK, Primary Examiner

U.S. Cl. X.R.

23—212; 48—196, 197, 214, 215; 252—376

Electronic Acknowledgement Receipt	
EFS ID:	48791783
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:	02-NOV-2023
Filing Date:	26-APR-2023
Time Stamp:	13:32:57
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		20231102_283386WOUS01_495230-44_Amendment_A.pdf	166705 a53fa295fbb2ebfc0ab263734df4384c9c96cfee	yes	21
	Multipart Description/PDF files in .zip description				
	Document Description		**Start**	**End**	
	Response after Ex Parte Quayle Action		1	1	
	Claims		2	7	
	Applicant summary of interview with examiner		8	8	
	Applicant Arguments/Remarks Made in an Amendment		9	21	
Warnings:					
Information:					
2	Miscellaneous Incoming Letter	20231102_283386WOUS01_495230-44_General-Authorization-to-Charge-Fees.pdf	16156 3f6eb6a6754b3a7159ef64b9ce7a931152a5183a	no	1
Warnings:					
Information:					
3	Information Disclosure Statement (IDS) Form (SB08)	20231102_283386WOUS01_495230-44_S1-IDS.pdf	1035111 1068465015452fc5f3d51fa66b77dfb6a5b699b5	no	4
Warnings:					
Information:					
4	Non Patent Literature	NPL_FertliserPolicyForSustainableAgriculture.pdf	3639527 6a79ba153d6d675be26cc6e28b408d5a2fa1dc9d	no	10
Warnings:					
Information:					
5	Non Patent Literature	NPL_LetterFromTopsoeCounsel.pdf	247323 74ed235867b4283a0baae45611cfb0303fbcbad6	no	3
Warnings:					
Information:					

6	Non Patent Literature	NPL_NoticeOfOpposition_EP1870297752_mailed_20220614.pdf	4777463 1ab79ee3c939c9be60b96f510640ed2a74ac048b	no	67
Warnings:					
Information:					
7	Other reference-Patent/Application/ Search Documents	US3479298A.pdf	818208 25332fef989c529032750454c904380f9ec530c2	no	4
Warnings:					
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		Total Files Size (in bytes):	10700493		

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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
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Document Code:WFEE

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Sale Accounting Date:11/02/2023

Sale Item Reference Number	Effective Date
96000424	11/02/2023

Document Number	Fee Code	Fee Code Description	Amount Paid	Payment Method
I2023A2G49396415	2822	REEXAMINATION CLAIMS IN EXCESS OF 20	$80.00	Deposit Account
I2023A2G49396415	2821	REEXAMINATION INDEPENDENT CLAIMS	$192.00	Deposit Account

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:				
REEXAMINATION INDEPENDENT CLAIMS	2821	1	192	192
REEXAMINATION CLAIMS IN EXCESS OF 20	2822	2	40	80
Miscellaneous-Filing:				
Petition:				
Patent-Appeals-and-Interference:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		**272**

Electronic Acknowledgement Receipt	
EFS ID:	48795537
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:	03-NOV-2023
Filing Date:	26-APR-2023
Time Stamp:	11:53:40
Application Type:	Supplemental Examination
Patent Number:	

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$272
RAM confirmation Number	E2023A3B54069807
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	Fee Worksheet (SB06)	fee-info.pdf	39866 9d68357c332bd6159decc0b664fd8f83f34e7538	no	2
Warnings:					
Information:					
		Total Files Size (in bytes):	39866		

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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
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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 11/14/2023
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
11/14/2023	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.

UNITED STATES DEPARTMENT OF COMMERCE
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APPLICATION NO./ CONTROL NO.	FILING DATE	FIRST NAMED INVENTOR/ PATENT IN REEXAMINATION	ATTORNEY DOCKET NO.
96/000,424	04/26/2023	11286168	283386WOUS01_4952

	EXAMINER	
Dorsey & Whitney / UT GENERAL 111 South Main Street 21st Floor Salt Lake City, UT 84111-2176	Jerry D Johnson	
	ART UNIT	PAPER
	3991	20231106

DATE MAILED: _____

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

Commissioner for Patents

The proceeding is terminated in view of Patent Owner's failure to submit a Patent Owner's statement of the August 25, 2023 interview which includes "a complete written statement of the reasons presented at the interview as warranting favorable action" as required by 37 CFR 1.560(b) and MPEP 2281. The brief statement presented with Patent Owner's November 2, 2023 response does not comply with 1.560(b).

Failure to promptly file a 37 CFR 1.137(a) petition to revive the proceeding with a separate complete written statement of the interview which complies with 1.560(b) will result in the issuance of a Notice of Intent to Issue a Ex Parte Reexamination Certificate (NIRC) which will cancel the rejected claims.

/Alan Diamond/ /Jean C. Witz/ Supervisor Patent Reexam Spec., CRU 3991	/JERRY D JOHNSON/ Patent Reexam Specialist, CRU 3991

PTO-90C (Rev.04-03)

VIA eFILE

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.:	9950	)
		)
Customer No.:	116407	)
		)
Examiner:	Jerry Johnson	)

PATENT OWNER'S STATEMENT OF THE INTERVIEW UNDER 37 C.F.R. 1.560(b)

Patent Owner received a Miscellaneous Communication from the U.S. Patent and Trademark Office ("PTO") dated November 14, 2023, indicating the Reexamination Proceeding was terminated in view of Patent Owner's failure to submit a Patent Owner's statement of the August 25, 2023 interview. Patent Owner respectfully submits that a good faith effort was made to submit a Patent Owner's statement of the interview with the Response filed November 2, 2023. In addition to the new Patent Owner's statement of the interview provided herein, a petition under 37 CFR 1.137(a) to revive the Reexamination Proceeding is filed concurrently with the new 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. Present on the telephone for the interview were Patent Reexamination Specialist Jerry Johnson, Patent Reexamination Specialist Alan Diamond, Supervisory Patent Reexamination Specialist Jean C. Witz, Patent Owner Representative Marcus Simon, and Patent Owner Representative Jonathan Rowe.

Topsoe, Inc. – EX1003
Page 750 of 1210

Multiple proposed amendments to independent claim 1 were discussed in the interview as set forth below in greater detail. No agreement was reached regarding patentable subject matter during the interview.

Patent Owner proposed amending independent claim 1 to further recite "addition of nitrogen to the synthesis gas." Patent Owner respectfully submitted this proposed amendment to claim 1 warranted favorable action because the PTO acknowledges Licht (U.S. Patent No. 8,137,422) does not disclose "addition of nitrogen to the synthesis gas," and one of ordinary skill in the art would not be motivated to combine the alleged addition of nitrogen of Reddy (U.S. Patent Application Publication No. 2004/0234426) or EP 2817260 ("EP '260") with the system of Licht because Licht is directed to hydrogen production. The Examiners asserted the indication in Licht that secondary reforming reactors are well-known and widely used for the production of ammonia (*see* Licht, col. 7, ll. 17-19) rendered such an addition obvious either in view of Licht or other references.

Patent Owner further proposed amending independent claim 1 to further recite "addition of nitrogen to the synthesis gas" and also "wherein the conversion of the charge of desulphurized natural gas includes a step of autothermal reforming or a step of partial oxidation." In addition to the reasons provided above, Patent Owner respectfully submitted this proposed amendment to claim 1 warranted favorable action because the alleged disclosures of EP '260 are steps expressly performed without a primary reformer that teach away from a combination with Licht, as Licht appears to require a primary reformer. The Examiners asserted that Licht teaches an autothermal reformer in the secondary reforming reactor of Licht, and that the process of EP '260 does not include a primary reformer.

Patent Owner further proposed amending independent claim 1 to further recite "addition of nitrogen to the synthesis gas," "wherein the conversion of the charge of desulphurized natural gas includes a step of autothermal reforming or a step of partial oxidation," and also "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." In addition to the reasons provided above, Patent Owner respectfully submitted this proposed amendment to claim 1 warranted favorable action because Licht appears to be silent about the trim fuel and its relation to total combustion heat, and 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 without the trim fuel accounting

Topsoe, Inc. – EX1003
Page 751 of 1210

for not more than 15% of a total combustion heat of the at least one furnace. The Examiners asserted that Licht teaches natural gas a trim fuel at col. 5, ll. 37-41.

Patent Owner further proposed amending independent claim 1 to further recite "addition of nitrogen to the synthesis gas," "wherein the conversion of the charge of desulphurized natural gas includes a step of autothermal reforming or a step of partial oxidation," and also "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." In addition to the reasons provided above, Patent Owner respectfully submitted this proposed amendment to claim 1 warranted favorable action because it incorporated dependent claim 10 while removing the "one or more burners of a primary steam reformer" present in claim 10. Thus, the PTO had 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." The Examiners asserted such an amendment would not result in patentability of claim 1.

Patent Owner further proposed amending independent claim 1 to further recite "addition of nitrogen to the synthesis gas," "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 also "conversion of the charge of desulphurized natural gas and steam is performed without any primary reforming." In addition to the reasons provided above, Patent Owner respectfully submitted this proposed amendment to claim 1 warranted favorable action because "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. The Examiners asserted such an amendment would not result in patentability of claim 1.

Patent Owner further proposed amending independent claim 1 to further recite "addition of nitrogen to the synthesis gas," "wherein the conversion of the charge of desulphurized natural gas includes a step of autothermal reforming preceded by a pre-reforming," "wherein said fuel

Topsoe, Inc. – EX1003
Page 752 of 1210

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." In addition to the reasons provided above, Patent Owner respectfully submitted this proposed amendment to claim 1 warranted favorable action because "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. The Examiners asserted that the use of a pre-reformer in the present specification is optional, and that the process of EP '260 does not include a primary reformer.

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 15th 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

UNITED STATES
PATENT AND TRADEMARK OFFICE

P.O. Box 1450
Alexandria, VA 22313 - 1450
www.uspto.gov

ELECTRONIC PAYMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
96/000,424	11/15/2023 05:37:03 PM Z ET	283386WOUS01_495230-44

Title of Invention

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

Application Information

APPLICATION TYPE	Utility - Reexamination based on supplemental examination	PATENT #	-
CONFIRMATION #	9950	FILED BY	Samantha Mayo
PATENT CENTER #	63267025	AUTHORIZED BY	Marcus Simon
CUSTOMER #	116407	FILING DATE	04/26/2023
CORRESPONDENCE ADDRESS	-	FIRST NAMED INVENTOR	- 11286168

Payment Information

PAYMENT METHOD	PAYMENT TRANSACTION ID	PAYMENT AUTHORIZED BY
CARD / 1083	E2023AEH38466064	Samantha Mayo

PRE-AUTHORIZED ACCOUNT
506181

PRE-AUTHORIZED CATEGORY
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)

FEE CODE	DESCRIPTION	ITEM PRICE($)	QUANTITY	ITEM TOTAL($)
2454	PETITION FOR THE DELAYED SUBMISSION OF A PRIORITY OR BENEFIT CLAIM, OR TO RESTORE THE RIGHT OF PRIORITY OR BENEFIT	840.00	1	840.00
			TOTAL AMOUNT:	$840.00

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 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.

Doc Code: PET.OP
Document Description: Petition for Review by the Office of Petitions

PTO/SB/64 (11-23)
Approved for use through 05/31/2024. 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 displays a valid OMB control number.

PETITION FOR REVIVAL OF AN APPLICATION FOR PATENT ABANDONED UNINTENTIONALLY UNDER 37 CFR 1.137(a)

Docket Number (Optional): 283386WOUS01_495230-44

First named inventor: Francesco Baratto

Application No.: 96/000,424 Art Unit: 3991

Filed: April 26, 2023 Examiner: JERRY D JOHNSON

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

Attention: Office of Petitions
Mail Stop Petition
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450
FAX (571) 273-8300

NOTE: If information or assistance is needed in completing this form, please contact the Office of Petitions at (571) 272-3282.

The above-identified application became abandoned for failure to file a timely and proper reply to a notice or action by the United States Patent and Trademark Office. The date of abandonment is the day after the expiration date of the period set for reply in the Office notice or action plus any extensions of time actually obtained.

APPLICANT HEREBY PETITIONS FOR REVIVAL OF THIS APPLICATION.

NOTE: A grantable petition requires the following items:

(1) Petition fee;
(2) Reply and/or issue fee;
(3) Terminal disclaimer with disclaimer fee – required for all utility and plant applications filed before June 8, 1995, and for all design applications; and
(4) Statement that the entire delay was unintentional.

1. **Petition fee (37 CFR 1.17(m))**

☑ Small entity fee $ 840 (Fee Code 2453). Applicant asserts small entity status. See 37 CFR 1.27.

☐ Micro entity fee $ _____ (Fee Code 3453). Applicant has established or is establishing micro entity status. See 37 CFR 1.29. Form PTO/SB/15A or B or equivalent must either be enclosed or have been submitted previously.

☐ Other than a small or micro entity (undiscounted) fee $ _____ (Fee Code 1453).

2. **Reply and/or fee**

A The reply and/or fee to the above-noted Office notice or action in the form of

Patent Owner's Statement of the Interview (identify the type of reply):

☐ has been filed previously on _____.

☑ is enclosed herewith.

B The issue fee and publication fee (if applicable) of $ _____

☐ has been paid previously on _____.

☐ is enclosed herewith.

A Federal agency may not conduct or sponsor, and a person is not required to respond to, nor shall a person be subject to a penalty for failure to comply with an information collection subject to the requirements of the Paperwork Reduction Act of 1995, unless the information collection has a currently valid OMB Control Number. The OMB Control Number for this information collection is 0651-0031. Public burden for this form is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the information collection. Send comments regarding this burden estimate or any other aspect of this information collection, including suggestions for reducing this burden to the Chief Administrative Officer, United States Patent and Trademark Office, P.O. Box 1450, Alexandria, VA 22313-1450 or email InformationCollection@uspto.gov. **DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS**. If filing this completed form by mail, send to: **Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450**.

If you need assistance in completing the form, call 1-800-PTO-9199 and select option 2.

Doc Code: PET.OP
Document Description: Petition for Review by the Office of Petitions

PTO/SB/64 (11-23)
Approved for use through 05/31/2024. OMB 0651-0031
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
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PETITION FOR REVIVAL OF AN APPLICATION FOR PATENT ABANDONED UNINTENTIONALLY UNDER 37 CFR 1.137(a)

3. **Terminal disclaimer with disclaimer fee**

☑ Since this utility/plant application was filed on or after June 8, 1995, no terminal disclaimer is required.

☐ A terminal disclaimer (and disclaimer fee (37 CFR 1.20(d)) of $ _____) disclaiming the required period of time is enclosed herewith (see PTO/SB/63).

4. STATEMENT: The entire delay in filing the required reply from the due date for the required reply until the filing of a grantable petition under 37 CFR 1.137(a) was unintentional.

Petitioner is reminded that a delay resulting from a deliberately chosen course of action on the part of the applicant does not become an "unintentional" delay within the meaning of 37 CFR 1.137 because:

- the applicant does not consider the claims to be patentable over the references relied upon in an outstanding Office action;
- the applicant does not consider the allowed or patentable claims to be of sufficient breadth or scope to justify the financial expense of obtaining a patent;
- the applicant does not consider any patent to be of sufficient value to justify the financial expense of obtaining the patent; or
- the applicant remains interested in eventually obtaining a patent, but simply seeks to defer patent fees and patent prosecution expenses.

Petitioner is further reminded that an intentional delay resulting from a deliberate course of action chosen by the applicant is not affected by:

- the correctness of the applicant's (or applicant's representative's) decision to abandon the application or not to seek or persist in seeking revival of the application;
- the correctness or propriety of a rejection, or other objection, requirement, or decision by the Office; or
- the discovery of new information or evidence, or other change in circumstances subsequent to the abandonment or decision not to seek or persist in seeking revival.

NOTE: Where the petition under 37 CFR 1.137(a) is filed more than two years after the date the application became abandoned, the United States Patent and Trademark Office requires an additional explanation of the circumstances surrounding the delay that establishes the entire delay was unintentional. This requirement is in addition to the requirement to provide a statement that the entire delay was unintentional. See *Clarification of the Practice for Requiring Additional Information in Petitions Filed in Patent Applications and Patents Based on Unintentional Delay*, 85 FR 12222 (March 2, 2020). See MPEP 711.03(c)(II)(C)-(F) for additional guidance on the information required to establish that the entire delay was unintentional.

☐ Because this petition under 37 CFR 1.137(a) is being filed more than two years after the date the application became abandoned, additional explanation of the circumstances surrounding the delay that establishes the entire delay was unintentional is enclosed herewith.

Doc Code: PET.OP
Document Description: Petition for Review by the Office of Petitions

PTO/SB/64 (11-23)
Approved for use through 05/31/2024. 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 displays a valid OMB control number.

PETITION FOR REVIVAL OF AN APPLICATION FOR PATENT ABANDONED UNINTENTIONALLY UNDER 37 CFR 1.137(a)

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

***This petition must be signed in accordance with 37 CFR 1.33. Please see 37 CFR 1.4(d) for the signature requirements. Submit multiple forms if more than one signature is required.**

/Marcus S. Simon, Reg.# 50258/	November 15, 2023
Signature*	Date
Marcus S. Simon	50258
Typed or Printed Name	Registration Number, if applicable
111 S. Main Street, Suite 2100, Salt Lake City, UT 84111	801-933-7360
Address	Telephone Number
Address	

Enclosures:

- [x] Petition fee under 37 CFR 1.17(m)
- [x] Reply and/or fee
- [ ] Terminal Disclaimer Form
- [ ] Additional sheet(s) containing statements establishing unintentional delay
- [ ] Other: _____

CERTIFICATE OF MAILING OR TRANSMISSION [37 CFR 1.8(a)]

I hereby certify that this correspondence is being:

- [ ] Deposited with the United States Postal Service on the date shown below with sufficient postage as first class mail in an envelope addressed to: Mail Stop Petition, Commissioner for Patents, P. O. Box 1450, Alexandria, VA 22313-1450.
- [ ] Transmitted by USPTO patent electronic filing system, or by facsimile to (571)273-8300, to the USPTO on the date shown below.

Date	Signature
	Typed or printed name of person signing certificate

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. The United States Patent and Trademark Office (USPTO) collects the information in this record under authority of 35 U.S.C. 2. The USPTO's system of records is used to manage all applicant and owner information including name, citizenship, residence, post office address, and other information with respect to inventors and their legal representatives pertaining to the applicant's/owner's activities in connection with the invention for which a patent is sought or has been granted. The applicable Privacy Act System of Records Notice for the information collected in this form is COMMERCE/PAT-TM-7 Patent Application Files, available in the Federal Register at 78 FR 19243 (March 29, 2013). https://www.govinfo.gov/content/pkg/FR-2013-03-29/pdf/2013-07341.pdf

Routine uses of the information in this record may include disclosure to:

1) law enforcement, in the event that the system of records indicates a violation or potential violation of law;

2) a federal, state, local, or international agency, in response to its request;

3) a contractor of the USPTO having need for the information in order to perform a contract;

4) the Department of Justice for determination of whether the Freedom of Information Act (FOIA) requires disclosure of the record;

5) a Member of Congress submitting a request involving an individual to whom the record pertains, when the individual has requested the Member's assistance with respect to the subject matter of the record;

6) a court, magistrate, or administrative tribunal, in the course of presenting evidence, including disclosures to opposing counsel in the course of settlement negotiations;

7) the Administrator, General Services Administration (GSA), or their designee, during an inspection of records conducted by GSA under authority of 44 U.S.C. 2904 and 2906, in accordance with the GSA regulations and any other relevant (i.e., GSA or Commerce) directive, where such disclosure shall not be used to make determinations about individuals;

8) 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));

9) the Office of Personnel Management (OPM) for personnel research purposes; and

10) the Office of Management and Budget (OMB) for legislative coordination and clearance.

If you do not furnish the information requested on this form, the USPTO may not be able to process and/or examine your submission, which may result in termination of proceedings, abandonment of the application, and/or expiration of the patent.

UNITED STATES
PATENT AND TRADEMARK OFFICE

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Alexandria, VA 22313 - 1450
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ELECTRONIC ACKNOWLEDGEMENT RECEIPT

APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
96/000,424	**11/15/2023 05:37:03 PM Z ET**	**283386WOUS01_495230-44**

Title of Invention

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

Application Information

APPLICATION TYPE	Utility - Reexamination based on supplemental examination	PATENT #	-
CONFIRMATION #	9950	FILED BY	Samantha Mayo
PATENT CENTER #	63267025	FILING DATE	04/26/2023
CUSTOMER #	116407	FIRST NAMED INVENTOR	- 11286168
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Marcus Simon

Documents

TOTAL DOCUMENTS: 2

DOCUMENT	PAGES	DESCRIPTION	SIZE (KB)
20231115_283386WOUS01_495230-44_Patent-Owners-Statement-of-the-Interview.pdf	4	Miscellaneous Incoming Letter	120 KB
20231115_283386WOUS01_495230-44_Petition-for-Revival.pdf	4	Miscellaneous Incoming Letter	427 KB

Digest

DOCUMENT	MESSAGE DIGEST(SHA-512)

20231115_283386WOUS01_495230-44_Patent-Owners-Statement-of-the-Interview.pdf	0160180BD0AD231ECCB3CC95009D67B4CA385FB4461FF953E1D143C7DF01539BE733E87404F71C0AF43B7FBA71428D15B7CE057A449770F335D9295DC41575B1
20231115_283386WOUS01_495230-44_Petition-for-Revival.pdf	66B8D5B027C3C5C2B97BF5B37CEBE54D2AA3590DAC8CD274EA32BAC0DC59858FE1129C6C199B72A4C6D9CB0815B7066BF998955DDCF465C500EF848865E2B888

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 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

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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 03/14/2024

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
03/14/2024	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.

UNITED STATES PATENT AND TRADEMARK OFFICE

Commissioner for Patents
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Dorsey & Whitney / UT GENERAL
111 South Main Street
21st Floor
Salt Lake City, Utah 84111-2176

In re Casale SA	:	
Ex Parte Reexamination Proceeding	:	**DECISION GRANTING**
Control No. 96/000,424	:	**PETITION UNDER**
Filed: April 26, 2023	:	**37 CFR 1.137(a)**
For: U.S. Patent No. 11,286,168	:	

This is a decision on the November 15, 2023, patent owner petition under 37 CFR 1.137(a) to accept an unintentionally delayed written statement under 37 CFR 1.560(b) and revive the present "terminated"[1] reexamination prosecution ("the November 15, 2023, petition to revive").

The November 15, 2023, petition to revive is before the Office of Patent Legal Administration for consideration.

The November 15, 2023, petition to revive is **granted**.

All citations to 37 CFR Part 1 (*e.g.*, 37 CFR 1.137) are to the regulations in effect as of the filing date of this petition.

STATUTES, REGULATIONS, AND PATENT EXAMINING PROCEDURES

35 U.S.C. 41(a)(7) provides, in pertinent part:

> REVIVAL FEES. — On filing each petition ... for the delayed response by the patent owner in any reexamination proceeding ...

35 U.S.C. 133 provides:

> Upon failure of the applicant to prosecute the application within six months after any action therein, of which notice has been given or mailed to the

[1] Although a Notice of Intent to Issue *Ex Parte* Reexamination Certificate (NIRC) has not been mailed to set forth the termination of the prosecution in this instance, the prosecution was "terminated" within the meaning of 37 CFR 1.550(d) for failure of the patent owner to timely file a compliant written statement, as required under 37 CFR 1.560(b), for the interview of August 21, 2023.

applicant, or within such shorter time, not less than thirty days, as fixed by the Director in such action, the application shall be regarded as abandoned by the parties thereto.

35 U.S.C. 305 provides, in pertinent part:

After the times for filing the statement and reply provided for by section 304 have expired, reexamination will be conducted according to the procedures established for initial examination under the provisions of sections 132 and 133.

37 CFR 1.137 provides, in pertinent part:

(a) *Revival on the basis of unintentional delay.* If the delay in reply by ... patent owner was unintentional, a petition may be filed pursuant to this section to revive ... a reexamination prosecution terminated under § 1.550(d) or § 1.957(b) or limited under § 1.957(c).

(b) *Petition requirements.* A grantable petition pursuant to this section must be accompanied by:

(1) The reply required to the outstanding Office action or notice, unless previously filed;
(2) The petition fee as set forth in § 1.17(m);
*
(4) A statement that the entire delay in filing the required reply from the due date for the reply until the filing of a grantable petition pursuant to this section was unintentional. The Director may require additional information where there is a question whether the delay was unintentional.

*

(d) *Terminal disclaimer.*

*

*

(3) The provisions of paragraph (d)(1) of this section do not apply to ... reexamination proceedings.

37 CFR 1.550 provides, in pertinent part:

(d) If the patent owner fails to file a timely and appropriate response to any Office action or any written statement of an interview required under § 1.560(b), the prosecution in the *ex parte* reexamination proceeding will be a terminated prosecution, and the Director will proceed to issue and publish a certificate concluding the reexamination proceeding under § 1.570 in accordance with the last action of the Office.

(e) If a response by the patent owner is not timely filed in the Office, a petition may be filed pursuant to § 1.137 to revive a reexamination prosecution

terminated under paragraph (d) of this section if the delay in response was unintentional.

37 CFR 1.560(b) provides:

In every instance of an interview with an examiner in an *ex parte* reexamination proceeding, a complete written statement of the reasons presented at the interview as warranting favorable action must be filed by the patent owner. An interview does not remove the necessity for response to Office actions as specified in § 1.111. Patent owner's response to an outstanding Office action after the interview does not remove the necessity for filing the written statement. The written statement must be filed as a separate part of a response to an Office action outstanding at the time of the interview, or as a separate paper within one month from the date of the interview, whichever is later.

MPEP 2268 provides, in pertinent part:

*

II. PETITION BASED ON UNINTENTIONAL DELAY

37 CFR 1.137(a), as amended in the final rule to implement the PLTIA, provides that if the delay in reply by patent owner was unintentional, a petition may be filed pursuant to 37 CFR 1.137 to revive a reexamination prosecution terminated under 37 CFR 1.550(d).

*

IV. FURTHER DISCUSSION OF THE PETITION REQUIREMENTS

See also MPEP § 711.03(c) for a detailed discussion of the requirements of petitions filed under 37 CFR 1.137.

DECISION

The Petition Under 37 CFR 1.137(a) is Granted

A grantable petition under 37 CFR 1.137(a) for a reexamination proceeding must be accompanied by: (1) a response to the outstanding Office action; (2) the petition fee set forth in 37 CFR 1.17(m); and (3) a proper statement under 37 CFR 1.137(b)(4) that the entire delay in filing the required response from the due date of the response to the filing of a grantable petition was unintentional. The present proceeding is a reexamination proceeding; thus, the petition does not require a terminal disclaimer.[2]

[2] See 37 CFR 1.137(d)(3).

Regarding item (1), this reexamination proceeding was terminated due to the failure to timely submit a compliant written statement pursuant to 37 CFR 1.560(b) for the interview of August 21, 2023.

37 CFR 1.560(b) requires the submission of the written statement as a separate part of a response to an Office action outstanding at the time of the interview, or as a separate paper filed within one month from the date of the interview, whichever is later. A response to a nonfinal rejection issued July 7, 2023, was outstanding at the time of the August 21, 2023, interview.

However, patent owner did not submit a written statement pursuant to 37 CFR 1.560(b) as a separate paper on or before September 21, 2023, i.e., within one month from the August 21, 2023, interview date. Nor did the amendment and response that patent owner filed on November 2, 2023[3], include a written statement pursuant to 37 CFR 1.560(b).

For the purpose of evaluating whether the November 15, 2023, petition to revive is a grantable petition, the submission of a written statement under 37 CFR 1.560(b) on November 15, 2023, satisfies item (1).

The petition fee set forth in 37 CFR 1.17(m) for the November 15, 2023, petition to revive has been paid, which satisfies item (2).

Item (3) has been satisfied by the statement provided in the November 15, 2023, petition to revive.

Accordingly, the November 15, 2023, patent owner petition to revive is **granted**. Prosecution in the above-identified reexamination proceeding is resumed.

CONCLUSION

1. The November 15, 2023, patent owner petition under 37 CFR 1.137(a) is **granted**.

2. The 96/000,424 proceeding is being forwarded to the Central Reexamination Unit to proceed as necessary consistent with the procedural status of this proceeding and this decision.

3. Any inquiry concerning the examination of this reexamination proceeding should be directed to the primary examiner, Jerry D. Johnson, of Art Unit 3991, at 571-272-1448.

[3] On August 25, 2023, the Office extended the time period for responding to the July 7, 2023, to November 7, 2023, in view of a petition for extension of time filed August 23, 2023.

4. Any inquiry concerning this decision should be directed to the undersigned at 571-272-7728.[4]

/Raul Tamayo/
Raul Tamayo
Senior Legal Advisor
Office of Patent Legal Administration
Office of the Deputy Commissioner for Patents

March 14, 2024

[4] Note that all practice before the Office should be in writing, and the action of the Office will be based exclusively on the written record in the Office. *See* 37 CFR 1.2. As such, petitioner is reminded that no telephone discussion may be controlling or considered authority for petitioner's further action(s).

UNITED STATES PATENT AND TRADEMARK OFFICE

UNITED STATES DEPARTMENT OF COMMERCE
United States Patent and Trademark Office
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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 04/22/2024

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
04/22/2024	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.

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 June 28, 2023.

A non-final Office Action rejecting claims 1-12, 14-17 and 19-23 was mailed July 7, 2023. An amendment amending claims 1, 10, 19 and 21, canceling claim 20, and adding new claims 24-26 was filed November 2, 2023 by patent owner.

Scope of Claims

The '168 patent, as amended November 2, 2023, contains claims 1-19 and 21-26. Claims 1, 21, 24 and 26 are representative:

> **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 <u>including an autothermal reformer downstream from a pre-reformer and without a primary reformer therebetween</u>;
>
> 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. (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.

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 compositions, 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.

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 including an autothermal reformer downstream 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 compositions, 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.

While the preamble of independent claims 1 and 26 recite "A process for synthesis of ammonia from natural gas", claims 1 and 26 do not require that ammonia is produced. In fact, the claims specifically state "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 these claims.

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 21-23 are rejected under 35 U.S.C. 103 as being unpatentable over the admitted prior art in view of U.S. Patent 8,137,422 to Licht et al. (Licht '422) and EP 2 817 260 (EP '260).

Under the section "PRIOR ART", the '168 patent teaches that ammonia synthesis plants of the prior art comprise a section adapted to convert the natural gas into a make-up gas containing hydrogen and nitrogen, and a synthesis section wherein said make-up gas reacts catalytically at high pressure to produce ammonia. The section which generates said make-up gas is referred to in the technical language as the "front end". The term "back end" is instead used to denote the section for ammonia synthesis . In the front end, 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 comprises (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.

Accordingly, Licht '422 teaches a "front end" process for producing a hydrogen-containing product gas with reduced carbon dioxide emissions compared to conventional "front end" hydrogen production processes.

EP '260 teaches a process for synthesis of ammonia from natural gas comprising an air separation unit (ASU). Nitrogen from the ASU is used to adjust the hydrogen to nitrogen ratio in the process. Preferably said nitrogen is produced in the same ASU unit which produces the oxygen for the reformer in oxygen-fired embodiments (i.e, "the oxygen-rich gas" of Licht '422) [0025]. Nitrogen is combined with the "front end" product steam and fed to the "back end" ammonia synthesis section (Figure 1).

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. In so doing, it would have been obvious to include an ASU as taught by EP '260 to provide nitrogen to the ammonia synthesis section as well as an oxygen-rich gas taught by Licht '422.

II. Claims 24 and 25 are rejected under 35 U.S.C. 103 as being unpatentable over EP '260 in view of "Ammonia: Principles and Industrial Practice" (hereafter "Ammonia").

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]. 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].

EP '260 differs from the claims in not teaching nitrogen wash of the carbon dioxide-depleted stream.

Ammonia, pages 137-138 teaches for partial oxidation processes

> [l] iquid nitrogen wash [754]-[756] delivers a gas to the synthesis loop that is free of all impurities, including inert gases and is also the means for adding some or all of the nitrogen required for synthesis.
>
> The nitrogen is liquefied in a refrigeration cycle by compression, cooling, and expansion. It flows to the top of a wash column, where it countercurrently contacts precooled synthesis gas from which most of the methane and hydrocarbons have been condensed. All of the cold equipment is installed in an insulate "cold box." The wash column temperature is about -190 °C. Liquid nitrogen wash systems are in operation at pressures up to 8 MPa corresponding to the highest gasification pressures. Careful surveillance of the inlet gases is required. As water and carbon dioxide in the inlet gas will freeze, causing operating difficulties, removal of these impurities down to a very low level is required. Traces of nitric oxide (NO) may react with olefinic hydrocarbons, causing explosions [757]. [758].
>
> Normally, an air separation plant is installed in conjunction with liquid nitrogen wash for economy in operation.

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 liquid nitrogen wash of the CO2-depleted synthesis gas to remove impurities and to supply some or all of the nitrogen required for ammonia synthesis in a process as taught by EP '260 because Ammonia teaches that a liquid nitrogen wash is conventionally used for partial oxidation processes, e.g., a partial oxidation

reactor, as taught by EP '260. In doing so, it would have been obvious to dry the inlet gas prior to the liquid nitrogen wash so as to remove water and avoid operating difficulties. Furthermore, as to claim 25, it would have been obvious to incorporate the liquid nitrogen wash after the fuel fraction has been separated from the CO2-depleted synthesis gas so as to avoid unnecessary purification of the fuel fraction and to minimize the cost of the liquid nitrogen wash process step.

III. Claim 26 is rejected under 35 U.S.C. 102(a)(1) as being anticipated by EP '260.

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]. 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; Figure 2].

The fuel gas can be entirely used as a fuel in the fired heater of the ammonia plant, to preheat the process feeds and superheat the steam, thereby containing the overall consumption of the natural gas fuel [0034].

Response to Arguments

Applicant's arguments filed November 2, 2023, to the extent they apply to the instant grounds of rejection, have been fully considered but they are not persuasive.

As to the rejection of claims 21 and 23, applicant argues

> EP '260 does not cure the 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. (Remarks, page 15)

Patent owner's argument is not persuasive because the teachings of EP '260 are not limited to "a tail gas having a different quality and pressure than a fuel fraction which is a portion of the CO2-depleted synthesis gas" as argued. Figure 3 of EP '260 discloses fuel gas 22 which is a portion of the CO2-depleted synthesis gas.

Claims Patentable

Claims 1-19 are patentable. The following is a statement of reasons for the indication of patentable subject matter: The claims, as amended, require an autothermal reformer downsteam from a pre-reformer and without a primary reformer therebetween which arrangement is not taught by the cited prior art.

Conclusion

Patent owner's amendment filed November 2, 2023 necessitated the new grounds of rejection presented in this Office action. Accordingly, **THIS ACTION IS MADE FINAL**. See MPEP § 706.07(a).

A shortened statutory period for response to this action is set to expire two months from the mailing date of this action.

Extensions of time under 37 CFR 1.136(a) do not apply in reexamination proceedings. The provisions of 37 CFR 1.136 apply only to "an applicant" and not to parties in a reexamination proceeding. Further, in 35 U.S.C. 305 and in 37 CFR 1.550(a), it is required that reexamination proceedings "will be conducted with special dispatch within the Office."

Extensions of time in reexamination proceedings are provided for in 37 CFR 1.550(c). A request for extension of time must specify the requested period of extension and it

must be accompanied by the petition fee set forth in 37 CFR 1.17(g). Any request for an extension in a third party requested ex parte reexamination must be filed on or before the day on which action by the patent owner is due, and the mere filing of a request will not effect any extension of time. A request for an extension of time in a third party requested ex parte reexamination will be granted only for sufficient cause, and for a reasonable time specified. Any request for extension in a patent owner requested ex parte reexamination (including reexamination ordered under 35 U.S.C. 257) for up to two months from the time period set in the Office action must be filed no later than two months from the expiration of the time period set in the Office action. A request for an extension in a patent owner requested ex parte reexamination for more than two months from the time period set in the Office action must be filed on or before the day on which action by the patent owner is due, and the mere filing of a request for an extension for more than two months will not effect the extension. The time for taking action in a patent owner requested ex parte reexamination will not be extended for more than two months from the time period set in the Office action in the absence of sufficient cause or for more than a reasonable time.

The filing of a timely first response to this final rejection will be construed as including a request to extend the shortened statutory period for an additional two months. In no event, however, will the statutory period for response expire later than SIX MONTHS from the mailing date of the final action. See MPEP § 2265.

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

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 02 November 2023.
☐ 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 1-19 and 21-26 are subject to reexamination.
1b. ☐ Claims _____ are not subject to reexamination.
2. ☐ Claims _____ have been canceled in the present reexamination proceeding.
3. ☑ Claims 1-19 are patentable and/or confirmed.
4. ☑ Claims 21-26 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)

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	04/16/2024							
	1	✓	=							
	2	✓	=							
	3	✓	=							
	4	✓	=							
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	17	✓	=							
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	19	✓	=							
	20	✓	-							
	21	✓	✓							
	22	✓	✓							
	23	✓	✓							
	24		✓							
	25		✓							
	26		✓							

Doc code: IDS
Doc description: Information Disclosure Statement (IDS) Filed

PTO/SB/08a (02-18)
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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
/J.D.J/	1	3479298	A	1969-11-18	SZE, et al.	

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	1							

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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

/J.D.J/	1	Notice of Opposition for European Patent Application No. 18702977.2 mailed June 14, 2022	
/J.D.J/	2	Response letter from Topsoe counsel dated June 13, 2023	
/J.D.J/	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	/JERRY D JOHNSON/	Date Considered	04/16/2024

*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.

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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.

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AO 120 (Rev. 08/10)

TO:	REPORT ON THE FILING OR DETERMINATION OF AN ACTION REGARDING A PATENT OR TRADEMARK
Mail Stop 8 Director of the U.S. Patent and Trademark Office P.O. Box 1450 Alexandria, VA 22313-1450	

In Compliance with 35 U.S.C. § 290 and/or 15 U.S.C. § 1116 you are hereby advised that a court action has been filed in the U.S. District Court Southern District of Texas, Galveston Division on the following

☐ Trademarks or ☑ Patents. (☐ the patent action involves 35 U.S.C. § 292.):

DOCKET NO.	DATE FILED	U.S. DISTRICT COURT
3:24-cv-00033	1/31/2024	Southern District of Texas, Galveston Division

PLAINTIFF	DEFENDANT
Topsoe, Inc.	Casale US, Inc. and Casale SA

	PATENT OR TRADEMARK NO.	DATE OF PATENT OR TRADEMARK	HOLDER OF PATENT OR TRADEMARK
1	11,286,168	3/29/2022	Casale SA
2			
3			
4			
5			

In the above---entitled case, the following patent(s)/ trademark(s) have been included:

DATE INCLUDED	INCLUDED BY ☐ Amendment ☐ Answer ☐ Cross Bill ☐ Other Pleading		
	PATENT OR TRADEMARK NO.	DATE OF PATENT OR TRADEMARK	HOLDER OF PATENT OR TRADEMARK
1			
2			
3			
4			
5			

In the above---entitled case, the following decision has been rendered or judgement issued:

DECISION/JUDGEMENT

CLERK	(BY) DEPUTY CLERK	DATE

Copy 1---Upon initiation of action, mail this copy to Director Copy 3---Upon termination of action, mail this copy to Director
Copy 2---Upon filing document adding patent(s), mail this copy to Director Copy 4---Case file copy

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January 31, 2024

Via Email (rbiazzi@zardi.ch)

Mr. Riccardo Biazzi
M. Zardi & Co. SA
Via G.B. Pioda 6 6900
Lugano CH

Via Email (collard.case@dorsey.com)

Mr. Case Collard
Dorsey & Whitney LLP
1400 Wewatta Street, Suite 400
Denver, CO 80202-5549

Dear Mr. Biazzi and Mr. Collard:

Earlier Topsoe filed the attached complaint against Casale US, Inc. and Casale SA (collectively "Casale") in the Southern District of Texas.

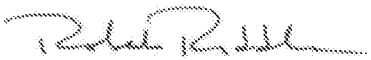
As a courtesy to your client, we have not yet served it. If your client wishes to discuss a possible resolution of this matter, please contact me by no later than close of business on February 7, 2024. Any such resolution would have to, at a minimum, include a covenant not to sue Topsoe or its licensees regarding U.S. Patent No. 11,286,168 and any related patents, including EP 3 583 067 B1, and an agreement to refrain from any further communications with Topsoe's customers or other third parties asserting or implying that Topsoe infringes these patents. As Topsoe has previously requested, we also would require Casale to identify in writing any third parties with whom it has had any communications asserting or implying that Topsoe infringes the patents, including the date of the communications, the parties to the communication, and a copy of any communications that were made in writing.

ReedSmith

In the event that your clients do not wish to discuss a resolution at this time, we ask you to let us know whether you will accept service of the complaint on behalf of your clients and waive service of a summons. Pursuant to Rule 4(d), we have attached the required notices and requests, as well as a form waiver.

We look forward to hearing from you.

Very truly yours,



Robert R. Riddle

Attachment

Cc: Kenneth A. Kuwayti

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Espacenet

CN102533365A Process for coproducing liquefied natural gas (LNG) and synthetic ammonia

Applicants: AEROSPACE CHANGZHENG ENG CO LTD

Inventors: HUI ZHAO,YONG HAN,DANYU LUO,YUYING ZHU,CONGBIN JIANG

Classifications:

IPC ***C01C1/04; C10L3/08; C10L3/10;***

CPC **F25J3/0219 (EP); F25J3/0233 (EP); F25J3/0276 (EP);** F25J2205/30 (EP); F25J2210/20 (EP); F25J2210/42 (EP); F25J2215/04 (EP); F25J2245/42 (EP); F25J2270/12 (EP); F25J2270/18 (EP); F25J2270/66 (EP); Y02P20/10 (EP); Y02P20/129 (EP);

Priorities: CN201110412589A 2011-12-12

Application: CN201110412589A·2011-12-12

Publication: CN102533365A·2012-07-04

Published as: CN102533365A;**CN102533365B**

Process for coproducing liquefied natural gas (LNG) and synthetic ammonia

Abstract

The invention belongs to the technical field of coal chemical industry and particularly relates to a process for coproducing gasified synthetic ammonia and liquefied natural gas (LNG). The invention provides a method and equipment for coproducing the LNG and the synthetic ammonia by using raw coal gas generated by a high-temperature entrained bed; the desulphurization and the decarbonization are carried out by using a mature and advanced physical and chemical absorption process, methane is obtained by using an advanced methanation conversion technology, then, a deep cooling technology is adopted to produce liquid methane and hydrogen through staged cooling and washing separation, the produced liquid methane is outputted as a product, i.e. the LNG, meanwhile, the produced hydrogen is mixed with nitrogen to form a synthetic gas, and the synthetic gas is conveyed to an ammonia synthesizer for the production of the synthetic ammonia after the cold energy is recovered. The coproduction of natural gas and liquid ammonia is achieved, the equipment has corresponding capability for load adjustment, and the emission of vent gas in synthesis is not needed, so that the raw coal gas is maximally used in the production of products.

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CLAIMS CN102533365A

1.

13 A method for co-producing liquefied natural gas and synthetic ammonia, characterized by comprising the following steps:

(1)

18 The coal gas is subjected to conversion treatment to obtain conversion gas;

(2)

22 After the condensate obtained by condensation separation of the shift gas is desulfurized and decarbonized to obtain purified shift gas;

(3)

27 methanating the purified converted gas to obtain a mixed gas including hydrogen and CH₄;

(4)

31 subjecting the mixed gas obtained in step (3) to cryogenic separation, and separating the liquid CH₄ as liquefied natural gas; and obtaining hydrogen;

(5)

36 The hydrogen obtained in step (4) is mixed with nitrogen to obtain a synthesis gas with a certain hydrogen-nitrogen ratio, which is sent to the ammonia synthesis process to obtain ammonia.

2.

41 The method according to claim 1 is characterized in that the coal gas is high-temperature coal gas produced by pressurized gasification of coal as raw material.

3.

46 The method according to claim 1 is characterized in that: the conversion process includes two-stage conversion, after the coal gas enters the heat exchanger and exchanges heat with the steam produced by the waste heat boiler at the outlet of the first-stage conversion furnace, a part of it enters the first conversion furnace, and the gas after the first-stage conversion passes through the waste heat boiler to produce steam and heat exchange with the coal gas before entering the second-stage conversion furnace, and the gas after the second-stage conversion passes through the steam superheater and the steam waste heat boiler to recover heat in stages.

4.

56 The method as claimed in claim 3 is characterized in that: the CO conversion rate in the first stage of conversion is 20-40% (v/v); the CO conversion rate in the second stage of conversion is 10-15% (v/v); 40%-60% (v/v) of the coal gas enters the first stage conversion furnace.

5.

62 The method according to claim 1, characterized in that: the methanation treatment includes a bulk methanation process and a supplementary methanation process; in the bulk methanation process, CO is converted into CH₄; in the supplementary methanation process, CO₂ is converted into CH₄.

6.

69 The method as claimed in claim 5 is characterized in that: the methanation treatment includes three stages of methanation; the purified conversion gas first enters the raw material heat exchanger, and the purified conversion gas is heated by the outlet gas from the third stage methanation furnace in the raw material heat exchanger; a part of the purified conversion gas after heat exchange is mixed with the gas at the outlet of the first stage methanation furnace and enters the second stage methanation furnace for methanation treatment; another part is mixed with a part of the gas at the outlet of the second stage methanation furnace as the circulating gas to dilute the CO concentration in the purified conversion gas, and then enters the first stage methanation furnace for methanation; another part of the gas at the outlet of the second stage methanation furnace enters the third stage methanation furnace for supplementary methanation treatment, and the gas after the third stage methanation treatment enters the raw material heat exchanger, and after heat exchange with the purified conversion gas, it is cooled and separated by a circulating water cooler, and then the water is adsorbed

by a molecular sieve for deep cold separation.

7.

95 The method according to claim 6 is characterized in that: the outlet gas of the second-stage methanation furnace is cooled by a waste heat boiler; the CO content in the gas entering the first-stage methanation furnace is less than or equal to 10% (v/v); the circulating gas passes through a desalted water preheater and liquid separation, is pressurized by a circulating compressor, and is mixed with the purified conversion gas to enter the first-stage methanation furnace.

8.

103 The method according to claim 1 or 7, characterized in that the cryogenic separation of the mixed gas obtained in step (3) comprises the steps of:

105 (1) The mixed gas enters the No. 1 raw gas cooler in the cold box for primary cooling, and the cooling capacity of the cooler is provided by the No. 1 mixed refrigerant circulating compressor and the returned synthesis gas after nitrogen addition;

108 (2) The mixed gas after primary cooling enters the No. 2 raw gas cooler. The cooling capacity of the No. 2 raw gas cooler is provided by the No. 2 mixed refrigerant circulation compressor and the returned synthesis gas after nitrogen addition;

111 (3) The mixed gas after secondary cooling enters the No. 3 raw gas cooler. The cooling capacity of the No. 3 raw gas cooler comes from the No. 2 mixed refrigerant circulation compressor, liquefied methane and returned nitrogen scrubbing gas. After this secondary cooling, part of the mixed gas is condensed;

114 (4) The mixed gas after tertiary cooling enters the No. 4 raw gas cooler, and the cooling capacity of the No. 4 raw gas cooler is provided by liquid methane and nitrogen scrubbing;

116 (5) The mixed gas after four coolings enters the nitrogen washing tower from the bottom, and liquid nitrogen is sprayed into the nitrogen washing tower from the top. The methane in the mixed gas entering the nitrogen washing tower is washed to the bottom of the tower. The purified nitrogen washing gas containing nitrogen leaves from the top of the tower, and is reheated by No. 4 and No. 3 raw gas coolers, and then an appropriate amount of high-pressure nitrogen is added to obtain synthesis gas. The synthesis gas is reheated to ambient temperature by No. 2 and No. 1 raw gas coolers, and then finely adjusted by nitrogen to achieve an accurate hydrogen-nitrogen chemical ratio to obtain refined synthesis gas, which then enters the synthetic ammonia process.

9.

127 The method according to claim 6 is characterized in that the liquid methane separated from the bottom of the nitrogen scrubber is sent to a methane storage device after recovering part of the cold energy through No. 4 and No. 3 raw gas coolers to be output as liquefied natural gas.

10.

133 The method according to claim 6 is characterized in that: the dissolved hydrogen and argon are separated by reduced pressure flash distillation before the liquid methane at the bottom of the tower is output, and the gas is returned to the system for recovery through a tail gas compressor.

11.

139 The method according to claim 6 is characterized in that the high-pressure nitrogen comes from the air separation unit, is cooled by No. 1 and No. 2 raw gas coolers, and is then mixed with the nitrogen-containing hydrogen from the top of the nitrogen scrubbing tower.

12.

145 The method according to claim 1 or 6 is characterized in that the concentrations of the acid gases H₂S, COS and H₂S in the purified conversion gas are below 0.1 ppm; and the molar ratio of hydrogen to nitrogen in the synthesis gas is 3:1.

13.

151 A process device for co-producing liquefied natural gas and synthetic ammonia, comprising:

152 The coal gasification unit includes an entrained flow pulverized coal gasification bed, in which the pulverized coal produces a raw coal gas, the raw coal gas mainly comprising: CO, carbon dioxide, methane, water vapor and hydrogen;

155 A conversion unit, comprising at least one reactor filled with a conversion catalyst, in which CO is catalytically converted into CO₂ and hydrogen;

157 Desulfurization and decarbonization unit, which removes acidic gases through desulfurization and decarbonization equipment;

159 Methanation unit, converting the remaining CO and hydrogen into methane gas;

160 Cryogenic separation unit, including nitrogen scrubber, condenses methane gas into liquefied natural gas and simultaneously separates hydrogen containing nitrogen;

162 Ammonia synthesis unit: uses medium-pressure synthesis process to produce liquid ammonia product.

163 The coal gasification unit is connected to the conversion unit; the conversion unit is connected to the methanation unit, the methanation unit is connected to the cryogenic unit, and the cryogenic unit is connected to the liquefied natural gas storage and the ammonia synthesis unit respectively; heat exchangers are evenly arranged at the inlet and/or outlet of the conversion unit, the methanation unit, and the cryogenic unit for recovering heat.

14.

171 The system as claimed in claim 13 is characterized in that the conversion unit includes two conversion furnaces, a heat exchanger is provided at the inlet of the first-stage conversion furnace, the outlet is connected to the heat exchanger at the inlet through a pipeline, and is connected to the inlet of the second-stage conversion furnace after passing through the heat exchanger, and the outlet of the second-stage conversion

furnace is connected to the desulfurization and decarbonization unit through a pipeline.

15.

183 In the system as claimed in claim 13, the methanation unit includes three methanation furnaces; a heat exchanger is provided at the inlet of the first-stage methanation furnace, the outlet of the first-stage methanation furnace is connected to the inlet of the second-stage methanation furnace through a pipeline, the heat exchanger is provided in the pipeline, the outlet of the second-stage methanation furnace is respectively connected to the inlet of the third-stage methanation furnace and the first-stage methanation furnace through pipelines, the outlet of the third-stage methanation furnace is connected to the heat exchanger located at the inlet of the first-stage methanation furnace, and is connected to the cryogenic unit after heat exchange.

16.

194 In the system as claimed in claim 13, the cryogenic unit includes four plate-fin heat exchangers, a mixed refrigerant circulation compressor and a nitrogen scrubber, the gas from the methanation unit passes through the four plate-fin heat exchangers once and then passes through the bottom of the nitrogen scrubber, the mixed refrigerant between the plate-fin heat exchangers circulates between the plate-fin heat exchangers through the circulation compressor; the hydrogen and nitrogen mixed gas flowing out of the top outlet of the nitrogen scrubber passes through the four-stage plate-fin heat exchanger and enters the ammonia synthesis unit after being heated.

(19)中华人民共和国国家知识产权局

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权利要求书 2 页 说明书 6 页 附图 1 页

(54)发明名称

一种液化天然气及合成氨联产工艺

(57)摘要

本发明属于煤化工技术领域；特别是一种煤气化合成氨和液化天然气的联产工艺。本发明提供了一种利用高温气流床产生的粗煤气生产液化天然气及合成氨联产的方法和设备，利用成熟先进的物理化学吸收工艺脱硫脱碳，利用先进的甲烷化转化技术获得甲烷后，采用深冷技术，经过阶梯式冷却、洗涤分离，生产的液态甲烷作为产品液化天然气输出，同时生产的氢气配氮回收冷量后送氨合成装置生产合成氨。从而实现天然气与液氨的联合生产，装置具有相应的调节负荷能力，且无需合成弛放气的排放。最大限度的将粗煤气用于产品生产。

CN 102533365 A

1. 一种液化天然气及合成氨的联产方法，其特征在于包括如下步骤：

(1)、煤气经变换处理，获得变换气；

(2)、所述变换气经冷凝分离所获得的冷凝液后，进行脱硫脱碳，得到净化变换气；

(3)、将所述净化变换气进行甲烷化处理，获得包括氢气和 CH_4 的混合气体；

(4)、将步骤 (3) 所获得的混合气体进行深冷分离，分离出的液态 CH_4 为液化天然气；并获得氢气；

(5)、将步骤 (4) 获得的氢气与氮气混合，得到一定氢氮比的合成气，送入合成氨工序，获得氨。

2. 如权利要求 1 所述的方法，其特征在于：所述煤气为以煤为原料经加压气化产出的高温煤气。

3. 如权利要求 1 所述的方法，其特征在于：所述的变换处理包括两段变换，煤气进入换热器与第一段变换炉出口废热锅炉产蒸汽进行热交换后，其中一部分进入第一变换炉，经过第一段变换后的气体，通过废热锅炉产蒸汽和煤气换热后进入第二段变换炉，经过第二段变换后的气体通过蒸汽过热器及蒸汽废热锅炉后分级回收热量。

4. 如权利要求 3 所述的方法，其特征在于：第一段变换中 CO 的转化率为 20 ～ 40% (v/v)；第二段变换 CO 转化率为 10 ～ 15% (v/v)；其中 40% -60% (v/v) 的煤气进入第一段变换炉。

5. 如权利要求 1 所述的方法，其特征在于：所述甲烷化处理包括大量甲烷化过程和补充甲烷化过程；在大量甲烷化过程中 CO 转化为 CH_4；在补充甲烷化过程中 CO_2 转为为 CH_4。

6. 如权利要求 5 所述的方法，其特征在于：甲烷化处理包括 3 级甲烷化；净化变换气先进入原料换热器，净化变换气在所述原料换热器中被来自第 3 级甲烷化炉的出口气加热；经过热交换的净化变换气一部分与第 1 级甲烷化炉出口的气体混合进入第 2 级甲烷化炉进行甲烷化处理；另一部分与第 2 级甲烷化炉出口的一部分作为循环气的气体混合，以稀释净化变换气中的 CO 浓度，然后进入第 1 级甲烷化炉进行甲烷化；另一部分第二级甲烷化炉出口的气体进入第 3 级甲烷化炉进行补充甲烷化处理，经第 3 级甲烷化处理后的气体进入所述原料换热器，与所述净化变换气热交换后，通过循环水冷却器冷却并分离冷凝液，然后通过分子筛吸附水份，进行深冷分离。

7. 如权利要求 6 所述的方法，其特征在于：第 2 级甲烷化炉出口气体经过废热锅炉冷却；进入第 1 级甲烷化炉的气体中 CO 含量小于等于 10% (v/v)；所述循环气经脱盐水预热器并分液后，通过循环压缩机加压与净化变换气混合进入第 1 级甲烷化炉。

8. 如权利要求 1 或 7 所述的方法，其特征在于：步骤 (3) 所获得的混合气体的深冷分离包括步骤：

(1) 所述混合气体进入冷箱中的 1 号原料气冷却器进行一次冷却，该冷却器的冷量由 1 号混合冷剂循环压缩机和返回的配氮后的合成气提供；

(2) 经过一次冷却的混合气进入 2 号原料气冷却器，2 号原料气冷却器冷量由 2 号混合冷剂循环压缩机和返回的配氮后的合成气提供；

(3)、经过二次冷却的混合气进入 3 号原料气冷却器，3 号原料气冷却器的冷量来自 2 号混合冷剂循环压缩机、液化甲烷和返回氮洗气，经过该次冷却后，部分混合气被冷凝；

(4)、经过三次冷却的混合气进入 4 号原料气冷却器，4 号原料气冷却器的冷量由液态

Topsoe, Inc. – EX1003
Page 797 of 1210

甲烷和氮洗气提供；

(5)、经过四次冷却的混合气由底部进入氮洗塔，液氮从氮洗塔的上部喷入，进入氮洗塔的混合气中的甲烷被洗涤至塔底，净化后的含有氢气的氮洗气由塔顶离开，经过 4 号和 3 号原料气冷却器复热后，配入适量的高压氮气，得到合成气，所述合成气经过 2 号和 1 号原料气冷却器复热到环境温度，再经过精细配氮调节实现准确的氢氮化学配比后得到精制合成气，然后进入合成氨工序。

9. 如权利要求 6 所述的方法，其特征在于：氮洗塔塔底分离出的液态甲烷，经过 4 号和 3 号原料气冷却器回收部分冷量后送往甲烷存储装置，作为液化天然气输出。

10. 如权利要求 6 所述的方法，其特征在于：塔底液态甲烷输出前减压闪蒸分离溶解的氢及氩气，通过尾气压缩机返回系统回收。

11. 如权利要求 6 所述的方法，其特征在于：高压氮气来自于空气分离装置，经过 1 号和 2 号原料气冷却器冷却后，与来自氮洗塔顶部的含氮氢气混合。

12. 如权利要求 1 或 6 所述的方法，其特征在于：所述净化变换气中酸性气体 H_2S、COS 和 H_2S 浓度在 0.1ppm 以下；所述合成气中氢气与氮气的摩尔比为 3 ： 1。

13. 一种液化天然气及合成氨的联产工艺装置，该装置包括：

煤气化单元，包括气流床粉煤气化床，煤粉在煤气化单元中产生粗煤气，粗煤气组要成分为：CO、二氧化碳、甲烷、水蒸气和氢气；

变换单元，包括至少一个充填有变换催化剂的反应器，在该单元中将 CO 通过催化变换为 CO_2 和氢气；

脱硫脱碳单元，通过脱硫脱碳装置去除酸性气体；

甲烷化单元，将剩余 CO 和氢气转换为甲烷气；

深冷分离单元，包括氮洗塔，将甲烷气冷凝为液化天然气，同时分离出含有氮气的氢气；

氨合成单元：采用中压合成工艺制取产品液氨。

煤气化单元与变换单元连接；变换单元与甲烷化单元相连接，甲烷化单元与深冷单元相连接，深冷单元分别连接液化天然气储存器和氨合成单元；在变换单元、甲烷化单元、和深冷单元的入口和 / 或出口处匀设有热交换器，用于回收热量。

14. 如权利要求 13 所述的系统，其特征在于，变换单元包括两个变换炉，第一段变换炉入口处设有热交换器，出口通过管线连接于入口处的热交换器，经过热交换器后连接于第二级变换炉的入口，第二段变换出口通过管线连接脱硫脱碳单元。

15. 如权利要求 13 所述的系统，甲烷化单元包括 3 个甲烷化炉；第一级甲烷化炉的入口处设有热交换器，第一级甲烷化炉的出口与第二级甲烷化炉的入口通过管线连接，该管线中设有热交换器，第二级甲烷化炉的出口分别与第三级甲烷化炉和第一级甲烷化炉的入口通过管线连接，第三级甲烷化炉的出口与位于第一级甲烷化炉入口处的热交换器连接，经过热交换后连接于深冷单元。

16. 如权利要求 13 所述的系统，深冷单元包括四台板翅式换热器、混合冷剂循环压缩机和氮洗塔，来自于甲烷化单元的气体经过一次经过四台板翅式换热器后经过氮洗塔的底部，所述的板翅式换热器之间的混合冷剂通过循环压缩机在板翅式换热器间循环流动；有氮洗塔顶部出口流出的氢气和氮气混合气，经过四级所述的板翅式换热器，升温后进入氨合成单元。

Topsoe, Inc. – EX1003
Page 798 of 1210

一种液化天然气及合成氨联产工艺

技术领域

[0001] 本发明属于煤化工技术领域。特别涉及一种煤气化合成氨和液化天然气的联产工艺。

背景技术

[0002] 天然气作为清洁能源是居民生活必须的首选燃料。随着国家对能源需求的不断增长，液化天然气产品将对优化中国的能源结构，有效解决能源供应安全、生态环境保护的双重问题，实现经济和社会的可持续发展发挥重要作用。作为天然气下游主要用户之一的城市燃气用户，其用气负荷波动量非常大，每天面临气源调峰的压力。因此，各城市燃气企业均需投巨资建设一些调峰设施。本专利技术满足合成氨与液化天然气 (LNG) 灵活调节生产的优点，且利用一套装置满足两种产品生产的先进性。

[0003] 传统的氨合成工艺流程为，粗煤气制备→变换→脱硫脱碳→精制→氨合成。

[0004] 传统的液化天然气工艺流程为，粗煤气制备→变换→脱硫脱碳→甲烷合成→甲烷分离。

[0005] 发明专利 CN1036375A 中记载了一种煤制备合成天然气的工艺，该工艺是煤加氢处理获得的煤气，经过净化，变换，甲烷化后经过深冷分离，获得合成天热气和氢气，氢气用于煤加氢处理；这样氢气的处理利用率不高。

[0006] 发明专利 CN101607694A 中记载了一种烃类物质通过变换，甲烷化和深冷分离后获得的合成氨原料，但是该专利中没有获得液化天然气，同时所用原料也不是煤气化的煤气。

[0007] 本发明利用一套化工装置实现两种产品方案的生产。

[0008] 此外，本发明也适用于利用现有化工装置进行技术改造，利用当地煤炭资源进行非催化部分氧化后的粗煤气。

[0009] 本发明具备先进的冷量及热量配备方案。且具备较强的可调节和可操作性，并达到了冷热能量的优化匹配。

[0010] 本发明在深冷过程中，使用了氮洗工艺，分离出的氢气中带有氮气，通过调整 NH 比回收冷量后用于氨合成，即减少了氮和氢气的分离工序，又节省了部分能量。

发明内容

[0011] 本发明的目的是一种利用煤联产液化天热气和合成氨的一种方法，提供一种可有效分离基本组分为氢气、甲烷的原料气，分离液化甲烷（液化天然气）作为清洁能源，纯度可达到 99.9% (vt)；净化氢气并配氮，使 H_2 ： N_2 = 3 ： 1，同时利用中压氮气节流的冷量，出界区的合成气送往下游合成氨装置；

[0012] 本发明还提供了一种联产液化天热气和合成氨的装置。

[0013] 本发明的技术方案如下：

[0014] 一种液化天然气及合成氨的联产工艺，其特征在于包括如下步骤：

Topsoe, Inc. – EX1003
Page 799 of 1210

[0015] (1)、煤气经变换处理，获得变换气；

[0016] (2)、所述变换气经冷凝分离所获得的冷凝液后，进行脱硫脱碳，得到净化变换气；

[0017] (3)、将所述净化变换气进行甲烷化处理，获得包括氢气和 CH_4 的混合气体；

[0018] (4)、将步骤 (3) 所获得的混合气体进行深冷分离，分离出的液态 CH_4 为液化天然气；并获得氢气；

[0019] (5)、将步骤 (4) 获得的氢气与氮气混合，得到一定氢氮比的合成气，送入合成氨工序，获得氨。

[0020] 本发明所述煤气为以煤为原料经加压气化产出的高温煤气。

[0021] 本发明所述的变换处理包括两段变换，煤气进入换热器与第一段变换炉出口废热锅炉产蒸汽进行热交换后，其中一部分进入第一变换炉，经过第一段变换处理后的气体，通过废热锅炉产生蒸汽和煤气换热后进入第二段变换炉，经过第二段变换处理后的气体通过蒸汽过热器及蒸汽废热锅炉后分级回收热量。

[0022] 第一段变换中 CO 的转化率为 20 ～ 40% (v/v)；第二段变换 CO 转化率为 10 ～ 15% (v/v)；其中 40% -60% (v/v) 的煤气进入第一段变换炉。

[0023] 所述甲烷化处理包括大量甲烷化过程和补充甲烷化过程；在大量甲烷化过程中 CO 转化为 CH_4；在补充甲烷化过程中 CO_2 转为为 CH_4。

[0024] 甲烷化处理包括 3 级甲烷化；净化变换气先进入原料换热器，净化变换气在所述原料换热器中被来自第 3 级甲烷化炉的出口气加热；经过热交换的净化变换气一部分与第 1 级甲烷化炉出口的气体混合进入第 2 级甲烷化炉进行甲烷化处理；另一部分与第 2 级甲烷化炉出口的一部分作为循环气的气体混合，以稀释净化变换气中的 CO 浓度，然后进入第 1 级甲烷化炉进行甲烷化；另一部分第二级甲烷化炉出口的气体进入第 3 级甲烷化炉进行补充甲烷化处理，经第 3 级甲烷化处理后的气体进入所述原料换热器，与所述净化变换气热交换后，通过循环水冷却器冷却并分离冷凝水，然后通过分子筛吸附水份，进行深冷分离。

[0025] 第 2 级甲烷化炉出口气体经过废热锅炉冷却；进入第 1 级甲烷化炉的气体中 CO 含量小于等于 10% (v/v)；所述循环气经脱盐水预热器并分液后，通过循环压缩机加压与净化变换气混合进入第 1 级甲烷化炉。

[0026] 本发明步骤 (3) 所获得的混合气体的深冷分离包括步骤：

[0027] 所述混合气体进入冷箱中的 1 号原料气冷却器 (E-5001) 进行一次冷却，该冷却器的冷量由 1 号混合冷剂循环压缩机 (k-5001) 和返回的配氮后的合成气提供；经过一次冷却的混合气进入 2 号原料气冷却器，2 号冷却器冷量由 2 号混合冷剂循环压缩机和返回的配氮后的合成气提供；

[0028] 经过二次冷却的混合气进入 3 号原料气冷却器，3 号冷却器的冷量来自 2 号混合冷剂循环压缩机、液化甲烷和返回氮洗气提供，经过该次冷却后，部分混合气被冷凝；

[0029] 经过三次冷却的混合气进入 4 号原料气冷却器，4 号冷却器的冷量由液态甲烷和氮洗气提供；

[0030] 经过四次冷却的混合气由底部进入氮洗塔，液氮从氮洗塔的上部喷入，进入氮洗塔的混合气中的甲烷被洗涤至塔底，净化后的含有氮气的氮洗气由塔顶离开，经过 4 号和 3

Topsoe, Inc. – EX1003
Page 800 of 1210

号原料气冷却器复热后，配入适量的高压氮气，得到合成气，所述合成气经过 2 号和 1 号原料气冷却器复热到环境温度，再经过精细配氮调节实现准确的氢氮化学配比后得到精制合成气，然后进入合成氨工序。

[0031] 氮洗塔塔底分离出的液态甲烷，经过 4 号和 3 号原料气冷却器回收部分冷量后送往甲烷存储装置，作为液化天然气输出。

[0032] 塔底液态甲烷输出前减压闪蒸分离溶解的氢及氩气，通过尾气压缩机返回系统回收。

[0033] 高压氮气来自于空气分离装置，经过 1 号和 2 号原料气冷却器冷却后，节流直接与来自氮洗塔顶部的含氮氢气混合。

[0034] 所述净化变换气中酸性气体 H_2S、COS 和 H_2S 浓度在 0.1ppm 以下；所述合成气中氢气与氮气的摩尔比为 3 ： 1。

[0035] 混合气深冷分离及生产液化天然气工艺主要设备包括混合冷剂循环压缩机 (K-5001、K-5002)、四台板翅式换热器 (E-5001 ～ 5004)、两台管壳式换热器 (E5005 ～ 5006)、氮洗塔 (C-5001)。

[0036] 气化炉生产的原料气，先后通过变换、低温甲醇洗、甲烷化装置，组分包括氢气、CH_4 和少量水、CO_2 的混合气最后经分子筛吸附器 (A-4001) 后送往深冷分离装置。吸附器为两台组成，一台吸附，另一台再生。常温分子筛吸附，可节省大量投资。

[0037] 本发明所述的液化天然气及合成氨的联产工艺装置，该装置包括：

[0038] 煤气化单元，包括气流床粉煤气化床，煤粉在煤气化单元中产生粗煤气，粗煤气主要包含 CO、二氧化碳、甲烷、水蒸气和氢气；

[0039] 变换单元，包括至少一个充填有变换催化剂的反应器，在该单元中将 CO 通过催化变换为 CO2 和氢气；

[0040] 脱硫脱碳单元，通过脱硫脱碳装置去除酸性气体；该单元主要是为了脱除对下游生产有危害的酸性气体 H_2S、COS，H_2S 可以脱除到 0.1ppm 以下，CO_2 可以脱除到≤ 1% (v/v)；该装置宜采用常温脱硫脱碳工艺，流程短，一次投资低；

[0041] 甲烷化单元，将 CO 和氢气转换为甲烷气。原料气是 CO 和 H_2，还有微量 CO_2 及过量的 H_2，由于 CO 转化为 CH_4 为大量放热反应，装置的核心为避免催化剂超温，在大量甲烷化段中 CO 完全转化为 CH_4，微量 CO_2 在补充甲烷化中，完全转化为 CH_4。

[0042] 深冷分离单元，包括氮洗塔，将甲烷气冷凝为液化天然气，同时分离出含有氮气的氢气；

[0043] 氨合成单元；

[0044] 以及，至少一个热交器；

[0045] 煤气化单元与变换单元连接；变换单元与甲烷化单元相连接，甲烷化单元与深冷单元相连接，深冷单元分别连接液化天然气储存器和氨合成单元；在变换单元、甲烷化单元、和深冷单元的入口和 / 或出口处匀设有热交换器，用于回收热量。以粉煤为原料加压气化技术，生产出的高温粗煤气经除尘后，从气化单元送出的粗煤气送下游装置。

[0046] 变换单元包括两个变换炉，第一段变换炉入口处设有热交换器，出口通过管线连接于入口处的热交换器，经过热交换器后连接于第二级变换炉的入口，第二段变换出口通过管线连接脱硫脱碳单元。根据下游产品对合成氨和液态甲烷的产量来调节变换单元 CO

Topsoe, Inc. – EX1003
Page 801 of 1210

的转化率，对于天然气合成氨联产装置，用宽温耐硫变换即可实现。该技术成熟可靠且普遍运用于现代化工装置，完全可以满足下游生产的需要。

[0047] 甲烷化单元包括 3 个甲烷化炉；第一级甲烷化炉的入口处设有热交换器，第一级甲烷化炉的出口与第二级甲烷化炉的入口通过管线连接，该管线中设有热交换器，第二级甲烷化炉的出口分别与第三级甲烷化炉和第一级甲烷化炉的入口通过管线连接，第三级甲烷化炉的出口与位于第一级甲烷化炉入口处的热交换器连接，经过热交换后连接于深冷单元。

[0048] 深冷单元包括四台板翅式换热器、混合冷剂循环压缩机和氮洗塔，来自于甲烷化单元的气体经过一次经过四台板翅式换热器后经过氮洗塔的底部，所述的板翅式换热器之间的混合冷剂通过循环压缩机在板翅式换热器间循环流动；有氮洗塔顶部出口流出的氢气和氮气混合气，经过四级所述的板翅式换热器，升温后进入氨合成单元。为了实现以煤为气头生产液化天然气联产合成氨工艺，深冷分离需要完成以下几个目的：(1) 液化天然气液化并分离；(2) 净化合成气满足合成氨需要；(3) 配氮：使氢氮比为 3 ： 1；(4) 冷量的提供和不同品味冷量的分配。

[0049] 本发明的装置还可以包括，空分单元：采用全低压、空气透平膨胀、空气预冷、分子筛吸附、内压缩工艺流程。采用分子筛净化空气；热交换器采用高效的板式换热器；采用高效的两级精馏工艺制取高纯度的氧气和氮气；采用增压透平膨胀机节省能耗，提高制冷量。空分产品氧气纯度为≥ 99.6%。且副产全厂消耗用各等级氮气及公用工程气体。

[0050] 本发明利用煤可以同时获得液化天热气和氨合成其，使煤气得到了充分的利用；本发明根据氮洗深冷技术的特点，使用深冷分离后的含氮氢气作为氨合成其，省略了分离氮气的步骤，节省了能量，简化的工艺；

[0051] 本发明对于热量和冷量都进行了回收利用，大量的节省了能量；其中工艺冷量主要是通过以下四个方面来提供：

[0052] 1) 混合冷剂循环压缩机 (K-5001、K-5002)，通过调整两种混合冷剂的组成，实现冷量的合理分级利用，减少了冷量的损失。甚至包括各种根据三种或三种以上制冷剂制冷方案确定的压缩方案；

[0053] 2) 中压氮气节流补充系统冷量；

[0054] 3) 喷淋液氮洗涤原料气，同时提供冷量；

[0055] 4) 氮洗塔 (C-5001) 底部分离出的液态甲烷，减压闪蒸尾气后，回收部分冷量。

[0056] 通过上述工艺同时实现了以下目的：

[0057] 1) 分离出液化天然气；

[0058] 2) 净化了氢气，洗涤了原料气中甲烷，避免了氨合成回路的驰放气排放；

[0059] 3) 在装置中实现气体配氮，氢氮比基本达到 3 ： 1，同时充分利用了中压氮气节流的冷量；

[0060] 4) 实现了冷量的合理分级利用，减少了冷量的损失；

附图说明

[0061] 图 1 为本发明先进天然气与合成氨联产流程的方块图。

[0062] 图 2 为本发明先进天然气与合成氨联产流程的系统说明图。

Topsoe, Inc. – EX1003
Page 802 of 1210

具体实施方式

[0063] 参考附图 1 和 2，以煤粉为原料加压气化生产出的高温粗煤气，根据下游产品对合成氨和液态甲烷的产量来调节变换单元 CO 的转化率，对于 12000Nm³/h 天然气及 500 吨 / 天合成氨联产装置，可按两段宽温耐硫变换即可实现。其变换催化剂的装填量及装填方案根据产品方案可相应调整。

[0064] 气化来的粗煤气通过与第 1 段变换炉出口废热锅炉 (E-2005) 产蒸汽后的换热器换热 (E-2001) 后，分 40 ～ 60％ (可根据产量比例适当调节) 粗煤气进入一段变换炉 (R-2001)，CO 转化到 20 ～ 40％ (v/v)，经废热锅炉产蒸汽 (E-2005) 和粗煤气换热后与未反应粗煤气混合后进第 2 变换炉 (R-2002)；二段变换出口 CO 转化到 10 ～ 15％ (vt)，变换气通过蒸汽过热器 (E-2004) 及蒸汽废锅 (E-2002) 后，分级回收热量 (E-2003)，并分离冷凝液后送往脱硫脱碳装置。

[0065] 通过脱硫脱碳装置脱除对下游生产有危害的酸性气体 H_2S、COS、CO_2，H_2S 需要脱除到 0.1ppm 以下，由于 CO_2 可以作为甲烷合成的原料，CO_2 脱除率并不是脱碳装置的要求的核心指标，因此 CO_2 可以脱除到≤ 50ppm 即可；该装置宜采用常温脱硫脱碳工艺，流程短，一次投资低。能耗低。

[0066] 甲烷化：该工艺主要包括两部分：大量甲烷化和补充甲烷化。净化变换气主要是 CO 和 H_2，还有微量 CO_2，由于 CO 转化为 CH_4 为大量放热反应，装置的核心为避免催化剂超温，在大量甲烷化段中 CO 完全转化为 CH_4，微量 CO_2 在补充甲烷化中，完全转化为 CH_4。

[0067] 净化后的变换气由界外提供到甲烷化装置。净化变换气在 1 号原料换热器 (E-4001) 中被第 3 级甲烷化出口气加热，合成气进入第 1 级甲烷化炉 (R-4001) 之前，分流出一部分去第 2 级甲烷化炉 (R-4002)，在第 1 级甲烷化炉入口前与第 2 级甲烷化炉出口的循环气混合后将 CO 稀释到～ 10％ (v/v) 或以下，进入第 1 级甲烷化炉 (R-4001) 进行甲烷化反应。出口气经废热锅炉 (E-4002) 冷却后，与新鲜气混合后进入第 2 级甲烷化炉 (R-4002)，出口气经废热锅炉 (E-4003) 冷却后，分流大部分循环气用于稀释第一级甲烷化入口的新鲜气，该循环气经脱盐水预热器 (E-4004) 并分液后，通过循环气压缩机 (K-4001) 加压后与新鲜气混合后进入一段甲烷化炉。

[0068] 补充甲烷化反应由第 2 级出口气经第 3 级甲烷化反应器 (R-4003) 反应后，在 1 号原料换热器 (E-4001) 加热入口新鲜气后，通过循环水冷却器 (E-4006) 冷却并水后，通过分子筛 (A-4001) 吸附水分后，进入深冷分离装置。吸附器为两台组成，一台吸附，另一台再生。常温分子筛吸附，可节省大量投资。

[0069] 混合气深冷分离及生产液化天然气工艺主要设备包括混合冷剂循环压缩机 (K-5001、K-5002)、四台板翅式换热器 (E-5001 ～ 5004)、氮洗塔 (C-5001)。

[0070] 气化炉生产的原料气，先后通过变换、低温甲醇洗、甲烷化装置，组分包括氢气和 CH_4 的原料气最后送往深冷分离装置。

[0071] 经分子筛吸附器处理后的原料气被送入冷箱中的 1 号原料气冷却器 (E-5001) 冷却，此换热器的冷量主要由 1 号混合冷剂循环压缩机 (K-5001) 和返回的配氮后的合成气提供；

[0072] 一次冷却的原料气再送入 2 号原料气冷却器 (E-5002) 冷却，此换热器冷量主要由

Topsoe, Inc. – EX1003
Page 803 of 1210

2 号混合冷剂循环压缩机 (K-5002) 和返回的配氮后的合成气提供；

[0073] 二次冷却的原料气进入 3 号原料气冷却器 (E-5003) 继续被冷却，此换热器的冷量主要由 2 号混合冷剂循环压缩机 (K-5002)、液化甲烷和返回氮洗气提供，经过此换热器，部分原料气被冷凝；

[0074] 三次冷却的原料气进入 4 号原料气冷却器 (E-5004) 继续被冷却，此换热器冷量主要由液态甲烷和氮洗气提供；

[0075] 原料气进入氮洗塔下部，液氮从塔顶喷入，其中氢气中含有的部分甲烷被洗涤出至塔底，净化后含有少量氮气的氮洗气自氮洗塔 (C-5001) 塔顶离开，经 4 号原料气冷却器 (E-5004) 和 3 号原料气冷却器 (E-5003) 复热，然后将高压氮气管线中来的氮气配入，基本达到氢氮比 3 ： 1，再经 2 号原料气冷却器 (E-5002) 和 1 号原料气冷却器 (E-5001) 复热到环境温度后，再经精细配氮调节实现准确的氢氮化学配比后作为精制合成气送入氨合成工序。

[0076] 塔底分离出液态甲烷，经过 4 号原料气冷却器 (E-5004) 和 3 号原料气冷却器 (E-5003) 回收部分冷量后，送往甲烷贮存装置，作为产品输出。

[0077] 塔底液态甲烷输出前减压闪蒸分离溶解的氢及氩气通过尾气压缩机返回系统回收。同时过冷产品甲烷并提高产品纯度。

[0078] 高压氮气来自界区外的空分装置，经过 1 号原料气冷却器 (E-5001) 和 2 号原料气冷却器 (E-5002) 冷却后，节流直接与自氮洗塔 (C-5001) 顶部来的精制气混合，实现配氮比例。

Topsoe, Inc. – EX1003
Page 804 of 1210

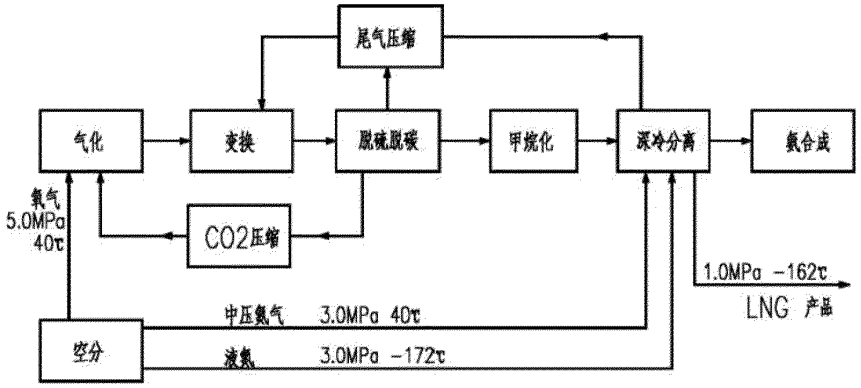


图 1

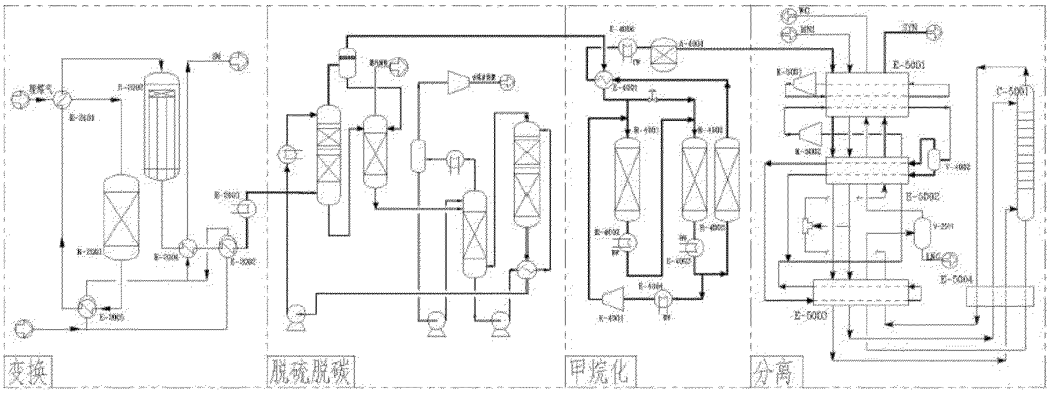


图 2

Topsoe, Inc. – EX1003
Page 805 of 1210

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APPLICATION #	RECEIPT DATE / TIME	ATTORNEY DOCKET #
96/000,424	**05/28/2024 03:39:41 PM Z ET**	**283386WOUS02_495230-102**

Title of Invention

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

Application Information

APPLICATION TYPE	Utility - Reexamination based on supplemental examination	PATENT #	-
CONFIRMATION #	9950	FILED BY	Samantha Stauffer
PATENT CENTER #	65696680	FILING DATE	04/26/2023
CUSTOMER #	116407	FIRST NAMED INVENTOR	- 11286168
CORRESPONDENCE ADDRESS	-	AUTHORIZED BY	Marcus Simon

Documents

TOTAL DOCUMENTS: 22

DOCUMENT		PAGES	DESCRIPTION	SIZE (KB)
20240528_283386WOUS02_495230-102_Amendment_B.pdf		10	-	193 KB
20240528_283386WOUS02_495230-102_Amendment_B-A.NE.pdf	(1-1)	1	Response After Final Action	107 KB
20240528_283386WOUS02_495230-102_Amendment_B-CLM.pdf	(2-5)	4	Claims	132 KB
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EXHIBIT A - 2024-01-31 1-0 Complaint with exhibit.pdf	54	District Court Trial Exhibit	11792 KB
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EXHIBIT C - 2024-02-01 9-0 US Patent and Trademark Office Notified. AO 120.pdf	1	District Court Trial Exhibit	202 KB
EXHIBIT D--2024-05-02 28-0 First Amended Complaint With Jury.pdf	43	District Court Trial Exhibit	8283 KB

Digest

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EXHIBIT D--2024-05-02 28-0 First Amended Complaint With Jury.pdf	F1B5B7F61A51983020A766FDFB6D7D952BABF27AF6C16FA723BDF5E7B8323E48B7ED89D168A393277ACE88CEEA1A2FBD8D13A9B1391B187D775F42103FDFD0E3

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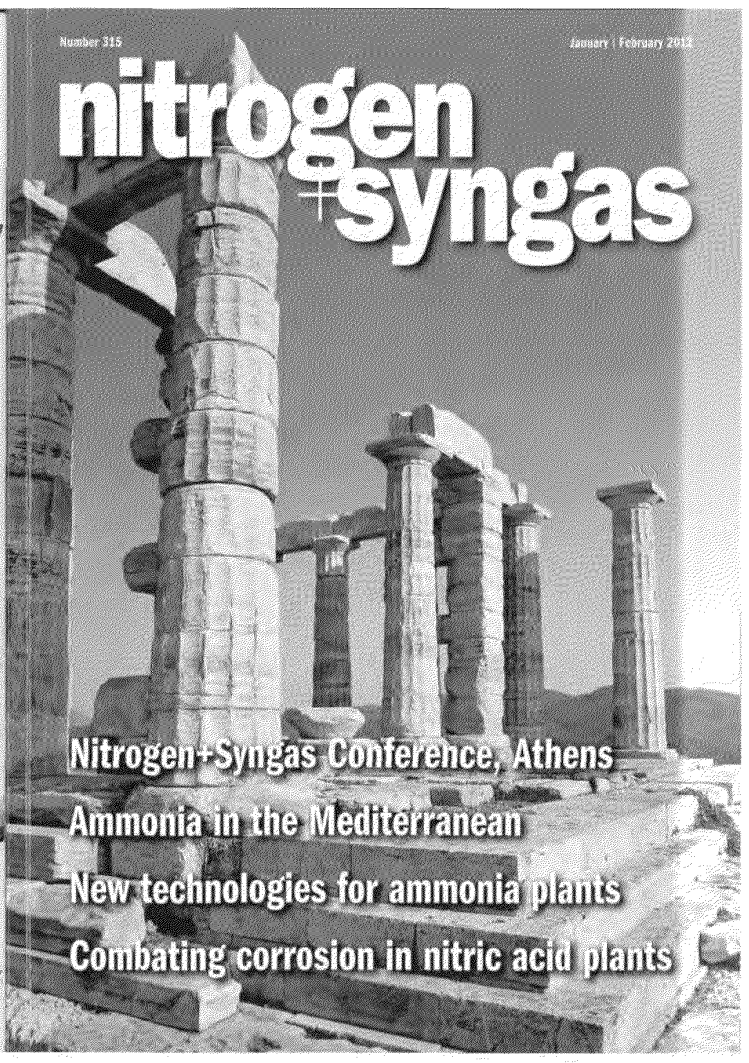
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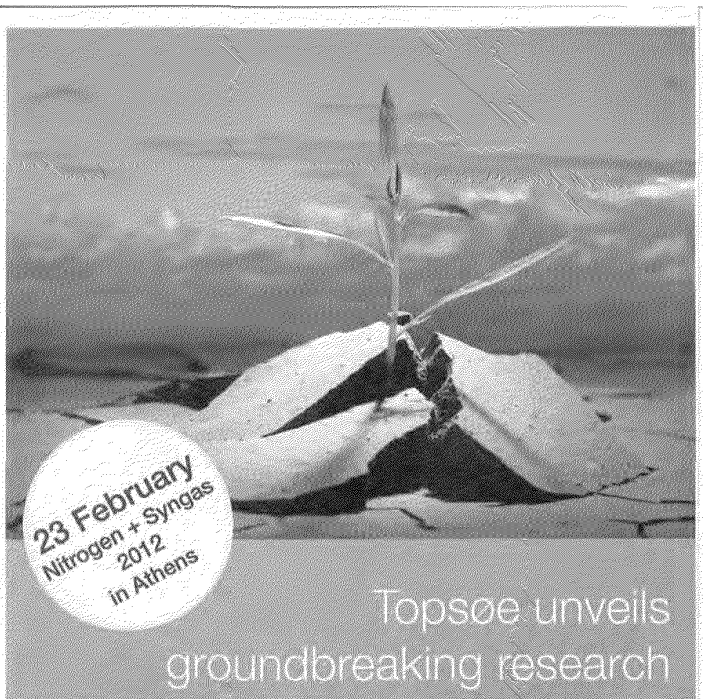
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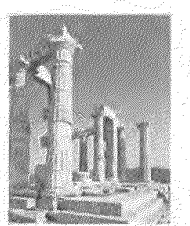
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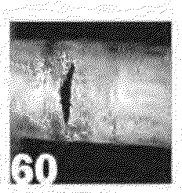


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46
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A project was recently completed on the development of an alternative process route for the removal of methanol, ammonia and carbon dioxide from process condensate in an ammonia fertilizer plant. The effect of stripper operating pressure and temperature and steam tonnage on the stripper performance is reported by S. Krishnaswamy, S. M. Nazir, P.V.K. Srikanth and K. Ponnani of BITS, Pilani – Goa Campus.

New approach to secondary catalyst installation
Secondary N_2O abatement in nitric acid plants with high nitrogen loading can be challenging. S.P. Tew of Johnson Matthey Noble Metals reports on the development of a new design approach to secondary catalyst installation utilising axial radial technology.

Combating corrosion in cooler condensers
The tube sheet and the inlet of the tubes of the cooler condenser in nitric acid plants are often subject to corrosion. In this article, Sandvik Materials Technology, ATI Wah Chang and Yara report on their experiences and solutions to this common corrosion problem in nitric acid plants.

DEPARTMENTS

4 **Editorial** Iran's challenge
5 **Price Trends**
6 **Market Outlook**
10 **Nitrogen Industry News**
14 **Syngas News**
18 **People & Diary**
20 **PlantManager+**
No. 10 High CO_2 content in liquid outlet of a high pressure CO_2 stripper in urea synthesis

Iran's challenge



The second decade of the 21st century is shaping up to be just as eventful as the first. Last year's Japanese tsunami and nuclear meltdown, a crisis in the Eurozone economies and the Arab Spring have already delivered major geopolitical shocks to markets, and the first crisis of 2012 already appears to be brewing in the Arabian Gulf.

Iran remains in deadlock with the United Nations over the country's nuclear programme. Although Iran insists that it is for peaceful purposes, the International Atomic Energy Authority (IAEA) went further than before in its report of November 2011 in stressing that uranium enrichment currently under way at the Fordo plant near Qom is to very high levels, beyond that required for civil nuclear use, and the clear implication is that Iran is pushing as quickly as it can towards developing a nuclear capability. A six-nation 'contact group' comprising France, Germany, the UK, US, Russia and China have been trying to argue Iran out of its ambitions for some time, but there are no signs that President Ahmedinejad is disposed to listen, and so the already significant regimen of sanctions that Iran operates under is being ratcheted up. At the start of this year the US tightened financial sanctions, and now the European Union has announced the imposition of an embargo on imports of oil from Iran.

> **The first crisis of 2012 already appears to be brewing in the Arabian Gulf.**

The oil embargo is a major step. The EU is Iran's second largest market after China, and 20% of its oil exports end up there, with France and Italy particularly large exporters. With oil sales representing the majority of government revenue in Iran, this will hit the country's already ailing economy hard. Iran's economy has been in difficulties because of the pre-existing sanction regime, and there are reports of rising unemployment and inflation. House prices are said to have risen 20% in the past few weeks and meat prices 40%. The removal of some price subsidies on fuel has caused popular discontent and rising utility prices are forcing companies to shut. On top of this is a groundswell of anger at the results of the 2009 elections which erupted into mass demonstrations and a heavy-handed security crackdown.

Iran clearly takes the embargo seriously. Indeed, the government has said that it is an "act of war". There has been a threat to close the Straits of Hormuz, which are the gateway for a large amount of the world's oil, and in response French, British and American warships, including an aircraft carrier, have passed through the straits in the past few days. While there seems to be no appetite in the West for an Iraq-style invasion and 'regime change', the prospect of military conflict or confrontation of some kind nevertheless appears to be looming closer than it has done for some years.

Rising oil prices could be a major headache at a time when the world economy is balanced on the edge of recession in Europe and North America. And of course it is not just oil; the Straits of Hormuz also carry a large volume of the world's ammonia, urea and methanol trade, and if there is a return to the 'tanker war' days of 1984-87, as happened during the Iran-Iraq conflict, then there will no doubt be major knock-on disruptions into all such petrochemical markets, with at the very least soaring insurance rates and rising freight prices, and possibly a complete blockade of the region.

But even if conflict is averted, the continuing and tightening sanctions mean that many gas-based petrochemical developments predicated on gas from Iran's development of its South Pars field are not likely to see the light of day. I was struck at the IHS Methanol Conference in San Diego (see report on pages 22-23) just how many new methanol plants were planned for Iran – several million tonnes' worth – the largest concentration of new capacity outside China. None of these look very likely in the current climate, and the same goes for the Venetian ammonia/urea complex.

The EU sanctions allow for existing contracts to play out as far as July this year. It can only be hoped that cooler heads prevail before then. ■





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Page 814 of 1210

Price trends

Key indicators

Cash equivalent	mid-Nov	mid-Sept	mid-July	mid-May
Ammonia ($/t)				
f.o.b. Caribbean	565	550	515	525
f.o.b. Arab Gulf	570-575	550	505-510	485-505
c.f.r N.W. Europe	650-655	640-650	560-570	560-570
c.f.r India	512-538	548-558	515-548	508-513
Urea ($/t)				
f.o.b. bulk Black Sea	483-485	507-513	445-460	380-388
f.o.b. bulk Arab Gulf*	495-510	505-530	470-500	380-390
f.o.b. bulk Caribbean (granular)	480	505-515	440	378-379
f.o.b. bagged China	490-500	505-508	460-470	355-360
DAP ($/t)				
f.o.b. bulk US Gulf	620-630	620-650	560	610-615
UAN (€/tonne)				
f.o.t. ex-tank Rouen, 30%N	250-254	248-250	250-255	215-225

*Notes: n.a. price not available at time of going to press; n.m. no market; * ngranul granular*

Source: fertilizer trade

NATURAL GAS

The US shale gas boom shows no sign of abating – two more joint ventures were announced at the end of 2011 – Total SA will partner with Chesapeake Energy Corporation and EnerVest in a $2.3 billion venture in the Utica shale, while Sinopec is partnering Devon Energy Corporation in a $2.2 billion venture in the Tuscaloosa and other shales. Shale gas production has increased 17-fold in a decade and now represents 20% of all US gas production.

On the pricing front, in spite of some spikes due to winter weather, temperatures have generally been relatively mild, and many Hub spot prices fell below $3.00/MMBtu at the end of December, with NYMEX futures contracts dropping accordingly to just $2.32/MMBtu. Inventories of working gas in storage are well above 5-year average levels and are 7.6% above the same period for the previous year. Gas prices are now at 10-year lows in the US, down 85% from their peak in 2005. Some industry forecasters have gone so far as to predict that gas prices could even drop as low as $1.00/MMBtu – making US gas cheaper than the Middle East.

The contrast with Europe remains all the more striking, where prices are averaging above $13.00/MMBtu, and there is a sign that demand destruction is occurring. Societe Generale reported that European gas consumption had fallen by 11% in 2011, and is set to fall still further. There were some signs that even Gazprom may be having second thoughts about turning the screws on European consumers as it lowered prices (by an undisclosed amount) to make buyers in western Europe, but for Ukraine the problems continue, with the energy regulator increasing the price of gas to industrial users from January to $12.50/MMBtu, excluding VAT, transportation and other charges. Ukraine and Russia have failed to reach an agreement on renegotiating the current gas contract and further meetings will be held in mid January.

AMMONIA

Ammonia prices began dropping sharply during November as demand began to dry up for December delivery. Industrial markets, which represent 40% of global ammonia trade, such as caprolactam and acrylonitrile, seemed to be particularly affected. Concern over the Eurozone crisis and a possible slide into 'double dip' recession is affecting most non-fertilizer sectors, which are concerned not to be left with too large an inventory on their hands. This coincided with the seasonal fall in fertilizer markets to create a 'perfect storm' for ammonia prices.

At Yuzhnyy, where prices peaked at over $665/t f.o.b. in October, prices fell from above $600/t to the low $500s during November, and continued falling in December, ending the year below $450/t. As prices fell, buyers inevitably began staying away from the market to wait and see how low they would go. Indian DAP markets were conspicuously oversupplied, with knock on effects for exporters in the US and Morocco. Mosaic in the US and OCP in Morocco announced cuts in output as DAP prices fell.

Exports from the Black Sea fell sharply in volume terms, with only 175,000 tonnes loaded in December, and some of that remained unsold. Falling prices finally began to trigger production cuts by the end of December, with Togliatti Azot closing three ammonia lines, and with expectations of fresh buying for the US spring ammonia application season there were hints that prices might have reached a floor. There was little fresh business in the US, however, and Caribbean prices fell from $485/t to $515/5 f.o.b. Tampa prices followed them down, from above $703/t at the start of November to $555/t c.f.r at the end of 2011.

UREA

Urea markets mirrored the losses in the ammonia market, as some of the anticipated extra southern Asian demand failed to materialise. There was also little buying interest in Europe, and US markets were also long, and urea prices dropped accordingly. Yuzhnyy prices made eye-catching falls from just under $500/t f.o.b. at the end of October to $315/t by year end, and some setbacks lower still, and there were indications that lack of interest for January could see more price drops in the New Year.

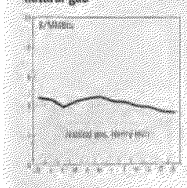
The situation was the same in all major markets. In Egypt the closure of the MOPCO plant due to local environmental opposition continued into a second month, but Egyptian prices nevertheless remained under pressure and fell from $524/t f.o.b. at the start of November to $380/t at the end of December.

Middle Eastern prices were supported a little in December by Indian buying, with over a million tonnes going to tender, although with the amount of competition around for tenders prices still dropped from $500/t f.o.b. to $380/t. Markets were waiting for a 200,000 tonne tender from Pakistan, but other Asian interest remained negligible.

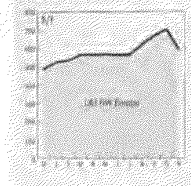
Falling prices eventually brought their own relief as urea began to be available at a discount compared to other nitrates, and European buying interest finally picked up. Turkey also took some tonnages from both the Black Sea and Baltic. There has been some Latin American business with buyers in Colombia, Central America and Peru. ®

WEB OR KOREN EXPORTERS

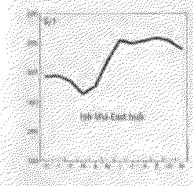
natural gas



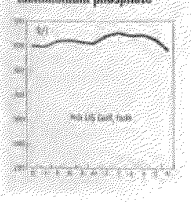
ammonia



urea



diammonium phosphate



METHANOL MARKET SPAIN

The December contract natural gas reference price was settled at $3.49/MMBtu for Texas, and $3.48/MMBtu for Louisiana, down $0.08 from November. On January 17th, Methanex announced that it would be relocating one of its idled methanol plants in Chile to Geismar, Louisiana. The company has begun engineering work and expects production to begin in the second half of 2014. With Pardora Methanol (850,000 t/a) restarting the Beaumont, Texas site this year and LyondellBasell (780,000 t/a) having announced that it will be restarting its Channelview, Texas methanol plant in late 2013, US methanol capacity will increase nearly fourfold by 2015. North America imported around 5.5 million tonnes of methanol in 2011 and these developments will impact on trade as supply shifts.

On the demand side, biodiesel continues to increase production as the industry reaches for the 1.0 billion gallon target for 2012. November US imports contracted from October levels, including 79,000t less from Trinidad, 42,000t less from Equatorial Guinea and 4,000t less from Canada. Total imports were down 119,000t. CMAI posts US spot markets at $1.125/gal ($374/t) f.o.b. Houston.

The three Iranian plants Farnavaran, Zagros (2x1.65 million t/a) and Kharg report continued operation at high rates. Varying statements are coming from NOC in Tripoli regarding a possible restart date for Marsa Al Brega, but all point to some time during Q2. With several vessels arriving in northern Europe, the need for prompt product has largely disappeared and with it bids and offers have fallen to €275/t f.o.b. Rotterdam T2. Based on January deals identified in the market, CMAI post the spot range at €278.5-280/t f.o.b. Rotterdam T2, with the forward month at €275 – 278.5/t. Indian inventory levels remain tight as less Kasias and Saudi product has arrived due to producers holding back shipments as contract negotiations for 2012 continued. GNFC maintained their non-discounted ex-tank price at Rps 23.7/kg.

EU sanctions against Iran have started to take coherent shape with actions planned against oil imports, further dual-use products and the Iranian Central Bank. Reports suggest that a grace period of several months will be allowed for current term contracts to elapse, with some option for extensions. If alternative suppliers cannot be put in place for those most dependent on Iranian supplies – Greece, Italy and Spain. The suggested date for the end of the, muted by several sources, is 1 July 2012. Whether oil products and petrochemicals are also included seems to be under debate. Methanol imports into the EU stood at 4.6 million tonnes to September, down 5.6% on 2011. The loss of Libyan imports following the civil war was compensated by Egyptian imports following the start up of EMethanex at Damietta in April.

The Asian market prices increased but with limited transactions in the week before Chinese New Year. Derivative markets were weak with a number of plants shut down. Asian spot prices are posted at $365-$381/t, c.i.f., depending on location, in southeast Asia. Petronas' large line remains down and the small line is operating at a low rate. Chinese inland domestic producers have fixed most of their production plans with end-users or traders before the Lunar New year. North China traders bought volume from inland producers during the last round of price decreases and recently began to sell part of their inventory as the market is positioned to rise again in the import market, bids were $375/t, c.fr, with offers at $390-$395/t, c.fr.

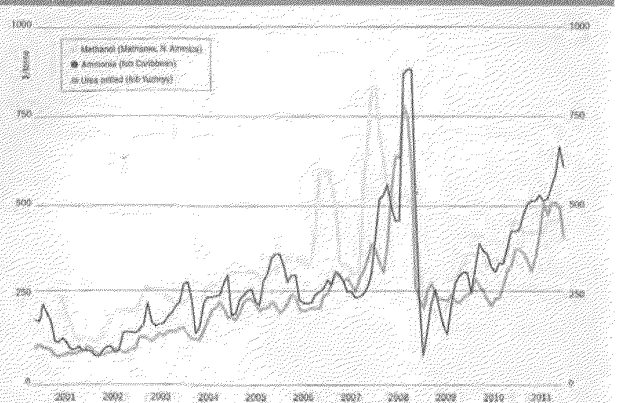
Most derivative markets in Korea are stable as the holiday approaches. Inventory levels in Korea are currently low with the market generally balanced between the weak demand and the low availability of Iranian volume. Bids from the main end-users are near $375/t while offers are higher. Notionally, CMAI posts prices at $375-$380/t. Taiwanese end-users engaged in some enquiries in the market this week. The notional price range was $365-$370/t c.i.f.

Methanex announced on 17 January that they plan to restart the second methanol plant at Motunui, New Zealand in mid-2012 with up to 650,000 t/a of incremental capacity. Methanex reported that they have signed a 10-year agreement with New Zealand-based Todd Energy to supply natural gas for up to half of the 1.5 million t/a of capacity at the Motunui site. The plant has been idle since 2004 and the estimated future capital cost to restart is US$60 million. ®

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Page 815 of 1210

Market outlook

Historical price trends, $/tonne



AMMONIA

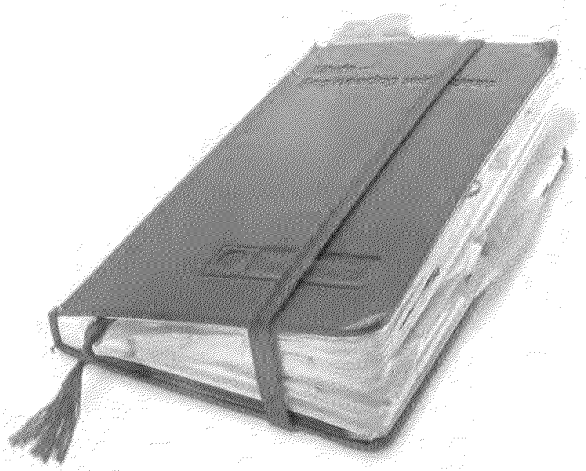
- Falling demand in industrial markets has coupled with a seasonal lapse in ammonia buying to create extremely bearish sentiment.
- DAP prices have also been falling and some phosphate producers have been scaling back output.
- Indian buyers have been trying to delay deliveries on existing contracts.
- The consequence has been a very significant and sustained drop in global ammonia prices across the board.
- Fresh demand is just around the corner for the US spring ammonia application season.
- Overall, world ammonia demand is predicted to be good for 2012, with strong fundamentals in both grain and phosphate markets.
- Lower ammonia prices have triggered some production cutbacks in Ukraine and Russia.
- However, for the moment oversupply in the market seems to indicate further price falls.

UREA

- The urea market has followed ammonia downwards, and there have been large price falls across all major markets.
- A large tranche of new production is still due to come on-stream, especially in China, where several million tonnes of new capacity is due to commence operations in 2012, including Xinjiang Yihua, China Blue, Haifeng Jinkai, Inner Mongolia Hubun.
- This is likely to see the market in oversupply throughout 2012, possibly to the tune of 13 million tonnes.
- Chinese export tariffs are likely to be similar to 2011, with 110% levied on all exports from January to June and November to December, restricting availability and leading to a glut on the Chinese market.
- Uncertainties in the global economy could dampen the market still further, especially for industrial applications.
- There are prospects for short-term improvements especially for granular, but overall the outlook remains bearish.

METHANOL

- Plants continue to restart in US to take advantage of favourable gas prices, potentially replacing US imports of methanol and therefore adding large unsold volumes to the international market.
- The situation regarding exports from Iran under the new sanctions regime remains unclear but could remove large tonnages from the market, possibly towards the middle of the year.
- Chinese markets have been in their traditional quiet period for Lunar New Year.
- However, new methanol trading contracts continue to make Chinese markets volatile.
- Industrial production is at a low ebb generally as confidence in any quick recovery in Europe wanes and the prospect of a Eurozone default remains.
- New capacity additions outside of the US are few, with the possible exceptions of the Mutaroi restart in New Zealand.
- The overall outlook remains very uncertain for methanol pricing.



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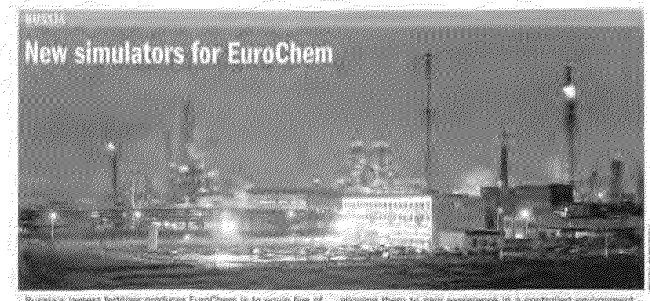
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RUSSIA

New simulators for EuroChem



Russia's largest fertilizer producer EuroChem is to equip five of its ammonia production units with Honeywell Process Solutions' UniSim operator training simulation (OTS) system. The installations will be at Nevinnomysskiy Azot and Novomoskovskiy Azot. EuroChem will use UniSim to create simulated process scenarios as part of its training programme for plant operators. The OTS system can enable process operators to familiarise themselves with the operation of plant equipment before entering the actual plant control room, and so reduce the risk of industrial accidents.

According to Honeywell, the Russian company will be able to train operators in a wide variety of simulated plant scenarios, allowing them to gain experience in a controlled environment. UniSim software, it said, also offers a pre-training preparation system – a suite of products that can be used to study cause-and-effect relationships in the process facility, analyse symptoms, diagnose problems and test emergency response.

"A common problem in our industry today is the shortage of skilled personnel," said EuroChem head of technological development German Tavetinsky. The new software, he said, "will be used to train new and experienced operators in a safe environment, and maintain their skills at a high level ... It also allows us to integrate technical systems from multiple vendors into one universal training programme, which is very important for us."

WORLD

World grain production fell in 2010-11

World grain production fell, to correlating a global food situation already plagued by rising prices, according to new research published by the Worldwatch Institute. Despite record rice and maize yields around the world, global wheat production dropped substantially enough to bring total grain output to just below 2008 levels. Nevertheless, preliminary data for 2011 indicate that grain production is recovering from the 2010 slump. The United Nations Food and Agriculture Organization (FAO) recently forecast that cereal output in 2011-12 will be 3 percent higher than in 2010-11.

Recent growth in agriculture production has been uneven, in many regions, climate change has brought irregular weather patterns such as rising temperatures, violent storms, and flash flooding. In Russia, where severe drought has plagued large farming regions, overall wheat yields plunged 40% in 2010, compared to a decline of only 5% worldwide. Subsequently, Russia banned all wheat exports, severely disrupting world grain markets. Poor weather took its toll elsewhere as well. El Niño in the west Pacific, for example, brought rice production down significantly in the Philippines, already the world's largest food importer.

Rising demand for ethanol fuel, which in the United States is produced almost exclusively from corn feedstock, is having an impact on grain prices as well. US maize production was down 5% in 2010 due to drought in the east and excessive rain in the west. The United States is the world's largest exporter of maize, accounting for 58% of global exports from 2006 to 2010.

EGYPT

Contract awarded for fertilizer project in Egypt

Technimont SpA has been awarded the engineering, procurement, construction and commissioning (EPCC) contract on a lump sum turnkey basis for a new fertilizer complex in Aswan, to be operated by Egyptian Chemical & Fertilizers Industries – KIMA. The new complex will comprise a 1,200 t/d ammonia unit based on KBR Purifier technology, a 1,575 t/d urea unit using Stamicarbon pool reactor technology, and a 1,575 t/d urea granulation plant, also using Stamicarbon technology, together with all necessary utilities and off-site facilities to support the process units. The overall project value is approximately $540 million, and completion is expected by the end of July 2014.

This contract will be the first EPC project for the Maire Tecnimont Group in Egypt and according to the company highlights synergies in the fertilizer sector between the Group's subsidiary sister companies Tecnimont SpA and Stamicarbon BV.

MOPCO shut by environmental protests

While battle lines remain drawn in Tahrir square between protestors and Egypt's new military-backed interim government, the Misr Fertilizer Production Company (MOPCO) ammonia-urea plant in Damietta has been closed by environmental protests in the Mediterranean city which turned violent, leading to clashes with security that left one person dead. MOPCO has faced a history of protest since it started production in 2008. Protesters claim that the unit does not adhere to environmental regulations and pollutes the Nile River, its marine life and surrounding agricultural land. What started as a small sit-in at the city's port quickly escalated to a protest of several thousand demanding closure of the factory. In November, the protesters blocked all roads leading to the city as well as forcefully closing down the port. After a failed attempt by central security forces and army perceived to quell the unrest, the Supreme Council of the Armed Forces (SCAF) ordered the factory to be shut down and all expansion operations to stop. The company denies the accusations of harming the environment.

MOPCO is 71% owned by Egyptian public-sector companies, including EGAS, GASCO, the National Bank of Egypt and Misr Insurance. Canadian-based Agrium owns 26% after MOPCO took over the bankrupt Egyptian project at a nearby site 15km away. The new ilnes are 90% completed, but work on them has now also been halted. The existing plant has 396,000 t/a of ammonia and 635,000 t/a capacity with the two new lines also both of similar size.

AUSTRALIA

Apache buys Burrup, sells to Orica

US independent oil producer Apache Corp has won the right to acquire 65% of Burrup Holdings Ltd, whose assets include a 760,000 t/a ammonia plant on the Burrup Peninsula in Western Australia and a 65% stake in a new $700 million industrial grade ammonium nitrate joint venture project at the site. The sale was made by PPB Advisory on behalf of Australia & New Zealand Banking Group Ltd (ANZ), after Burrup had defaulted on an ANZ loan amid alleged financial improprieties by former owners Parkia and Radhika Oswal. The terms of the deal with Apache were not disclosed, but were reported in the Australian media as a sum of $560 million. Yara, which under the terms of the Burrup Holdings joint venture agreement holds the right to match any offer made for the shares, is reported to be "considering its position" and has until January 31st 2012 to exercise that right.

Apache has been the main gas supplier to Burrup since 2006, and locked in its own legal struggle with Burrup over gas pricing. The company indicated that it intended to sell on the rights to the AN plant to Australian-based explosives manufacturer Orica, and that it did not intend to operate the ammonia plant, preferring to rely on "those with intensive experience in this sector," according to G. Steven Farris, Apache's chairman and chief executive officer. He added that the deal would "secure a long-term economically viable market for our natural gas production in Western Australia".

However, the commercial viability of the new AN plant depends on how quickly it can be completed. There are two other civil protests for Western Australia – Incitec Pivot also has a plant planned for the Pilbara region, while CSBP Wesfarmers has signed off on a $550 million expansion of its ammonium nitrate facilities at Kwinana, south of Perth, bringing capacity up by 260,000 t/a to 750,000 t/a in 1H 2014, sufficient to cover demand in WA until about 2020.

Urea plant okayed

Perdaman Chemicals and Fertilisers' planned coal-based urea plant has been approved by the local Collie Shire Council. Department of Mines and Petroleum (DMP) and Environmental Protection Authority (EPA) requirements will also have to be met before work on the plant can begin. However, Perdaman remains locked in litigation with coal supplier Griffin, now owned by India's Lanco. Lanco is reportedly close to a deal with the Bluewaters Power Station, where the new owner threatened to halt coal deliveries unless the prices paid were raised and moving the dispute to court, a move which caused Perdaman to sue Lanco over its own 25-year coal supply deal.

Orica re-starts AN plant but ammonia remains closed

Orica has been given permission by the New South Wales Environmental Protection Agency to re-start downstream nitric acid and ammonium nitrate production at its Kooragang Island site near Newcastle, following leaks from the site in August. However, the ammonia plant remains closed for the time being and Orica has been buying in ammonia to run the nitric acid plant. Orica shut down the ammonia plant following the release of an amount of sodium chromate containing hexavalent chromium on August 8th, whilst the unit was being brought back on stream following a maintenance turnaround. That incident was followed a few days later by the discharge of effluent containing concentrations of arsenic above EPA licensing limits into the nearby Hunter River. The company shut down the AN plant at the site on November 9th following an ammonia vapour release from a containment tank. A leak of 20,000 litres of weak AN solution occurred on December 7th following an overflow from a tank into dikes around it, forcing a temporary halt to restart activities, but permission was granted to continue the AN re-start on December 9th.

The EPA said it is continuing its investigations and will be appointing Orica's Environment Protection Licence to require the company to appoint an independent engineer to report back to the agency on the incident and appropriate next steps to address this and any similar problems with this part of the plant.

Orica is also being required to undertake ground water monitoring to ensure that there are no offsite impacts from the December 7th incident, the agency said. It added that it will determine appropriate regulatory action once its investigation is complete.

The ammonia plant is said to require further pressure testing before it can be given the go-ahead for a restart. Orica has said that the shutdowns have impacting company earnings before interest and tax by approximately A$4 million (US$4.1 million) per week.

The Kooragang Island ammonia plant has an installed capacity of around 285,000 t/a; a 75,000 t/a expansion was completed in the August turnaround but has not yet been commissioned. The AN facility has a capacity of 430,000 t/a.

UNITED STATES

Rentech completes nitrogen IPO, plans debottleneck

Synthetic fuels developer Rentech has completed its IPO of Rentech Nitrogen Partners LP, which operates an ammonia urea and UAN nitrogen fertilizer complex at East Dubuque, Illinois. Rentech's ownership in Rentech Nitrogen is valued at $403 million based on Rentech Nitrogen's closing stock price on December 14, 2011 and the company says it currently intends to maintain its majority (60.8%) ownership interest. Rentech Nitrogen used $150.8 million of IPO proceeds to repay in full its outstanding debts, retaining $48 million of cash which will be used for working capital and to help fund debottlenecking at the site. A

Topsoe, Inc. – EX1003
Page 817 of 1210

project is under way to increase ammonia production at the facility by approximately 23%, or 70,000 t/a and to increase on-site ammonia storage capacity by approximately 20,000 tonnes. Work is intended for the plant's 2013 turnaround. The entire project is expected to cost approximately $100 million, and generate attractive project returns given current expectations for pricing of products and costs of natural gas. The company is also expanding urea capacity by 17,500 t/a and work has begun on a mixing and loading facility for Diesel Exhaust Fluid (DEF), a urea solution for diesel emissions control which is the US equivalent of AdBlue. The urea expansion and DEF project are expected to be completed by the end of 2012 and will cost approximately $5.8 million.

While Rentech Nitrogen is the major source of company earnings at the moment, Rentech says that it continues to seek investment opportunities "that would combine Rentech's biomass gasification technologies with third-party technology for the production of renewable fuels or power". Research and development work continues at the Rentech-ClearFuels Integrated Bio-Refinery (IBR) Project at the Rentech Energy Technology Center (RETC) in Colorado.

Dakota Gasification expansion

Dakota Gasification Co. is expanding capacity at its site near Beulah, North Dakota. The company is in the design and procurement stages of a new 30,000-tonne ammonia storage facility to increase availability of anhydrous ammonia, which should be complete by 1Q 2013. The company also is in a pre-engineering and design phase for a proposed urea expansion. At present the site produces 1,100 t/d of ammonia, with downstream ammonium sulphate.

New ammonium sulphate nitrate plant

US firms Honeywell and JR Simplot Co. have agreed to build a facility to produce Honeywell's SuN-N 26, a granular ammonium sulphate nitrate (ASN) fertilizer made from a patented Honeywell process which the company claims makes it more chemically stable and resistant to being misused as an explosive. The fertiliser is 26% nitrogen and 14% sulphur by weight.

Under the terms of the agreement, Honeywell will engineer, construct and own the modular manufacturing unit at Simplot's Lathrop, California, production plant. Simplot will operate the facility and have exclusive rights to market and sell the fertilizer in the Western US, Western Canada and Northern Mexico. The companies aim for the unit to be completed and on and running by early 2013.

EGYPT

Notore claims productivity milestone

Notore Chemicals Industries Ltd say that the company's ammonia/urea unit at Onne, Port Harcourt, has achieved 90% of nameplate capacity utilisation during November 2011, and is aiming to reach 100% by the end of 2011. Notore bought the closed unit from the National Fertiliser Company of Nigeria (NAFCON) in August 2005 and re-started operations in 2009 following extensive refurbishment. The plant was shut down for scheduled maintenance during August and September 2011 and since its re-start has been ramping up to its full nameplate capacity, producing 900 t/d of ammonia and 1,350 t/d of urea.

QATAR

Qafco V inaugurated

The Qatar Fertiliser Company (Qafco) formally inaugurated its new Qafco V ammonia-urea line at the company's Mesaieed site December 20th. Qafco says that the new plant will bring its annual production capacity to 3 million t/a of ammonia and 4.3 million t/a of urea, and urea production will rise to 5.6 million t/a with the start-up of Qafco VI in 2012, at which time Qatar will account for about 12.5% of the world's traded urea. A new 60,000 t/a melamine line at the site is now running at 100% capacity according to the company.

PAKISTAN

Gas supply troubles continue

Shortages of natural gas in Pakistan have continued to force shutdowns and disruption to urea plants fed from the Sui Northern Gas Pipeline (SNGPL) network. Gas supplies to Engro's new 1.3 million t/a fertiliser plant at Daharki have been curtailed "indefinitely" and the shutdown of plants on the SNGPL network was expected to drastically increase Pakistan's ongoing urea shortage in December. On November 17th the government committed to a continuous gas supply to the fertiliser sector until December 31st 2011 in order to meet the urea demand for the Rabi (winter) season. There were 300,000 tonnes of urea in stocks in the country at the end of November, but demand during December was projected to be 900,000 tonnes, and with many urea plants shut down, Pakistan faced a shortfall of 300,000 – 450,000 tonnes.

The four plants fed by the SNGPL network have a total capacity of 2.2 million t/a. They include Engro's new urea plant, which has spent 158 days idle in 2011 due to gas curtailments, producing only at 40% of capacity, Dawood-Hercules, which has lost 50% of production, Pak-Arab, which has lost 26%, and Agritech, which has lost 62%.

BULGARIA

Neochim re-starts production

Neochim Plc, one of the largest Bulgarian fertilizer manufacturers, has restarted production after being shut down for a two month turnaround. The Neochim plant, based in the southern town of Dimitrovgrad, was built in 1951, but has now been fully revamped to produce 2,100 t/d of ammonium nitrate and 970 t/d of ammonia. For the first time since it was opened in 1987 the nitric acid facility at the plant will be powered with hydrogen instead of the nitrogen and hydrogen mix previously used, he added.

OMAN

Oman to withdraw from urea project

Oman will withdraw from a project to build an ammonia/urea plant in southern Iran, according to a statement by National Iranian Petrochemical Co. (NPC). The stated reason was a dispute over gas pricing according to NPC, and not the imposition of international sanctions against Iran. The deal to construct the plant in the southern port town of Assaluyeh was signed between the two countries in 2009. Iran expects the Hormuz plant, which requires an investment of $500 million, to produce 1.8 million tons of ammonia and urea annually.

PERU

Nitratos del Perú to begin construction in 2012-13

Nitratos del Perú expects to begin construction of its nitrates project in Ica region's Pisco province by the end of 2012, or early 2013 at the latest, according to general manager Iain Shackleton. The project



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The project involves the construction of a 2,000 t/d ammonia plant, 925 t/d nitric acid plant and 1,000 t/d ammonium nitrate plant in the industrial sector of Paracas district. The company expects to award the contract for basic engineering studies soon, which will be take four to five months to complete, before awarding the detailed engineering studies, construction and procurement contracts. Nitratos expects earthmoving works to begin in 2H12 and construction by end-2012 or the beginning of 2013, with operations startup likely in early 2015. Investment in the project is estimated at $800 million. Swissen said the firm remains in contract negotiations with Contugas, which holds the concession to distribute gas in its region. The project is estimated to require 78 million cubic feet/day (2.15 million m3/d) of natural gas from Camisea. Ammonium nitrate production will be mainly for domestic consumption by the industrial and mining sectors, replacing imports that currently represent 90 – 95% of domestic demand. Nitratos del Perú is a joint venture between Breca of Peru and Chile's Sigdo Koppers.

CHINA

China XLX Fertiliser in bond issue

China XLX Fertiliser Ltd says that Primavera Capital Group has agreed to purchase convertible bonds worth approximately $51 million. The global private equity fund will indirectly hold 14.97% of the company's enlarged capital and become its third largest shareholder and largest institutional investor upon full conversion of the bonds. The 5-year Renminbi-denominated convertible bonds carry an annual interest rate of 4.5%. Net proceeds of Rmb 322 million raised will be used for the development of the company's fourth urea plant, acquisition of coal resources and as general working capital. Primavera Capital will appoint a non-executive director at China XLX as part of the deal.

China XLX Fertiliser Ltd. is one of the largest coal-based urea producers in China. Its current production capacities are 1.25 million t/a of urea, 600,000 t/a of compound fertiliser and 200,000 t/a of methanol. The Company is planning to develop its fourth plant in Xinxiang City, Henan Province. The plant is expected to be fully completed in 2013 and the company's annual urea capacity will then increase to over 2 million tonnes.

SAUDI ARABIA

Saipem to build new Safco plant

The Saudi Arabian Fertilizer Company (Safco) has awarded a turnkey project to Italy's Saipem SpA to design and build a 2 million ryal ($533 million) urea plant at Jubail. Production capacity at the new plant, which will be funded internally, is expected to reach 1.1 million t/a of urea, Safco said. Ammonia feedstock will come from existing capacity at the Jubail site. Construction of the new plant is expected take 26 months, with commercial production due to start within the third quarter of 2014.

Safco currently operates 2.2 million t/a of ammonia and 2.5 million t/a of urea capacity at al-Jubail, as well as 380,000 t/a of ammonia and 580,000 t/a of urea at the Ibn al-Baytar plant, also in Jubail. There is also a joint venture at Jubail (al-Bayroni) with the Taiwan Fertilizer Company with a further 320,000 t/a of ammonia and 620,000 t/a of urea capacity. Toyo Engineering recently announced that it has been awarded an energy optimisation project for the al-Bayroni ammonia plant. The project implementation is scheduled to be completed in the second quarter of 2013, and includes engineering, procurement, construction, pre-commissioning and commissioning assistance on a lump sum turnkey basis.

NETHERLANDS

Sluiskil urea plant handed over

ThyssenKrupp Uhde says that it has formally handed over the Sluiskil urea plant in the Netherlands, which it supplied and commissioned as EPC contractor for owner Yara. The new production facility, which came on stream in mid-July, is Europe's largest urea plant, with a capacity of 3,500 t/d. Construction took three years, and Yara invested €400 million ($550 million) for its construction.

Urea technology was licensed from Stamicarbon, with Uhde responsible for engineering, supply of all equipment and the construction of the plant on a fixed-price, turnkey basis. The new unit will replace the outdated US and UE urea solution units at Sluiskil, increasing production capacity from 700,000 t/a to 1.28 million t/a. Solid urea (granular and prill) output will increase by 300,000 t/a and other liquid products (UAN and AdBlue solutions) by a further 200,000 t/a of urea equivalent.

BRUNEI

Mitsubishi to conduct ammonia feasibility study

Mitsubishi is reported to have been contracted by the Brunelan government to conduct a feasibility study on setting up a 500,000 t/a ammonia plant in the Sultanate, with construction to begin immediately upon completion if the study proves favourable. It is believed that the plant would be a joint venture between Brunei and a Japanese partner.

ANGOLA

Design engineering to begin on ammonia-urea plant

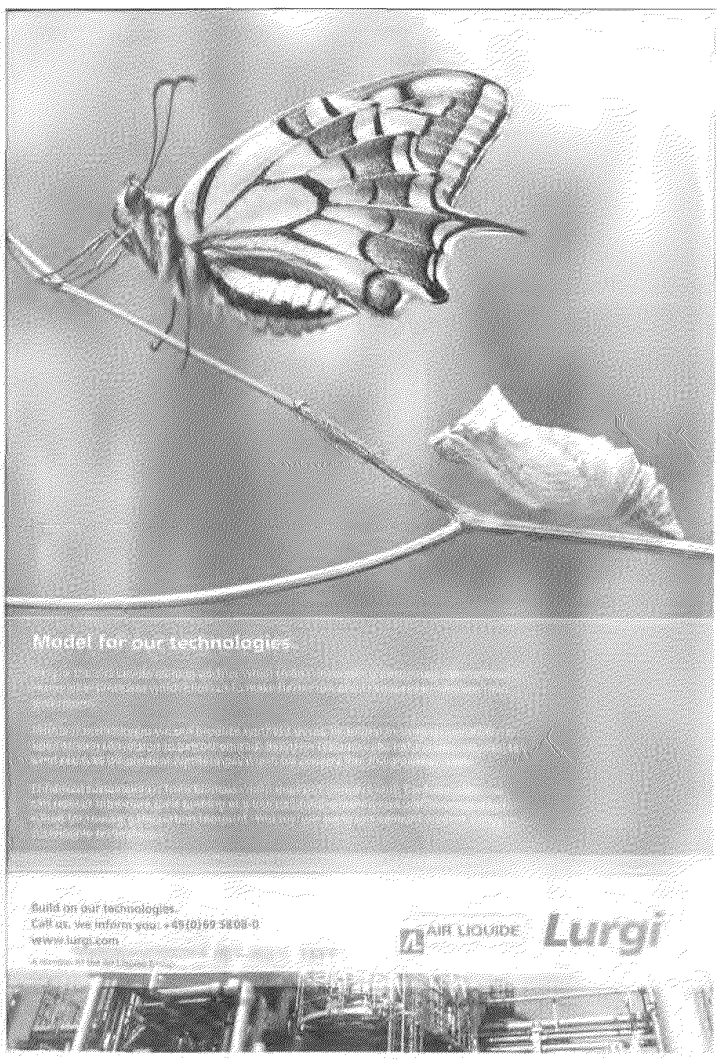
The Angolan Ministry of Geology, Mining and Industry has signed an Early Work Agreement with a consortium of Japanese firms including Mitsubishi Heavy Industries, Ltd. and Toyo Engineering Corporation, Sojitz and Sumitomo for design engineering work on an ammonia and urea fertilizer plant in Angola. The agreement covers the basic design of the plant, preparation of engineering documents and contracts, site surveys, and other work.

The ammonia/urea plant is to be constructed in Soyo in Zaire province, about 300km north of Luanda. Construction, including production and shipping facilities, is scheduled to be completed by the end of 2015, according to Mitsubishi. Planned capacity is 2,000 t/d of ammonia and 1,750 t/d of urea. The engineering, procurement and construction contract will be awarded to the consortium following completion of the design engineering, and the entire project is expected to cost $1.3 billion. According to Mitsubishi, the plant will use excess natural gas supplied to the LNG plant under construction in Soyo.

CAMEROON

Ammonia-urea plant feasibility study

Cameroon's state-owned National Hydrocarbons Corporation has signed a Memorandum of Understanding (MoU) with Ferrostaal for a nine month feasibility study on a proposed gas-based ammonia/urea in the country. The projected size of the complex is 800,000 t/a of ammonia and 700,000 t/a of urea, intended for both domestic and export markets. The location of the proposed plant has yet to be determined.



United States

LyondellBasell to restart methanol plant in 2013

LyondellBasell plans to re-start its methanol unit near Houston, Texas in late 2013. Chief executive Jim Gallogly said that the 780,000 t/a unit at Channelview would be brought back on-stream in late 2013 to take advantage of lower US natural gas prices. The plant aims to generate $130-150 million/year in annual earnings before interest, taxes, depreciation and amortisation (EBITDA). In October last year, there had been rumours that LyondellBasell was trying to sell the plant, and company spokesman David Harpole said the producer had explored "various options" for the unit before deciding to restart it. The plant was closed in March 2003 because of the then high cost of natural gas feedstock. US natural gas prices jumped above $15/MMBtu by the end of 2005, but have since dropped considerably in the US and Canada to as low as $3.55/MMBtu because of the shale gas boom in North America. Lower natural gas prices in North America have prompted the restart of at least two North American plants at a fraction of the cost of building new units. Methanex reopened a mothballed methanol plant in Medicine Hat, Alberta and another closed plant in Beaumont, Texas, was purchased in May 2011 for $65 million and is now owned solely by Egyptian-based OCI Nitrogen.

Foreclosure sale for Range Fuels

The commercial-scale cellulosic biofuels facility in Soperton, Georgia owned by Range Fuels Inc. will be put up for sale in January 2012. Prior to 2011, Colorado-based Range Fuels was widely hyped to become one of the first commercial-scale cellulosic biofuels producers in the US. The wood-to-ethanol/methanol facility aimed to use locally sourced wood to produce cellulosic biofuels using a proprietary technology it had spent years developing. The company garnered the attention of private investors, including Vinod Khosla, and the federal government, which provided a $50 million grant through the Department of Energy in 2007 and a conditional commitment for an $80 million USDA loan guarantee in January 2009, of which half was eventually approved. The state of Georgia also provided grants to the project.

Ground was broken in 2010, but technical difficulties were experienced during the commissioning phase and the company was forced to spend the rest of the year trying to overcome these problems. In January 2011, Range Fuels announced a shortlived run of methanol production, but it ceased operations just days after the announcement and laid off employees at its office in Colorado and the plant in Georgia. At the same time, the defaulted on its USDA loan guarantee and went into Chapter 11 bankruptcy proceedings. The company failed to refinance itself during 2011 and late moves are afoot to liquidate its assets, including a foreclosure sale for the Soperton plant, scheduled to take place on January 3rd. According to the USDA, Range Fuels has repaid only $2 million of its $40 million federal loan, and the company has been roundly criticised for "over-hyping" its cellulosic alcohol technology.

Valero to build new hydrogen plant

Valero Energy, the largest refiner in the US, plans a $298 million upgrade of its Memphis refinery over the next four years. The company will build a new hydrogen plant, make cooking lower additions and improve tanks and other facilities at the 70-year-old facility.

Europe

Uhde buys Otto Corporation

ThyssenKrupp Uhde has bought the Tokyo-based Otto Corporation, as part of its move to expand its market presence in the field of coke plant technologies, particularly in the Asian region. Otto Corp. will in future operate in Japan as a wholly-owned subsidiary, under the name of ThyssenKrupp Otto. According to an Uhde company statement, the acquisition is the result of very close business relations over many years. Back in 1952 Nihon Otto K. K. of Tokyo was founded as a subsidiary of Dr. C. Otto GmbH of Bochum, Germany, and from 1991 onwards it became an independent company trading under the name of Otto Corporation.

Australia / Europe

Compact GTL forms strategic partnership with Fluor

Compact GTL plc, pioneering its own commercial modular gas-to-liquids (GTL) technology, has entered into an agreement with Fluor Ltd, the UK operating division of the US-based Fluor Corporation, for the delivery of front end engineering and design (FEED) and pre-FEED studies for potential commercial scale modular GTL projects. In addition, the five-year framework contract will also cover putting the results of data from CGTL's various demonstration plants into commercial practice, execution of feasibility and scoping studies and support the delivery of EPC contracts.

Nicholas Gay, CEO of Compact GTL said: "our commercial development has gone from strength to strength, and we are attracting world class partners. Fluor has proven experience in the relevant process technologies and a worldwide record of project delivery, making them an ideal strategic partner. The company adds strength to our technical and international footprint needs. The agreement with Fluor is one of the latest components of our strategy to form an organisation amongst world-class partners that can deliver commercial-scale plants."

Compact GTL currently has several project studies underway on behalf of multiple clients worldwide.

Oil / Australia

Tassie Shoals project seeks restructuring

MEO Australia has terminated its 2004 joint development agreement (JDA) with Air Products concerning the proposed Tassie Shoal Methanol Project offshore northern Australia. MEO will pay Air Products a termination fee of A$1 million and a contingent payment of A$8 million from the sale of an interest in the project.

The Tassie Shoals methanol project envisaged the construction of two 1.75 million t/a methanol plants on shallow underwater shoals about 15 m down in the Timor Sea, around 270km northwest of Darwin. There are numerous large, undeveloped gas fields in the area, some with high CO_2 levels (up to 10%), which would make the gas acidic and require additional processing, making it less economical to produce. Conversely, however, it would also be highly suitable for methanol production. A 3 million t/a USD plant was also proposed for the site. When the joint development agreement was formed in 2004, MEO said that it expected the project would attract third party gas suppliers to monetise holdings in the region. However, the company says this business model has not been successful, and it intends to pursue a fresh approach by restructuring the Tassie Shoal gas processing projects during the first part of 2012 to facilitate separate ownership of each of the methanol plants and the LNG plant. MEO will invite participation from interested parties in 2Q 2012.

Europe

Total to sign $3 billion contract for methanol complex

Total is reportedly close to signing a contract with the Egyptian Petrochemicals Holding Company to build a $3 billion plant to produce various olefins from natural gas via a methanol route. The olefins complex is expected to produce 470,000 t/a of polypropylene, 185,000 t/a of gasoline, 40,000 t/a of LPG and 330,000 t/a of acetic acid. Current plans envisage production beginning by late 2014 at a site in the northwest of the Gulf of Suez. The complex will include a methanol-to-propylene processing unit.

Europe

New methanol plant

Russia's Ural Methanol Group, a joint venture between Austria-based OCP Chemicals AG and Russian energy major Neva Oil and Gas, has finalised contracts for the construction of a 500,000 t/a methanol plant at Nizhny Tagil near Sverdlovsk. Construction is to begin in 2012 with completion scheduled for 2015. Total cost for the project is put at $400 million. Ural Methanol Group signed the turnkey engineering, procurement and construction contract with Czech-based engineering company ALTA in July 2010, with 71% of financing provided by the Czech Export Bank.

Europe

Expansion work on renewable methanol plant

Icelandic firm Carbon Recycling International (CRI) has begun work on an expansion to its methanol demonstrator plant at Svartsengi which produces 'renewable' fuels using energy from the nearby Grea Geothermal power plant. CRI says that it aims to be the first in the world to produce renewable fuel on a commercial scale from waste CO_2, using the tail gas stream from the geothermal plant, which consists of 90% carbon dioxide. The CO_2 is combined with hydrogen generated using electrolysis of water, with the electricity for this also coming from the geothermal plant. A 1,200 t/a pilot plant started operation at the site towards the end of 2011, and the expansion will take production to 3,000 t/a of methanol production by 2Q 2012. The methanol will be blended locally with gasoline as a vehicle fuel by Icelandic fuel company Olis, although the Icelandic authorities currently only allow a 3% methanol blend. CRI says that 4,800 t/a of CO_2 will be 'recycled' in this way, as an alternative to underground storage. CRI has plans to build a larger-scale unit to produce up to 30,000 t/a of methanol by 2013.

Middle East / Europe

US sanctions may halt Veniran plants

A new package of sanctions approved by the United States and other countries against Iran could halt work on the Venirao methanol plants, according to Venezuela. President Barack Obama has signed an Executive Order authorising new sanctions against any person who sells or provides goods, services, and technology to Iran or supports Iranian oil development with specific amounts of money. The US can mete out sanctions to those who "contribute to the maintenance or expansion of Iran's petrochemical sector through the sale, lease, or provision of goods, services, and technology." Canada also imposed economic sanctions on Iran, and banned sales to Iran of inputs for the petrochemical, oil and gas industries. By targeting the Iranian oil and petrochemical sectors, Washington intends to cut off Tehran's foreign currency flow.

However, the move against the Iranian oil and petrochemical sectors has caused alarm in Venezuela, which is involved in a number of joint petrochemical projects with Iran, including a 140,000 bbl/d refinery in Syria announced in 2010 and due to come on-stream in 2012, and two large-scale 3.65 million t/a methanol plants, one to be built in Iran, the other in Venezuela. The so-called Venirao methanol project agreement was signed in 2007, but work on the Iranian plant at Asaluyeh, at an investment cost of some $700 million, has stalled in spite of EPC contracts being awarded in 2010. In 2010, Venezuela also authorised a joint venture between the Venezuelan Petroleum Corporation (CVP) and Iran's Petropars in the Dobokubi field in the state of Anzoategui in northeastern Venezuela, at a total cost of $1.5 billion.

Canada

Uhde to build hydrogen plant

Linde is set to build and operate a new hydrogen plant in the Jilin Chemical Industrial Park (JCIP) in northeastern China. The company will be investing around euro 42 million in the first phase of this new project. The hydrogen plant is expected to come on stream by the end of 2013, supplying several companies in the Jilin chemical complex with high purity hydrogen. This park is home to the production facilities run by Evonik Industries and Jilin, a joint venture between the PetroChina Jilin Petrochemical Group and the Jilin Sherman Group.

"The project further strengthens our leading position as a gases and engineering player in China," said Sanjiv Lamba, Linde's board member responsible for Asia. "We are delighted to see more and more large-scale industrial developments in this dynamic region and – together with our partners – we are committed to supporting the development of these projects as we move forward."

The new hydrogen plant will use steam methane reforming to produce 25,000 Nm³/h of hydrogen. It will be built by Linde's Engineering Division and operated by its Gases Division. In addition, Linde will set up a subsidiary, Linde Gases Jilin, to focus on further expanding the gas supply infrastructure in and around the JCIP chemical complex.

Canada

Hydrogen plant to start in 1Q 2012

Work on a hydrogen plant at the Syncrude Canada oil sands upgrader was completed in December, according to Canadian Oil Sands Ltd., the biggest holder in the venture. Syncrude has been struggling bitumen, which will be processed into a light, low-sulphur synthetic oil, at its northwestern Alberta facility in anticipation of the restart.

Topsoe, Inc. – EX1003
Page 820 of 1210

People

Haldor Topsoe has appointed **Dr. Bjorne S. Clausen** as its new Chief Executive Officer following the resignation of Niels Kegel Sørensen, who has held the post since September 2007. The company's board expressed their sincere recognition of Niels Kegel Sørensen's 35 years of employment with the company and in particular his great efforts, first as CEO of the subsidiary Haldor Topsoe, Inc. and later as CEO of Haldor Topsøe A/S, during which time the company has achieved excellent results in spite of difficult times in the global market.

Bjørne Clausen has been employed in the company since 1979, first as a researcher in R&D with the responsibility for many of the company's international collaborations and later as Director of R&D. In 2008, Bjørne Clausen was asked to take over the management of the Technology Division, and as Executive Vice President, initiated many changes and more efficient procedures.

Chairman of the Board, Dr. Haldor Topsøe said: "Haldor Topsøe A/S is facing some very exciting and interesting development opportunities and the Board is very pleased that Bjørne Clausen with his unique experience and background has accepted to manage the company on the way forward."

Jörg Hoffmann has been appointed as to the board of Aumund Fördertechnik GmbH. Hoffmann was previously a member of the management at Schade Lagertechnik in Herne, part of the Aumund Group. In conjunction with Franz-Walter Aumund and Dr. Volker Brandenburg he will assume responsibility for the operational side of the business.

From Germany's Westphalia region, his professional career began in January 1998 as sales manager at SMS AG in Hilchenbach. After further positions of responsibility in the USA and as a management board member both in China and Canada, he returned to Germany and in December 2008 assumed a new management role at Schade Lagertechnik in Herne.

Helm Fertilizer Corp. has added **Jerrod Greene** and **Adam Dye** to its marketing team as from the start of 2012. Greene will serve as Southwest Region sales manager responsible for sourcing product and sales in Oklahoma, Texas and New Mexico.



Dr. Bjørne S. Clausen of Haldor Topsøe.

Dye will be West Region sales manager, responsible for Iowa, Kansas, Missouri, Minnesota, Nebraska, North Dakota and South Dakota.

Origin Fertilisers UK Ltd. has appointed **Michael Pater** as managing director. He succeeds Mike Redden who is stepping down from the position of managing director after 10 years, although he will continue as purchasing director. Pater studied agriculture and graduated from the Royal Agricultural College, Cirencester in 1984, and subsequently joined Seabright Chemicals/Industries, working in various capacities within the fertiliser business until he joined IAWS Fertilisers/Origin Fertilisers in 1997. Since 2000, he has held the position of sales director.

Engro Corporation Limited (ENGRO) has appointed **Khalid Mansoor**, currently chief executive of Engro Powergen Qadirpur Limited, as chief executive of Engro Fertilizers Limited with effect from January 1, 2012, according to the company. At the same time, **Khalid Siraj Subhani**, currently chief executive of Engro Fertilizers Ltd, will take over as chief executive of Engro Polymer & Chemicals Ltd on the early retirement of its current chief executive, Asif Qadir.

Oswal Chemicals & Fertilizers Limited has changed the name of the company to Oswal Green Tech Limited with effect from October 21, 2011.

Diary 2012

FEBRUARY

AFA 18th Annual Fertilizers Forum and Exhibition, Cairo, Egypt.
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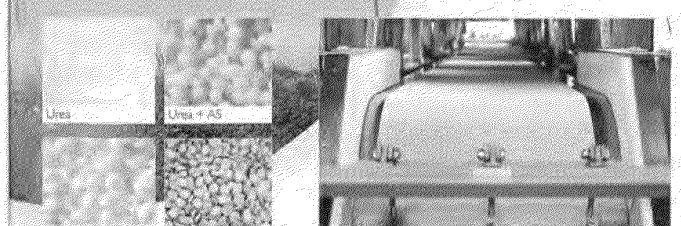
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Problem No. 10 - High NH$_3$ content in liquid outlet of a stripper handling CO$_2$ effluent in urea synthesis

It is well known that the high pressure CO$_2$ stripper efficiency in a urea plant is defined by the ammonia content in the liquid bottom outlet. The ratio NH$_3$/CO$_2$ in the bottom outlet is determined by equilibrium equations. Problems have been experienced with a relatively high CO$_2$ content.

Several possible causes are explored. One cause could be that CO$_2$ slips through with the liquid bottom outlet due to a defective level measurement in the stripper bottom. Measuring the liquid level is not an easy task due to the corrosive nature and the risk of crystallisation. Sometimes a delta-P level transmitter is applied with flushes in its legs, but this is not a reliable option. Radioactive level measurements are often used but still safety risks, complicated calibrating procedures, limited lifetimes and maintenance costs are significant concerns. The radar level measurement developed by Stamicarbon offers a new and reliable solution.

Mr Amir Hamzah of PT Petrokimia Gresik in Indonesia introduces an interesting topic to the round table:
In March 2010 we carried out some maintenance on our high pressure CO$_2$ stripper due to high NH$_3$ content in the liquid bottom outlet. After start-up, the NH$_3$ outlet improved (down from 15.8 wt% to 14 wt%, while the design figure is 12.8 wt%). However, CO$_2$ is still high (before shutdown 16.4 wt%, now 16.2 wt%, design is 13.28 wt%). Now our recovery section is getting hotter. In my opinion, the higher the decomposition rate of carbamate in the stripper, the lower the NH$_3$ content in the bottom of the stripper, as with CO$_2$. However in my case, the NH$_3$ content in the outlet is lower but the CO$_2$ is still high... I welcome comment on what's going on with this high CO$_2$ problem.

Mr Hadi Mohammadian of Pidamco in Iran comes up with a possible cause:
Check for gaseous CO$_2$ slip from the bottom of the stripper if N/C ratio in the synthesis section is normal.

Mr Emilson Acevedo of Qatar Fertilizer Company (Qafco) in Qatar shares his experiences:
We had the same problem some years ago. I suggest you check the stripper level indication, which can be wrong due to bad calibration or vortex formation. Incorrect level indication will permit CO$_2$ bypassing, which you cannot easily figure out. Try to close the stripper outlet valve more than usual (by 5%) and wait, the high stripper level alarm comes on, you will see a change in the stripper bottom temperature and in the recirculation pressure.

We have installed a box inside our stripper. This device is used to avoid vortex formation and allow us to obtain the correct level indication. Your ammonia content seems to be very high, which kind of urea process are you talking about?

Mr Mohammad Rahmanifar of Pidamco in Iran introduces new process parameters to double check and correct:
It seems the stripper efficiency is low. I suggest you investigate the saturator drum pressure and its level, N/C ratio and adjust reactor temperature.

Mr Muhammad Salman of Fatima Fertilizer Ltd in Pakistan confirms that unreliable level measurement could be a possible cause:
I am of the same opinion that there is every possibility of CO$_2$ slippage to the recovery section. Another explanation could be that urea hydrolyses into NH$_3$ and CO$_2$ but in your case as the NH$_3$ contents are the same this can be ruled out. From your design conditions it seems that you have a TEC ACES process. If this is correct then the only thing could be the problematic flushing water pumps to the stripper level transmitter.

Address the issue and hopefully you will get a positive result.

Mr Mark Browne of UreaKnowHow.com provides and asks for some more information:
Gensik operates a TEC ACES urea plant. The reactor pressure is higher than in a Stamicarbon plant and the stripper efficiency is lower. A medium pressure recirculation section is therefore part of an ACES plant. What are your design and actual reactor pressure and design and actual stripper efficiency?

Mr Rahmat provides some answers:
Yes, we have the ACES process. Before posting this topic, we had already taken some action.

We regulated the stripper bottom level. Normal operation is 40%, we increased it to 50% and the CO$_2$ content is still the same. We also decreased it to 25% and had no effect.

We regulated the saturation drum level. Normal level is 61%, steam pressure 17.4 kg/cm^2.g. We decrease it to 50%, the steam pressure was also run down to 16.4 kg/cm^2.g), bottom stripper temperature was increased to 170°C. The CO$_2$ content is still high.

Our conditions for the reactor and stripper are: reactor design pressure 175 kg/cm^2.g, actual is 170 kg/cm^2.g; N/C ratio design is 4, we maintain it in the range 3.96-4.04; design stripper efficiency is 72.8%, actual is 67.2%.

Mr Ashraf of Fatima Fertilizer Ltd. in Pakistan shares his experiences:
We have the same conditions at our plant but have never had this high CO$_2$ content problem. Can you tell me what the results at the reactor outlet and stripper outlet? Can you tell me whether CO$_2$ in the reactor remains OK? I still believe that it is CO$_2$ slippage from the stripper. Does your ammonia feed to the reactor have the same rate as earlier at the same CO$_2$ load?

As the stripper bottom temperature you are operating at is not favorable for hydrolysis I would rule this cause out.

Try to further increase the stripper level. When we had similar problems we increased it up to 100%. There are two temperature indicators at the stripper bottom which can give you an idea about level position. Moreover the CO$_2$ compressor discharge pressure will start increasing when the level approaches the sparger area.

Mr Kamal Hussain of Pak Arab Fertilizers in Multan, Pakistan suggests another way to determine the cause:
There may be a problem in the level transmitter of the stripper, low level of stripper causes passing of the gases to the lower pressure recovery section. It can be judged by the temperature of the stripper off gases, if it is lower than normal than the stripper efficiency is will be lower with a low level in the stripper bottom.

Mr Muhammad Adnan Hanif of Fauji Fertilizer Company Ltd in Pakistan provides some suggestions:
In my opinion, you should post more details such as the current and design operating parameters; pressure and temperature of the stripper, reactor inlet and outlet compositions along with conversion, steam to stripper pressure, and stripper bottom and top temperatures. These are necessary to investigate the higher CO$_2$ at the stripper outlet.

With the available information, I can only suspect the N/C ratio is on the lower side than that reported. How do you measure the N/C ratio i.e. through laboratory or some instrument? In the stripper there are two types of stripping in progress; chemical stripping and mechanical stripping. So, if NH$_3$ is stripped off there is no reason that CO$_2$ does not strip-off, based on the same N/C ratio.

Mr Mohammad Khalid Hussain of SABIC in Saudi Arabia contributes to the discussion:
Many assumptions can be made for this case but I suggest the following:

- first check that the reactor conditions are normal, in particular the N/C ratio;
- check the calibration of the stripper bottom level transmitter;
- operate your stripper at higher level set point than normal. This problem is probably CO$_2$ slippage caused by wrong indication of the level transmitter.

Mr Ramzan provides some more answers:
The N/C ratio is measured by laboratory analysis. We have a normal N/C ratio as stated earlier. Last week we increase the saturation drum pressure from 16 K to 17 K. The result is quite good, the bottom stripper temperature increase to 174°C, the efficiency of the stripper increased to 68.4% from 67.2%, the synthesis loop pressure also increased from 170 K to 171.4 K. Now the NH$_3$ outlet stripper is 14.13% while CO$_2$ is 15.4%.

Mr Bikramjeet asks for some more information and makes some suggestions:
What is the condition of your recovery system condition after increasing the steam pressure of the stripper shell? Your design N/C ratio for the stripper outlet stream is 2.5 and at present this ratio is 2.36, so I think that first of all, you should try to reach the design N/C ratio.

I think it is better to decrease the amount of CO$_2$ outlet to the recovery section with throttling of level control valve in the stripper outlet to reach the higher ratio.

Mr Mark Browne introduces another cause:
Another cause could be that the relatively high CO$_2$ content is caused by a bad sampling method. Taking a good sample from the liquid bottom outlet is not easy due to the high pressure, high temperature, crystallization of the media, formation of a gas phase due to the pressure drop and the hazardous ammonia. BASF in Austria has developed a no dead volume high pressure sampling valve which makes taking a sample much safer and easier.

Mr Muhammad Salman of Pak-American Fertilizers Ltd in Pakistan contributes to the discussion:
I have seen this plant and am familiar with Toyo ACES loop of technologies, hence I would like to add that the problem you are facing is due to little or too little CO$_2$ conversion in your reactor which can be improved to obtain optimum results.
The steps required are:

- increase steam saturation drum pressure (UFA-101 in your case) gradually 0.2 to 0.5 kg/c only 17.1 - 17.6 kg/cm^2, so that the stripper bottom remains in your desired range. Keep synthesis pressure around 172 kg/cm^2. Try to maintain N/C ratio of 4.0 in the urea reactor.
- Counter the risk of the pressure rise by R/C.

An increase in synthesis pressure will gradually reduce your CO$_2$ content at the stripper outlet and recovery will dictate these changes.

Mr Muhammad Shahid Nawaz adds the following suggestions:
I suggest you check the following:

- loop pressure is normal;
- condenser bottom temperature is normal;
- calculate stripper efficiency based on ammonia looking on but on basis of CO$_2$ in leak;
- check that the stripper bottom level transmitter is working normally. I think the level at the bottom of the stripper is less and CO$_2$ slipping.

Mr Waqar Malik of Engro Fertilizers Ltd contributes to the discussion:
If the level of the stripper is the reason, the CO$_2$ usually increases from the bottom only if the level is high and is near the CO$_2$ sparger i.e. somewhat above the bottom nozzup. This is because the direction of CO$_2$ sparger holes in the TEC stripper is downwards and not upwards. I think the following two possibilities also need consideration.

In the TEC stripper, the bottom CO$_2$ sparger has pipes with holes of variable size. It is quite possible that these sparger pipes are not reinstalled as per drawings and there is a mal-distribution of CO$_2$ at the bottom so check this at the next available opportunity.

There may be some level build up in the bottom of the stripper shell due to higher steam flow or some restriction in piping. This causes the stripper bottom temperature to decrease more than expected and thus increases the solubility of CO$_2$ in the stream leaving the stripper bottom. This can be verified by comparing the change in delta-T with change in stripper efficiency. ■

This series of discussions is compiled from a selection of round table topics discussed on the UreaKnowHow.com website. UreaKnowHow.com promotes the exchange of technical information to improve the performance and safety of urea plants. A wide range of round table discussions take place in the field of process design, operations, mechanical issues, maintenance, inspection, safety, environmental concerns, and product quality for urea, ammonia, nitric acid and other fertilizers.

Topsoe, Inc. – EX1003
Page 822 of 1210

Methanol: the future remains bright

Nitrogen+Syngas reports from the IHS World Methanol Conference in San Diego, held in December 2011, on how the rapidly changing market for this important syngas derivative is shaping up.

It is just short of 100 years since Dr Alwin Mittasch of BASF made the first synthetic methanol from carbon monoxide and hydrogen at Ludwigshafen. By the time that his invention reaches its centenary in 2013, the methanol market will exceed 90 million tonnes per annum. Most of that growth has occurred in the past 40 years, as countries discovered natural gas in remote parts of the world and used methanol as a way of monetising it, replacing older, higher cost capacity in Europe, North America and Japan, as gas costs there rose. Methanol derivatives, however, still tended to be produced in the developed world, and so a large seaborne methanol trade developed.

As we move into the 21st century, the market is changing more rapidly than at any time since the 1970s. New consumption of derivatives is moving to newly industrialising countries, particularly China, and economies of scale and falling production costs mean that new and some like fuel blending and even on-purpose propylene production are coming to the fore.

Energy markets

To bring sufficient new supply into oil markets will require all new sources of supply, including oil sands, deep water drilling etc. The likelihood is thus that the price will remain above $100/barrel for the foreseeable future, which provides a basis for investment in new technologies such as coal, gas and biomass to liquids, and of course methanol. Biofuels will continue their push into the refined product market, but there is unlikely to be any great "second generation" breakthrough. However, these still represent a small slice globally.

Shale gas productivity per well continues to rise and risk and well completion break-even costs are averaging $4.00-4.50/MMBtu, with the presence of natural gas liquids bringing this down. However, in spite of some progress in China and Poland, the shale gas boom remains slow to spread elsewhere. Rising coal and feedstock gas prices in China are expected to impact on the long-term average pricing of methanol, but it remains underpinned on an energy equivalent basis.

Methanol markets

Dewey Johnson gave the usual overview of the global methanol market. He expected the global methanol supply-demand balance will tighten through 2016, becoming even more pronounced after 2017 unless new capacity comes on-stream. The methanol market has been at a low point after the most recent large tranche of capacity, while demand continues to ratchet up. In general, methanol demand for conventional derivatives – mainly chemicals – tracks GDP, or GDP plus – on average by a factor of two. However, fuel uses have the potential to create a step change in global demand for methanol just as they have in China. He did not expect rising methanol prices to stop growth in fuel applications, as these are driven by differentials in energy prices (especially between natural gas and oil), which are expected to remain large, as noted above. Methanol remains cheap compared to gasoline on an energy equivalent basis. Meanwhile, large-scale production and large scale downstream uses like MTO/MTP, MTG or however also bring the potential for shocks in the supply/demand balance. Process technology continues to advance, with feedstock diversity, increased scale, yield improvement, and integration options. Feedstock dynamics also continue to affect supply location, with new capacity generally coming from advantaged feedstocks, these days including low cost gas and stranded coal in China.

China and Asia

Several papers focused on China, which has come to dominate the global methanol market. The Chinese government is trying to move away from the smaller, dedicated coal production of the past and towards larger-scale, more integrated complexes. Although there are reportedly 291 methanol producers in China, more than half of all production is accounted for by 30 companies, and this consolidation is set to continue. A series of mega-scale integrated complexes is planned to be established by the end of 2015, and many of the smaller scale units will probably close.

Coal is of course the feedstock of choice. China has 319 billion tonnes of reserves, but these are mainly in the north of the country, and often far from end use markets. As well as fuel blending, other downstream opportunities like methanol to olefins, and now coal to monoethylene glycol (MEG) are set to take an increasingly large share of coal demand. By 2016, fuel, chemical and olefin demand will all be roughly one third each of China's methanol demand. China's massive coal imports mean that it is a global market setter, but since additional new capacity is using cokе oven gas as a feed, Chinese coke-based methanol capacity has grown from 300,000 t/a in 2006 to 6.6 million t/a in 2011, although its operation is very dependent on the steel and other markets.

China has somewhat overshadowed the rest of Asia, but southeast Asia, where capacity continues to increase, much of it for export, is also seeing increased demand growth, especially in Indonesia and Singapore.

Other regions

While China has become the major consumer of methanol in the world, India has lagged behind, with 3.75 million t/a of domestic production and less than 1.5 million t/a of demand. Is there any sign of this changing? The short answer is yes, but not rapidly. Formaldehyde, methylamines, chloromethanes, and pharmaceutical uses have been the fastest growing derivatives, and are set to take demand above 2.0 million t/a by 2015, but a large scale fuel/energy use such as has been seen in China remains unlikely, and the government has privileged ethanol blending over methanol.

European methanol demand is relatively mature, likely to rise from 8.1 million t/a today to 9.3 million t/a in 2016 according to IHS. Gasoline/fuel blending is likely to be the fastest growing sector, but formaldehyde remains the bedrock of demand at 51%. FSU demand is likewise growing slowly, from 3.1 million t/a to 3.4 million t/a over the same period, but capacity is likely to increase over the same period. The same is true of the Middle East and Africa, where capacity runs far in excess of the relatively modest domestic demand, mostly for fuel components such as TAME and MTBE. Capacity additions are particularly siloed for Iran, where there are 22 million t/a of new projects, but given the country's international isolation at present, how many of these can be financed and built is a moot point. Another 8 million t/a of capacity is planned or projected in North Africa and other parts of the continent such as Nigeria, Tanzania or Mozambique.

In North America, demand has been dominated by the US and supply by Trinidad, but the shale gas situation has led to many restarts in the continental USA and Canada, and over a million tonnes of new capacity. Demand continues to increase modestly, with fuel blending, biodiesel and MTBE for export all contributing. In the rest of the Americas, Venezuela is the largest producer since Chile has suffered from the supply issues, but this situation could reverse by the 2015-16 time frame as new gas supplies are brought on line offshore of Chile. Biodiesel and fuel blending are also set to make an impact here, especially in Brazil and Argentina.

Downstream markets

Formaldehyde remains the largest consumer of methanol on a global basis, with resins, especially urea-formaldehyde, responsible for the majority of demand. Needless to say China is the fastest growing area for both demand and production, with over 30% of the market already. However, formaldehyde still faces challenges in the US and Europe over its alleged carcinogenic properties. EPA draft legislation in the US would set ridiculously low values for permissible formaldehyde levels, although the good news is that the National Academy of Sciences has commented unfavourably on the EPA's report. Nevertheless, the uncertainty over the compound continues. There is the potential for a major impact on demand, although at the moment there are no real feasible alternatives.

Acetic acid is the second largest chemical use for methanol. Shale gas production in the US has not only brought down natural gas costs but also the cost of producing acetic acid, significantly changing the industry cost curve, leading to re-starts, debottlenecks and new construction there. Meanwhile demand for acetic acid stood at 13.0 million t/a in 2010 and is forecast by Lyondellbasel to rise at an average annual growth rate of 3% per year over the period 2011-2017, much slower than the 11% AAGR that it averaged from 2007-2011. Within that overall demand picture, vinyl acetate monomer and purified terephthalic acid are the fastest growing areas.

On the fuels side, MTBE demand declined from 20 million t/a in 2002 to 15 million t/a in 2008 due to the ban in the United States, and capacity fell at the same time to 18 million t/a, mostly in China and the Middle East. Demand has been slowly recovering, with China, Saudi Arabia, Iran and South Korea the largest consumers, and Mexico and Venezuela have also been increasing their blending of the compound. Demand is forecast to increase fastest in China, which will have a 22% market share in 2016.

Biodiesel is hit a low point in 2010 in the US as the tax credit lapsed, but is forecast to grow quickly under the new renewable fuel standard to 1.28 billion gallons in 2013.

DME has been a big hit as an LPG blendstock in Asia, but whilst about the US? Elliott Hicks of Oberon Fuels shared a vision of small-scale modular US production from bio-feedstock and cheap natural gas to produce DME "in sync" with market growth. However, commercialisation of the modular production technology was still out in 2015, he admitted.

Methanol to gasoline is a technology which has come back into vogue now that oil prices seem set to remain high for the foreseeable future. The 1980s vintage plant in New Zealand has now been joined by a 100,000 t/a demonstrator unit at Jincheng Anthracite Mining in China. ExxonMobil rehearsed the advantages of the process, and announced that Jincheng now plan to build a 1.0 million t/a unit at the same site.

Of course, methanol has also taken off as a fuel in its own right, and Lotus looked at the inclusion of ethanol-methanol-gasoline blends and how they might work in the Flexible Fuel Vehicles now being mandated in the US.

'Giga' methanol

Large scale production is nothing new for the methanol industry, with Lurgi and Haldor Topsoe both showcasing their ability to construct plants of 5,000 t/d, in both cases based on innovative catalyst technology from Sud-Chemie or developed in-house respectively. But now the move is towards even larger units of 10,000 t/d. Topsoe believe that by running conventional steam methane reforming and autothermal reforming in parallel this can be achieved in a single train. Perhaps the most intriguing paper was saved until last, with methanol entrepreneur Dan Van Wyk also discussing a 10,000 t/d plant, based on Lurgi's established 5,000 t/d Atlas plant on Trinidad – which Dan also helped develop. The idea is to double the pressure of the plant (reducing the load on the syngas compressor) and hence the throughput, based on Lurgi's high pressure autothermal reformer. He believed that there were plenty of opportunities globally for plants of such a "giga" size for in fact double that, since the Jubail project relies on two such trains, producing 20,000 t/d, not intended for the merchant market, which it would swamp, but with downstream methanol to olefins or methanol to gasoline capacity – much larger downstream markets. There is abundant gas, he said, to feed such an enterprise, especially when shale gas – not just in the US but around the world – is taken into account. In the meantime Dan has been working on the Pandora project, re-starting the Beaumont methanol plant in Texas, which has now been handed over to partners OCI. ■

Topsoe, Inc. – EX1003
Page 823 of 1210

AN/NA conference report

Papers presented and subjects discussed at the ammonium nitrate/nitric acid (AN/NA) meeting, held in Denver, Colorado late last year.

Ammonium nitrate has been in the news recently for all of the wrong reasons, and safety and security concerns were to the fore at the AN/NA meeting in Denver, this year hosted by Dyno Nobel, based just across the state line in nearby Cheyenne, Wyoming. However, as usual technical concerns and operator experiences were also aired, making for a varied and informative conference.

Safety and security

Pam Griffin of The Fertilizer Institute (TFI) went into more detail on the US Secure Handling of Ammonium Nitrate Act, which was passed by Congress in 2007 but which did not finally see a Notice of Proposed Rule-making until 2011. It requires registration with the Department of Homeland Security (DHS) anyone who sells, purchases and takes possession, or transfers ownership of ammonium nitrate (AN) – AN defined as not less than 33% nitrogen by weight in its pure form, as well as in any mixture amount in by determined by DHS – currently any mixture of 30% or more AN falls under the law. There will be point of sale verification via an approved DHS database, and if an unregistered agent is used to make a transfer (eg a haulage company) then there must be telephone verification with an authorised dealer. The onus is on the seller to verify, and there are considerable record keeping requirements. There are exemptions for AN made into ANFO explosive (which falls under existing explosives legislation) and for parcel sizes of 25lbs or less, although the industry opposes this latter as it could easily be used piecemeal to assemble sufficient AN to make a sizeable explosive. There are also questions about civil liability if AN is later used as an explosive.

Consultant **Kish Shah** ran through the European situation on AN under REACH and UN Transport regulations. He considered in some detail the case of an EU Chemical Safety Report for AN which had concluded that it was an eye irritant, and what this meant for mixtures involving AN. Using 'dredging' principles Fertilizers Europe has carried out a series of tests on mixtures containing less than 80% AN, confirming that these were not eye irritants.

In tackling the subject of best practice for AN plant design, **Alkiviadis Burch** of CPI ran through a series of serious accidents in the AN industry, presented at earlier AN/NA conferences, and their implications for plant designers.

The conference was also addressed by US Army Lt General **Michael Barbero**, who is the director of JIEDDO (see side bar page 26). General Barbero has been in discussions with the government of Pakistan, amongst others, on ways of tackling the threat from improvised explosive devices (IEDs), particularly to US troops in central Asia, but more generally both at home and abroad. He outlined the work of JIEDDO and invited industry participation.

Technology

A slightly off the wall beginning to the technology papers, as **Bruce Peters** of Atmergic LLC presented what he described as a single-step synthesis of AN using a pulse jet process. It is a refinement of the old Birkeland/Eyde process, which generates NO using an electric arc in air, oxidising this to HNO_3 in water. Here however a hydrogen-fueled pulse jet generates the ammonia and NO at incredibly high temperatures, and a water quench converts this to ammonium nitrate. However, as for the system remains largely conceptual, with some lab experiments completed.

Next, **Peter Hein** of CSEP showed that analysis and sampling for CO and N_2O in AN prill storage can act as an early warning system for AN breakdown, and presented some results from live testing.

Jean-Francois Granger of GPN presented a prill tittering process developed by GPN in the 1980s which can increase capacity in existing prilling plants by up to 50%.

Neville Jordaan of Spies showed some illustrations of indirect heat exchanger coolers and showed how the technology had changed from its earlier immersion, when AN phase changes had not been taken into account, and caking on the plates made some installations require frequent cleaning. The caking issue is solved by avoiding condensation on exchanger plate surfaces by maintaining the dew point of air in the void space below the plate temperature. Different fertilizers require different control over humidity in the cooler, and AN with its hygroscopic nature needs particular attention to water temperature profile through the cooler.

German Lanuza of Enaex in China described work that his company has conducted on loosening LDAN prills for the mining industry. The ULD ammonium nitrate (Ultra Low Density) prills have a density of 0.58 g/cm³ and are designed for higher blasting efficiency for underground mining of smaller diameter holes (2 to 3 inch).

Operator experiences

John May of Orica began the section on operator experiences with a report on how one of the company's AN plants had begun producing red-coloured AN after a restart. The elemental profile suggested corrosion products from 304 stainless steel, with the issue eventually traced to mesh pads that had been incorrectly specified as SS304 and not 304L.

A second paper from **Kish Shah** described his involvement in the demolition of an AN plant following the closure of the Gewirtow plant in Seemanpie in the UK. Among the facilities taken down were two ammonia plants, two nitric acid plants, an AN prill plant, and associated plant utilities, ammonia storage spheres etc. He took the delegates through a decommissioning worksheet, paying particular attention to potential hazardous operations, especially around chemicals still remaining in situ in pipes and storage areas.

Nick Vogels of OCI Nitrogen described modifications made to the CAN granulation line at Geleen as a result of closure of the Ymuiden site and relocation of the nitric acid unit there to increase production at Geleen. The company is examining whether to replace the existing fluid bed coolers and several belt flow cooler options were examined, along with whether or not to use purge air. A Coperion cooler is now in place on one line, and if tests prove successful, the plan is to replace the other two lines. Failing that, dust emission reduction measures will have to be taken on the existing coolers.

M Venkatesh of AECOM looked at handling of waste water within an AN complex, and how his firm goes about identifying possible areas for reuse and remediation options.

Jose Frirrer of Exondesa reported on one year of operating experience with the new Enaex PANNA 4 plant in Chile. The new line is a 925 t/d nitric acid unit (160% basis), using a dual pressure process at 60% concentration, and the AN unit 1,000 t/d (100% basis) producing low density AN prills. Operator experience is increasing with the new plants, and plant downtime has decreased markedly over the year. Some improvements have been identified, including automatic control of ammonia dosage to solution and automatic blow down in the air refrigeration system. It is believed that capacity can be increased to 109% of design.

Finally, **Bert Butler** of Geneva Nitrogen presented a paper on operator training, reviewing the positions and skill sets for his company's nitric acid, AN solutions and AN solids plant, and how the 'Seven Deadly Sins' of AN were instilled into them: Contamination, Contamination, Confinement, Time, Temperature, pH and Density.

AN pumps

Handling ammonium nitrate solution under heat and pressure makes AN pumps a particular area of concern, and several papers tackled that subject. **Frank Wolf** of AN Resources Inc from Brandon, Manitoba first reported on an AN pump survey conducted by the AN/NA secretariat during 2011 as a result of comments from the previous year's conference. As well as profiling the number and type of pumps in the industry a series of incidents were reported back, including leaking mechanical seals, an explosion in a 1/4% concentration pump, and high percentages of AN in sumps leading to no flow situations and line blockage.

Mark Gibbons of Willey looked at thermal safety in centrifugal pumps. The key risk area is in a low/no flow situation during pump operation, he said, and he recommended the use of two independent thermocouples to monitor pump temperature, one in the casing and one in the impeller cavity. A design that encourages fluid exchange in the impeller cavity is to be preferred.

Dan Kilpatrick of CF Industries used an explosion in an AN pump at Yazoo City in 2007 as an introduction to look at risk factors and safety integrity levels (SIL) in AN pump operation. As tempting as it is, he said, assigning SILs is not easy to generalise from plant to plant, and needs to be considered on a case by case basis.

Francois Ladoux of Yara described an incident in March 2010 involving an explosion of dilute AN solution in a pump. Although there were no injuries and general damage was slight, large fragments of the pump were dispersed over a wide area. The pump had been allowed to keep pumping from a dry tank, building up heat and pressure inside it. Changes to procedure and staff retraining resulted from what could easily have been a fatal incident.

Steve Olsen of Geneva Nitrogen also spoke on AN pump safety, detailing work done at his own company's plant, and he was followed by **Dan Schuler** of Potash Corp, who looked at safety instrumentation systems for AN pump protection, with a risk-based assessment of failure scenarios and how instrumentation and automated safety systems should catch them.

Nitric acid

The second half of the conference is devoted to nitric acid, and began with a paper by **Jan Sandvig Nielsen** of Weir and Sandvig, who spoke to delegates on behalf of the International Energy Agency (IEA) technology agreement on industrial energy efficiency (IEA IETS). Founded by the OECD in the wake of the 1973 energy crisis, the IEA is a body for gathering information and statistics on energy use. However, it is also involved with evaluating and promoting technologies for increased energy efficiency, and Jan encouraged delegates to get involved with its work in energy intensive industries like fertilizers.

Moving to markets, **Jim Glauser** of IHS consultants looked at global nitric acid supply and demand. Global capacity stood at 72 million t/a in 2010, with demand at 54.5 million t/a. Demand is likely to rise to 80 million t/a by 2015. Capacity remains dominated by Europe and the FSU (about 50% of all capacity), with China growing rapidly to 13 million t/a and North America at 9.8 million t/a. China is, perhaps unsurprisingly, the fastest growing area of demand. Ammonium nitrate accounts for 80% of consumption, with nitrobenzene, toluene diisocyanate (TDI) and nitroaromatic plastics next. AN capacity stood at 21.5 million t/a in 2010, with a similar regional breakdown to nitric acid (although China is relatively underrepresented on AN production; AN consumption was 18.9 million t/a, with fertilizer representing 75% of this and the rest being accounted for by explosives and other industrial uses. Fertilizer is however overwhelmingly a European/Eurasian use, with explosives dominating in the Americas and Oceania.

An interesting paper on the nitric acid industry in China followed, presented by **Lihui Sun**. The Chinese nitric acid industry has been growing at amazing rate – 20% year on year in the past few years. By the end of 2010, the total production capacity of nitric acid had reached 9.2 million t/a, with another 4.2 million t/a of capacity under construction in 2011. Total capacity is set to reach 15 million t/a by the end of 2012, driven by rapidly increasing demand for MDI, TDI, adipic acid, and chemical compounds. There are now more than 80 plants in China now, of varying size, vintage and technical specification. Older atmospheric plants are no longer granted state approval, so new plants after 2005 have all been dual pressure, with oxidation pressure 4.2 - 5.2Mpa, and absorption pressure 10.4 - 11.8Mpa. More than 95% new capacity is dual pressure, and 67% of all Chinese nitric acid production is using dual pressure at the end of 2010, up from 53% in 2009. The size of plants has gradually increased, and 450,000 t/a plants are now under design. Chinese requirements for N2O emissions are gradually tightening, with old plants having to achieve 500ppm, and new plants 300ppm, or 200ppm in specially designated areas. A lot of plants are using tertiary abatement systems.

Operating issues

Karl Hohenwarter of Borealis Agrolinz Melamine discussed why his company had installed monitoring equipment for hydrogen and methane at the company's nitric acid plant in Linz, Austria, briefly, there are fears that in an ammonia process stream, contamination with these gases can lead to process mixes in excess of the lower explosion limit (LEL) during start-up conditions.

Nenad Zebevic of Petrokemija at Kutina, Croatia, took delegates through

Topsoe, Inc. – EX1003
Page 824 of 1210

the company's revamp of the site's nitric acid plant acetylene systems as a risk-based analysis.

Jean-Francois Granger of GPN presented the results of a survey that GPN had conducted on washing of NOx converters. He found that 75% of those companies surveyed washed the converters to avoid/eliminate nitrate build-up. The washing was mainly (32%) manual, with most of the operators washing once per shift and 75% at least once a day. About 68% use demineralised water, but a minority use steam. Perhaps most surprisingly, 38% of respondents did not know the origin of the procedure they are currently using!

Sam Corenti of IneosPivot looked at operating a compressor train with a variable frequency motor following the replacement of the steam turbine at the company's 900 t/d acid plant. The company had been able to realise utility cost savings through improved compressor speed control.

Dylan Charles of Apache Nitrogen at Benson, Arizona described using hydrogen peroxide to reduce NOx emissions during plant start-up. The company found that it was able to reduce NOx emissions by 99% by using H_2O_2 injection.

Enaex has installed new power management systems at its nitric acid and ammonium nitrate complex, and **Ricardo Camus** of Enaex reported on how the critical loads had been distributed to keep the maximum capacity operating in the event of interruptions to the power supply.

Corrosion is the perennial problem in acid plants, and **Marcello Senatore** of Sandvik took delegates through the company's range of high performance steels, including IRE10, which can achieve a 25 degree improvement in the temperature of 65% acid that it can tolerate compared to 304L. It is particularly suitable for cooler/condensers and tail gas pre-heaters.

And talking of cooler/condensers, **Andre de Smet** of Yara presented a look at a new design Yara had installed at Sluiskil following tube/tube sheet failures due to corrosion, using Sandvik's 2RE10 material.

Donald Hopner of Yara looked at liquid sampling points in a nitric acid plant and how it can be achieved safely.

Chetan Shah of PT Hidroflex Indonesia presented some tips on maintenance of expansion joints in nitric acid plants, including the right choice of materials and how poor installation can lead to premature failure.

Rowan Harvey of Orica reported on a bellows failure at an Uhde nitric acid plant – the number 3 unit at Yarwun, a 650 t/d dual pressure plant built in 1979, relocated from Denmark in 2005 and recommissioned in 2008. In May 2010 small cracks were discovered in an expansion bellows between the NOx compressor and tail gas preheater, and in June this had become a leak, forcing a shutdown. The issue was corrosion – internally from reheating acid and externally from chlorides, and preventative maintenance had not picked it up quickly enough. A replacement was ordered which would avoid the reheating acid problem.

N_2O abatement

As a major greenhouse gas reduction in nitrous oxide emission continues to be a major focus for the nitric acid industry. **Steve Dams** of IneosPivot reported on issues with a NOx abatement catalyst basket which had been causing ever-greater N_2O slip at the plant, and design modifications to the basket which appeared to cure the problem.

John Williams of ClimeCo looked at the company's first tertiary (tailgas) N_2O reduction system in the US, at the Rentech Energy Mid-West plant at East Dubuque, Illinois, a 200 t/d plant built in 1978. The N_2O abatement system, designed by CRI Catalyst, came on-stream in July 2011. John took delegates through the pre-commissioning planning which allowed down-time to be kept to just 65 hours. At normal operating temperatures, N_2O reduction is 99%.

Control of plant tail gas temperature is crucial in this kind of situation, and **Steve Olsen** of Genoa Nitrogen reported on some more real life data from the Genoa Nitrogen facility in Green, Utah, where a 200 t/d Montecatini acid plant and a 105 t/d Weatherly unit are both installed. As well as an 8% increase in acid production, a higher tail pipe temperature allowed the plant to run tertiary N_2O abatement technology without hydrocarbon injection.

More 'end of pipe' N_2O abatement, this time from **Martin Voorwinden** of OCI Nitrogen in the Netherlands. BAT regulations for N_2O emissions levels specify a baseline level of 270ppm in 2008 falling to 210ppm in 2012, with the benchmark level from 2013-2020 to be 160ppm. OCI runs two Stamicarbon nitric acid plants at the site, one with 1,600 t/d capacity, the other 700 t/d. Uhde EnviNOx tertiary abatement systems were installed in 2008-09 and brought N2O emissions levels down to almost zero. However, there were problems during 2009-10 relating to broken ammonia spargers due to nitriding corrosion.

Finally, **Bill Federbach** of ClimeCo looked at the company's first secondary N2O emission project in the US, at the 1,000 t/d El Dorado Nitrogen nitric acid plant at Baytown, Texas, including the plant monitoring and baseline level studies required to get the project registered under CAR (Climate Action Reserve).

What is JIEDDO?

JIEDDO is the Joint Improvised Explosive Device Defence Organisation, a US Department of Defence agency which is attempting to bring together military, scientific and industry personnel to try and tackle the threat of improved explosive devices, which have become the weapon of choice for terrorists around the globe.

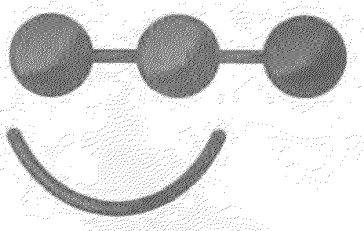
In November 2011 they hosted a Homemade Explosives Focus Forum in Washington to discuss approaches towards tackling the IED threat via new formulations of ammonium nitrate and possible regulatory, procurement, transport, storage and tracking policies.

In essence, JIEDDO is looking at various strands of thinking, including new AN-based fertilizer formulations, additives and methods to disrupt IED manufacture (whether it is possible to 'de-sensitise' AN via adding other compounds) and additives and methods for increased detection or identification of explosive mixtures – possibly so-called 'taggants', which were considered during the 1990s in the wake of the Oklahoma City bombing, but possibly something as simple as dyes or colourants. A particular problem at the moment is smuggling across the Pakistan-Afghanistan border, and one anonymous white pill looks much like another – the theory is that if it were coloured in some way this might aid the work of customs and security forces.

Anyone in the AN industry wanting to get involved should contact: kara.ewell@jieddo.dod.mil

CRI

Controlling N_2O emissions is no laughing matter.



With an environmental impact 310 times higher per unit than carbon dioxide (CO_2), N_2O has been identified as a significant source of greenhouse gas. To help combat this environmental threat and enable nitric acid plants and other manufacturing facilities to both meet clean air requirements and participate in carbon credit programs, CRI offers an innovative, energy-efficient tertiary solution for Nitrous Oxide decomposition based on our unique LFR technology.

What are the benefits of our unique removal system?

- Up to 99% N_2O reduction
- Low pressure drop designs
- Operating range of 380°C – 620°C
- Axial, radial and lateral flow reactors (LFR)
- Minimal impact on plant operations
- No reagents/hydrocarbons
- Earn tradable carbon credits

To learn more about CRI's Tertiary N_2O Abatement System visit us at the Nitrogen & Syngas Conference & Exhibition, February 20-23 in Athens.

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OCI and Yara: old and new

Nitrogen+Syngas looks at two leading figures of the nitrogen industry – one a long-established player, the other a new entrant that has grown rapidly by acquisition to become one of the largest fertilizer companies in the world.

Yara International

Yara International is the world's largest publicly traded nitrogen fertilizer supplier, with a truly global reach. It operates production facilities on six continents and has sales or other operations in more than 50 countries, selling its products to 150 countries around the world. In sales terms it is a world leader, with global sales of 85.37 billion krone ($11.0 billion) in 2010, and EBITDA of 15.32 billion krone ($2.0 billion). Total sales of ammonia and finished fertilizers were 17.20 million tonnes, an increase of 3% on 2009.

More recently, 3Q 2011 results announced in October 31 saw an 85% rise in net income after non-controlling interests to 3.57 billion krone ($634 million), compared with the same period for 2010, and EBITDA excluding special items of 4.21 billion krone ($710 million).

The company was originally founded in 1905 as Norsk Hydro, and used a novel electric arc process (the Birkeland-Eyde Process), to form nitric oxide (NO) from atmospheric nitrogen and oxygen. The nitric oxide was then oxidised to NO_2 and combined with water to form nitric acid. The process was however very energy inefficient, and it was replaced in 1928 with a Haber Process ammonia plant using technology licensed from BASF, with downstream Ostwald Process ammonia oxidation to nitric acid.

From these pioneering beginnings, Norsk Hydro grew to be a major player in the European fertilizer industry. The company has made many major acquisitions down the years in order to speed growth in sales, including NSM, Netherlands in 1979; Supra, Sweden in 1981; Pivora, UK (1982); Ruhr Stickstoff, Germany (1984); Windmill/Hamel Chemie, Netherlands/Germany (1986); Cofaz, France (1986); DMV Rostock, Germany (1991); Enichem Agricoltura, Italy (1990); Phosyn, UK (part share, 1997).

In 2004 Yara International was demerged from the parent company to run the fertilizer operations of Norsk Hydro, which were at the time run as the Hydro Agri business unit. Further acquisitions continued under the Yara International banner, including shares in Rossosh, Russia in 2005, the full purchase of Phosyn in 2006 and the company's largest acquisition to date – that of Scandinavian Iisalmi Growhow of Finland in 2007. The Norwegian government retains a large minority share (36%) in the company.

Joint ventures

The company has also proceeded via a number of joint ventures around the world, beginning with Qatar Petroleum in 1969, to found the Qatar Fertilizer Company (Qafco). Norsk Hydro took a 25% stake in this far-sighted venture, one of the first to exploit the vast reserves of natural gas in the Arab Gulf region. In 1977 it began the Trinigas joint venture with the Trinidadian government, building a 500,000 t/a ammonia plant to use stranded gas from Trinidad's rapidly-developing fields, and then a second plant in 1980. In 1991 Hydro also acquired an older 1959 vintage plant at the same site – the first to have been built on Trinidad – from WR Grace.

Hydro and then Yara also has entered joint ventures with Adubos Trevo, Brazil (2000); Ameriya, Mexico (2006); Fertiberas, Brazil (2006/07); Sweetwater Canada (2008), Libeco, Libya (2009), and has taken financial stakes in Kynoch, South Africa (1990); Borrup, Australia (2005) and Balderton, Switzerland (2006). The latter company was wholly acquired in 2010.

NOx reduction

One of Yara's signature products in recent years has been the AdBlue urea solution for selective catalytic reduction (SCR) of diesel exhausts, but the company has also worked on NOx reduction for industrial processes, which was why another recent acquisition for the company was Sweden's Pemo Miljo, formerly a subsidiary of Petrokraft AB, a leader in selective non-catalytic reduction (SNCR). Yara confirmed that Pemo Miljo will become a wholly-owned subsidiary of Yara International, and says that as a result of the deal, it will be able to offer one of the most comprehensive and effective NOx emission reduction solutions to utilities, refineries, manufacturing centres, and other industrial facilities as the company's Nox-Care capabilities will now include everything from building SNCR systems and storage facilities to supplying the right reagent to advising on chemical storage and handling.

Strategy

Going forward, the company believes that its ever-increasing global market footprint brings increased responsibilities in its wake. The company's declared strategic goals reflect this broad focus, with eight targets:

- Profitability: Yara seeks to achieve a 10% return on investment over the business cycle.
- Competitiveness: Yara seeks to achieve a gross return (EBITDA/Total Assets) in the top quartile of a peer group of leading chemical companies.
- Solidity: Yara's goal is to retain a mid investment grade credit, a minimum BBB in Standard & Poor's methodology.
- Cash returns: Cash returns to shareholders should average 40-45% of net income, with dividends at a minimum 30% over the business cycle.
- Growth in low-cost gas supply: Yara's goal is to increase its proportion of production in low-cost gas regions.
- Overall growth: Yara's target is to double its fertilizer sales to 40 million t/a.
- Citizenship: Yara seeks to positively address major global challenges and to pursue industry-leading standards in all its operations and activities.
- Environment: Yara seeks to be among the most energy-efficient companies in the industry and to reduce greenhouse gas emissions by 40% from 2004 to 2013.

At its Capital Markets Day on December 6th in Oslo, Yara International has said that it is "well positioned in an attractive market" and presented "new scenarios for future earnings". The company believes an 8.0 million t/a increase in own-produced and joint venture product sales from 2010 to 2018 is "realistic".

Orascom

A name that is gaining increasing prominence in world fertilizer markets is that of Orascom. Based in Egypt, the group holds a diverse portfolio covering construction, railways, hotels and telecoms. The company can trace its origins back to 1950, when it was founded by Onsi Sawiris. His three sons run the business today and the Sawiris family retain 55% of the Orascom ordinary shares, with the remainder held under a free float.

In the fertilizer sector, the company's holdings began with the Egyptian Fertilizer Company (EFC) and a share in the Egypt Basic Industries company (EBIC) plant, which began production in 2009. The company was also instrumental in the setting up of Sorfert in Algeria in 2005, which is a 51:49 joint venture between OCI and the Algerian state-owned oil and gas company, Sonatrach. In April 2008, the partners secured a 1.1 billion loan to develop an ammonia and urea facility which is in the process of starting up, and a second ammonia plant with a capacity for 800,000 t/a ammonia is planned at the Arzew complex.

The largest expansion to date was the acquisition of the fertilizer assets of DSM Agro in the Netherlands in March 2010, for €310 million ($417 million) on a cash and debt-free basis, enabling OCI to expand its customer base in European markets via DSM Agro's well-established distribution chain, as well as a subsequent acquisition of Dutch company Nitro Chemie BV, whose assets include an ammonia terminal in Rotterdam with a combined storage capacity of 30,000 tonnes and a permit to receive up to 600,000 t/a of ammonia.

The company has also gained a marketing foothold in Brazil via a trade and distribution agreement with FITCO International B.V., a subsidiary of the Grupo Fertipar fertilizer group, and a 20% stake in US trading company, Gavilon Group. There is also a 13.5% stake in Nokoni Chemical Industries Ltd, in Nigeria, the successor to the National Fertilizer Company of Nigeria (NAFCON), where the company's shuttered ammonia/urea plant has been refurbished and re-started. Originally OCI held a 24% stake but downgraded this in 2010 to gain working capital.

Company comparison

	Yara International	Orascom*
Total sales, 2010 ($ million)	11,020	2,021
Net income, 2010 ($ million)	2,590	557
Employees	7,438	4,190
Debt: Equity ratio	27%	63%
Share price (Jan 2011)	$41.90	$35.59
Fertilizer sales (million tonnes)	20.3	8.8

* Fertilizer Group only

OCI's plants

Location	Company	Capacity (t/d)
Suez, Egypt	EFC (100% owner)	Ammonia 2 × 1,200; Urea 2× 1,925
Suez, Egypt	EBIC (50% owner)	Ammonia 2,000
Arzew, Algeria	Sorfert (51% owner)	Ammonia 2 × 2,200; Urea 3,500
Onne, Nigeria	Nitrogen Chemicals (13.5% owner)	Ammonia 1,000; Urea 1,500
Beaumont, TX, USA	OCI North America (100% owner)	Ammonia 800; Methanol 2,000
Geleen, Netherlands	OCI Nitrogen (100% owner)	Ammonia 2 × 1,500 Nitric acid 520 + 1,800 + 730 = 2,850 CAN 4,000; UAN 600-1,600; Urea 1,800 Melamine 360 + 90 = 440
Ningxia/China	OCI Nitrogen (100%/50% owner)	Melamine 200 + 150 = 350

OCI reported 1H results for 2011 as EBITDA of $695 million on sales of $2.7 billion, the former up 38% on the previous year, the latter up 17%. Fertilizers accounted for 69% of the profits, with 38% of revenue coming from Europe, and 45% from Egypt, the Middle East and North Africa. However, Fertilizer Group revenue was overwhelmingly (71%) from sales in Europe.

Demerger

On December 21st, OCI file an application with the Egyptian Financial Supervisory Authority (EFSA) to begin the demerger of its construction and fertilizer activities. OCI will continue to run the fertilizer business unit, with the new demerged company holding the construction business. The demerger is expected to be completed during 1Q 2012. Existing shareholders will each receive one free share in the new company for every share held in OCI at the time of the demerger.

Methanol

Meanwhile, Orascom's latest move has been into methanol. In November OCI Fertilizer Group signed an agreement to completely acquire its Texas-based joint venture Pandora Methanol LLC. Pandora has been re-starting an idled ammonia-methanol plant in Beaumont, Texas. The company will now become OCI North America. OCI Nitrogen bought the former Eastman Chemical Company ammonia-methanol plant in May 2011 through a 50:50 joint venture with Jenya Methanol AG. The plant has 250,000 t/a of ammonia and 750,000 t/a of methanol capacity, plus storage for 18,000 tonnes of ammonia and 44,000 tonnes of methanol, and pipeline connections to adjacent customers.

Capacity expansions

The Fertilizer Group continues add capacity in Egypt, Algeria, the Netherlands and the US. Once those initiatives are complete by the end of 1Q 2012, total production capacity would increase by approximately 60%. Expansion of the CAN line at Geleen to 1.45 million t/a is expected to be complete in 1Q 2012, and a 30,000 t/a melamine plant is also to be re-started at the same time as debottlenecking of A/N and UAN capacity at the site. EFC will complete debottlenecking work at both urea lines by the end of 1Q 2012, with production increasing to 1.55 million t/a.

Topsoe, Inc. – EX1003
Page 826 of 1210



Ammonia in the Mediterranean

The gas-rich nations of North Africa have become a southern adjunct to the European market, supplying ammonia and other downstream products to the European market. However, some production continues in southern Europe, mainly in the hands of large, integrated companies like Yara and Fertiberia.

Table 1. Natural gas production, reserves, 2010

	Production	Consumption	Reserves
Algeria	80.4	29.9	4,500
Egypt	61.1	45.1	2,200
Greece	0.0	3.7	1
Italy	7.6	76.1	84
Libya	15.8	6.0	1,500
Morocco	0.0	0.6	1
Portugal	0.0	5.0	0
Spain	0.0	34.4	3
Tunisia	3.6	4.9	65
Turkey	0.0	39.0	8

The Mediterranean Sea has long been one of the major crossroads of the world, and continues to be so, with both natural gas and downstream products crossing it in increasing volumes. This has become particularly so of the ammonia industry, as capacity has closed in Europe and begun to migrate to lower gas cost locations which increasingly include the countries of North Africa.

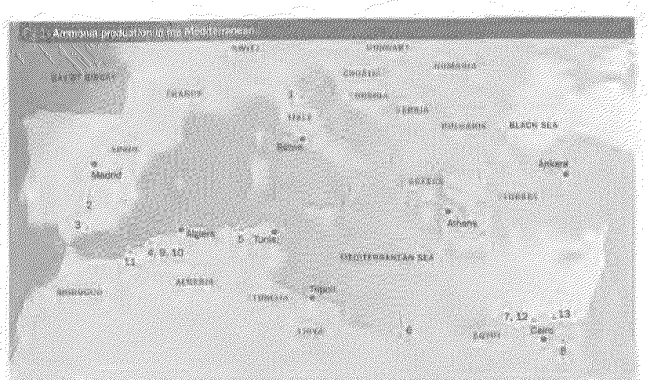
As Table 1 shows, natural gas reserves are concentrated on the North African side of the Mediterranean, with Egypt, Libya and Algeria holding large reserves. Europe has long been a net consumer, and in fact much of the gas consumption in southern Europe is fed from those three north African states, via pipelines that cross the sea from Algeria to Spain and Italy, and from Libya to Sicily. There is also LNG export from all three of the resource-rich states, although Libya's export is relatively minor compared to the larger volumes from Algeria and Egypt.

Algeria

As Table 1 shows, Algeria has North Africa's largest reserves of natural gas, and with a relatively small population domestic demand remains modest. Algeria consequently exports large volumes of its gas: 28bcm to Italy and 12bcm to Spain by pipeline in 2010, and another 19 bcm as LNG to France, Turkey and the UK, amongst others. It has also allowed the country to monetise the gas domestically by the development of a downstream nitrogen fertilizer industry. Previously this was mostly in the hands of the state-owned Asmidal group. Asmidal Fertilizer Co. was established in 1964 when the Sonatrach Algerian state oil group was restructured. It remains under 100% state ownership and operates two subsidiary companies, Fertial and Alzofert. Fertial, based at Annaba in the east of the country, operates 330,000 t/a of ammonia capacity, while Alzofert at Arzew near Oran has two 330,000 t/a ammonia plants. Asmidal also owns



Fig. 1 Ammonia production in the Mediterranean



Key:

1. Yara, Ferrara, Italy: 600,000 t/a of ammonia, 500,000 t/a of urea
2. Fertiberia, Puertollano, Spain: 200,000 t/a of ammonia, 135,000 t/a of urea
3. Fertiberia, Palos, Spain: 400,000 t/a of ammonia, 250,000 t/a of urea
4. Asmidal, Arzew, Algeria: 2 x 330,000 t/a of ammonia
5. Fertial, Annaba, Algeria: 330,000 t/a of ammonia
6. Libyan Norwegian Fertilizer Company, Libya: 700,000 t/a of ammonia, 900,000 t/a of urea
7. Abu Qir Fertilizers & Chemicals, Abu Qir, Egypt: 2 x 330,000, 1 x 400,000 t/a ammonia, 510,000 t/a + 570,000 t/a urea
8. EFC, EBIC, Suez, Egypt: 700,000 t/a of ammonia, 1.3 million t/a of urea
9. Sofert, Arzew, Algeria: 2 x 660,000 t/a ammonia, 1.3 million t/a of urea
10. Algeria-Oman Fertilizer Company, Arzew, Algeria: 2 x 660,000 t/a of ammonia, 2 x 1.1 million t/a of urea
11. El Bahia Fertilizers, El Bahia, Algeria: 1.1 million t/a of ammonia (projected)
12. Alexandria Fertilizers, Alexandria, Egypt: 400,000 t/a of ammonia and 660,000 t/a of urea
13. MOPCO, Damietta, Egypt: 400,000 t/a of ammonia and 635,000 t/a of urea

635,000 t/a of ammonium nitrate capacity, with downstream UAN and NPK plants, although these tend not to operate at full near capacity. In 2005, the Spanish industrial group Grupo Villar Mir, the holding company of Fertiberia, acquired a 66% stake in Fertial. The Algerian government, via Asmidal, retains the remaining 34%.

Algeria currently exports most of its ammonia, around 500,000 t/a on average.

New capacity

While the Asmidal plants have been operating for some time, during the early 2000s the Algerian government made a move to increase domestic ammonia and urea capacity, via the development of new world-scale plants. There are currently three major projects under development:

Based at Arzew, Sofert is a joint venture between Sonatrach and Egypt's Orascom Construction Industries (OCI). OCI is the lead project developer, with a 51% stake, and the engineering, procurement and construction (EPC) contract went to Uhde in 2008 to build a 660,000 t/a ammonia plant and a 1.1 million t/a urea plant. A second ammonia plant with a capacity of 660,000 t/a is also being built. The ammonia plants are based on Uhde's ammonia process, with the urea license coming from OCI subsidiary Stamicarbon. Uhde Fertilizer Technology (UFT) has provided the licence for its fluid-bed urea granulation process. Investment costs have been estimated at $1.5 billion.

The Sofert facility is in the process of being commissioned and is expected to come on stream in early 2012, providing up to an additional 800,000 t/a of merchant ammonia. OCI plans to handle the marketing of the merchant ammonia itself, which will be targeted almost entirely at export markets.

A second complex is also under development at Arzew, via the joint venture Algeria Oman Fertilizer Company. AOFC is a joint venture between Sonatrach (51%) and Suhail Bahwan Group of Oman (49%) to build two 2,100 t/d ammonia production units and two 3,500 t/d granular urea plants. Japan's Mitsubishi Heavy Industries (MHI) and Daewoo Engineering & Construction Co. of South Korea were awarded the EPC contract to build the new plants, which will be based on Haldor Topsøe ammonia and Saipem (Snamprogetti) urea technology, with UFT again licensing its granulation technology. Production at the complex is scheduled to begin in the second half of 2012.

Finally, El Bahia Fertilizers, based just to the west of Arzew, is a joint venture between Fertiberia (51%) and Sonatrach (49%), where a 1.1 million t/a merchant ammonia plant is under development at a cost of $1.1 billion. The project was originally scheduled for completion in 2010 but the timescale has slipped several times and there is currently no firm date for start-up.

Egypt

Over the past decade, monetisation of Egypt's natural gas reserves have driven a major boom in fertiliser production. The ammonia fertilizer industry is not a new one for Egypt; the country had a very old ammonia/urea plant, Kima, at Aswan, going back to the 1950s, with 150,000 t/a ammonia produced from hydrogen generated from electrolysis, fed by the nearby hydroelectric dam. There was also Al Nasr Coke and Chemicals at Helwan with 56,000 t/a of capacity, although that closed in 2000. Gas-based capacity began during the 1970s: Semadco opened a plant at Suez in 1979, producing 133,000 t/a of ammonia from natural gas, and El Delta Fertilizer Co at Talkha operated another 400,000 t/a. However, the largest producer for many years was Abu Qir Fertilizers and Chemicals, which began producing in 1976 at Abu Qir bay, near Alexandria, with a 330,000 t/a ammonia and 510,000 t/a urea plant. A second train started in 1981, feeding nitric acid and ammonium nitrate capacity, and a third train with 400,000 t/a of ammonia and 570,000 t/a of urea capacity started production in 1998.

A new wave of expansion occurred during the 2000s, with Alexandria Fertilizers starting production of its 400,000 t/a of ammonia and 660,000 t/a of urea capacity in 2006, and the Helwan Fertilizer Company began operations of a 400,000 t/a ammonia and 580,000 t/a urea plant at Helwan in 2007. Helwan is considering doubling capacity at the site.

At Suez, the Egyptian Fertilizer Co (EFC) operates a total of 1.3 million t/a of urea capacity in two trains, and the Egypt Basic Industries Corporation (EBIC) began operating its 700,000 t/a ammonia plant in 2009, and also operates downstream ammonium sulphate production. EFC is now 100% owned by Egypt's new international fertiliser giant Orascom, while EBIC is 60% owned by Orascom.

And finally, at Damietta, the Misr Oil Processing Company (MOPCO) began construction of a 400,000 t/a ammonia and 635,000 t/a urea plant in 2008. The plant was finally completed in 2011, but has had operating difficulties due to local environmental opposition. Agrium had also planned a joint venture plant in the country, also at Damietta, to be known as EAgrium, but left the project in 2008, at which time the project was passed to MOPCO and is now projected to become MOPCO II. A third MOPCO plant has also been planned, but both expansions are also under threat from the current disturbances.

Italy

Italy is one of the few European countries to remain self sufficient in ammonia production. Yara maintains two manufacturing sites in Italy, at Ferrara and Ravenna. Ferrara is the upstream site, with ammonia and urea production, and nearby Ravenna has more downstream production, with nitric acid, calcium ammonium nitrate, and NPKs.

Libya

Libya's nitrogen production is in the hands of what is now Lifeco, the Libyan Norwegian Fertilizer Company. Originally developed as the Sirte Oil Company, Lifeco is now a joint venture between the Libyan National Oil Company (NOC) and the Libyan Investment Authority, each with a 25% stake, and Yara International, with the remaining 50%. There are two ammonia-urea trains at Marsa el Brega, built originally in 1978 and 1982 respectively, which have now been revamped and re-started in 2009, and which now have a total capacity of 700,000 t/a of ammonia and 900,000 t/a of prilled urea. Natural gas is supplied by NOC under a long term contract, with all ammonia and urea sales handled by Yara.

While the uprising against Colonel Gaddafi which became Libya's civil war raged up and down the coast last year, the plant was shut for most of 2011, but damage to the plant itself was not reported to be serious, and Yara has indicated that it aims to re-start production there in the second half of 2012.

Morocco

Although Morocco has no native ammonia production, it is nevertheless a major consumer of ammonia via its huge phosphate industry. Morocco operates 3.4 million t/a of mono- and di-ammonium phosphate capacity (MAP/DAP), and in 2010 imported 428,000 tonnes of ammonia. Office Chérifien des Phosphates (OCP), which operates the majority of the country's phosphate capacity, has huge expansion plans over the coming years. At Jorf Lasfar it plans to open an addition 4 million t/a of MAP/DAP capacity over the period 2013-15.

Spain

Fertiberia, purchased in 1995 by major industrial conglomerate Grupo Villar Mir, is the major fertilizer producer in the Iberian peninsula. There has been considerable rationalisation down through the years, with the closure of the plants at Seville and Cartagena in 2003, and the Sefanitro plant in 2005. However, Fertiberia has expanded into growth markets via its 66% stake in Fertial in Algeria in 2005 and in 2008 the company also bought Portuguese producer Adubos de Portugal (ADP). As noted above, it is also in partnership with Sonatrach over the El Bahia ammonia plant in Algeria.

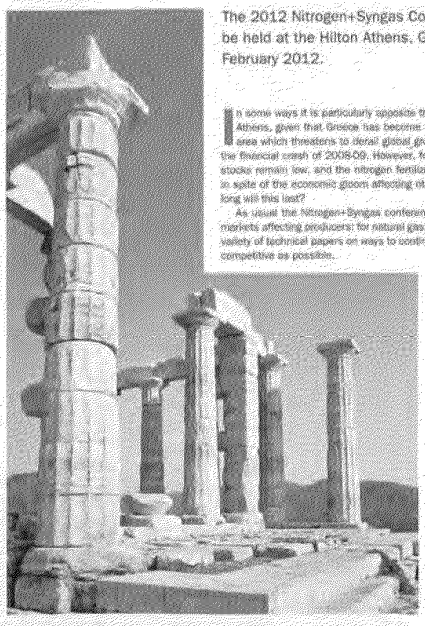
Fertiberia operates 600,000 t/a of ammonia capacity within Spain: a 200,000 t/a plant at Puertollano and a 400,000 t/a plant at Palos de la Frontera. Puertollano is integrated with downstream urea, nitric acid, ammonium nitrate and solutions capacity. Palos also has some urea capacity. Fertiberia operates additional urea capacity in Portugal under the umbrella of subsidiary Adubos de Portugal.

Looking ahead

The largest amount of new ammonia and urea capacity outside China is planned for North Africa. The European market will probably not be able to absorb all of this new capacity, and producers in Algeria and Egypt will likely have to find new markets for their urea outside of the region, particularly in North and South America.

Topsoe, Inc. – EX1003
Page 828 of 1210

Nitrogen+Syngas 2012



The 2012 Nitrogen+Syngas Conference and Exhibition will be held at the Hilton Athens, Greece from 20th – 23rd February 2012.

In some ways it is particularly apposite that the Nitrogen+Syngas conference meet in Athens, given that Greece has become symbolic of the wider crisis in the Eurozone area which threatens to derail global growth as it recovers from recession following the financial crash of 2008-09. However, for the moment, oil prices remain high, grain stocks remain low, and the nitrogen fertilizer industry continues to enjoy good margins in spite of the economic gloom affecting other sectors. As always the question is: how long will this last?

As usual the Nitrogen+Syngas conference will begin with an overview of the major markets affecting producers: for natural gas, ammonia, urea and methanol, followed by a variety of technical papers on ways to continue to make operations as cost-effective and competitive as possible.

Pre-conference workshop on urea manufacturing

A new departure this year is a pre-conference workshop on aspects of urea manufacturing, organised by UreaKnowHow.com, to be held on Monday February 20th.

This workshop offers attendees the opportunity to discuss operational and maintenance topics with experts in the industry and fellow urea producers. The workshop will have the format of round tables and be moderated by UreaKnowHow.com. It will consist of two modules of two hours each, and will cover two important topics in urea production technology:

- Urea product quality and higher margin urea products.
- Safety risks and reliability problems caused by corrosion in urea plants.

As usual, associated with the main Nitrogen+Syngas conference will be an exhibition. This time with 40 exhibitors.

Highlights of the technical papers to be presented over three days include:

- Capacity-enhancing revamps in synthesis gas plants
- Commissioning and operation of the world's largest urea plant
- New GigaMethanol process
- Latest developments in plate fertilizer coolers
- Capacity-enhancing revamps in ammonia plants
- Experience with urea pastillation
- New high-stability LTS catalysts
- Enhancing ammonia plant efficiency with advanced process control and operator training systems
- Operating experience in a large methanol plant
- Optimization of nitric acid plant ammonia burners
- The 6,000-t/d urea plant
- Combined ammonia and methanol production
- Revision of CO_2 removal systems



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New technologies for ammonia plants

Research and development continues to yield novel concepts for ammonia production and some of these are now ready for their first commercial application. In this article, we report on new technologies and process enhancements from Ammonia Casale, Haldor Topsøe and KBR.

Casale ammonia plant design

Casale's policy has long been based upon the development and application of new advanced technologies to get the best improvements in ammonia plant performance in terms of energy consumption, capacity, or a combination of the two.

Many articles have been written on Casale technologies for plant revamping, whose application can lead to a capacity increase of 50% or more, and a significant energy saving. For this reason, this article presents the new technologies developed by Casale for new ammonia plants only.

Casale advanced ammonia-urea process

Through the continuous development of its technologies, Casale has developed innovative processes for world-scale ammonia and urea grass-roots plants at conventional capacities and is now in the unique position of owning proprietary technologies for the design of ammonia-urea grass-roots plants.

Having designed and built two grass-roots ammonia plants according to the Casale advanced ammonia process and one grass-roots urea plant according to the Split Flow Loop™ urea process, Casale is ready to offer the Casale advanced ammonia-urea process for the design of a combined and fully integrated ammonia-urea fertilizer complex featuring very low energy consumption.

The ammonia and urea plants are designed to be best integrated, with optimised exchanges of energy and materials. In practice this translates in an overall consumption per tonne of urea of only 4.6 Gcal/tonne, including feed and fuel, electricity and utilities (Fig. 1). This result has been obtained by integrating the steam balance of the two plants in such a way that there is no export of steam from the ammonia-urea complex and the import of electric power is 0.025 kW/tonne urea.

Steam consumption of the urea plant is completely fulfilled by export of HP and MP steam (HP for the CO_2 compressor and MP as process steam) from the ammonia plant, while there is no back export of LP steam from urea to ammonia. The CO_2 production is balanced with ammonia production with a slight excess of air in the secondary reformer and by burning a small amount of synthesis gas as fuel upstream of the methanator. Necessary electric power is produced in two expanders in the ammonia plant.

The high efficiency of the Casale ammonia-urea advanced process, makes it possible to reduce, for a given capacity, the size of the equipment and, therefore, to build a plant with lower investment costs.

In addition, the Casale ammonia-urea process has been designed to minimise the environmental impact. In fact, the only liquid wastes are the boiler blow down, the air compressor inter stage coolers condensate and the urea process condensate.

The boiler blow down, after flashing and cooling, is used as cooling water make-up for the cooling water loop. The same for the air compressor inter stage condensate, which is returned to the cooling water return header. The process condensate from the urea plant is, as described above, returned clean as boiler feed water.

The only gaseous wastes are the flue gas from the primary reformer, the inerts from the urea plant and the air exhaust from the prilling tower. The flue gas from the primary reformer contains less than 110 mg/Nm³ of NOx. The guaranteed figure of NOx is lower than the figure required by the European Community for new plants (140 mg/Nm³ calculated at 3% oxygen excess). The ammonia content in the other gaseous waste can be kept below the allowable emission levels.

Casale advanced ammonia process

The main features of the Casale advanced ammonia process are:

- high efficiency design for the secondary reformer;
- axial-radial technology for the shift conversion;
- ejector ammonia wash process;
- axial-radial technology for the ammonia converter;
- advanced waste heat boiler design in the synthesis loop;
- coupling of converter and downstream exchangers;
- low temperature heat recovery;
- hydrogen recovery unit.

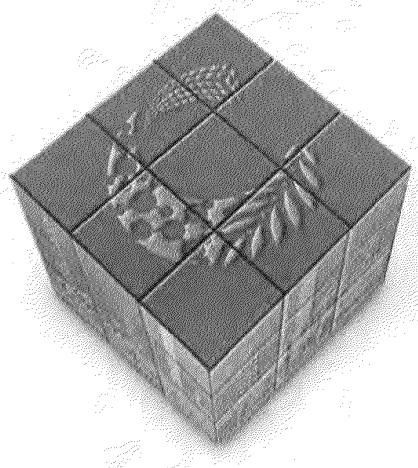
Most of this equipment and these technologies were first applied in revamping projects, allowing performance improvement, before being installed in Casale grass-roots plants.

Ammonia process performance and implementation

Thanks to the features listed above, the Casale ammonia process offers:

- Steam to carbon ratio (referred to NG steam only): 2.9
- CO slip from LTS: less than 0.3% vol. (dry base, EOR)
- CO_2 slip from absorber: less than 300 ppm vol.
- Ammonia loop pressure: 140-160 bar
- Ammonia conversion: about 21 %
- Very low total energy consumptions (evaluated as feeds + fuel + electricity and steam export to urea) of less than 6.5 GCal/tonne of produced ammonia.

AmmoniaCasale
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MethanolCasale
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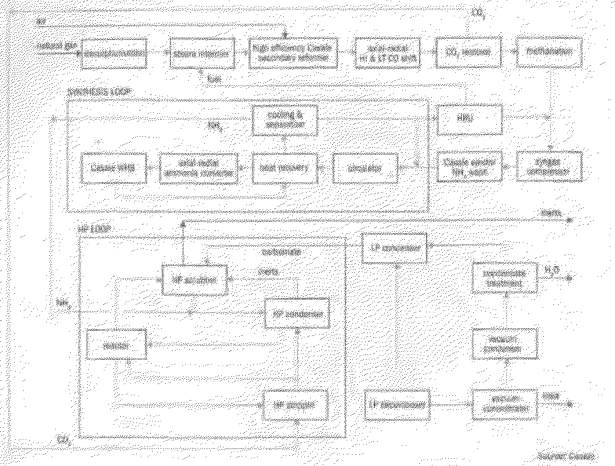
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Fig. 1: Casale advanced ammonia/urea process



Source: Casale

The Casale advanced ammonia process is currently operating in a 2,050 t/d plant in Iran operated by Razi Petrochemical Company. The new plant, which was designed by Casale and built by the Iranian contractor Pidaco, has been in operation since the beginning of 2008.

A second 2,050 t/d ammonia plant is under advanced implementation in Iran to be built for Shiraz Petrochemical Company. More recently, Casale has been awarded with three more contracts for the design of three new 2,050 t/d ammonia plants in various locations in Iran.

Casale Split Flow Loop™ urea process

The Casale Split Flow Loop™ process for grass-roots urea plants is an improved CO_2 stripping process in which urea is formed in a reactor fitted with high efficiency trays. The solution from the reactor is first treated in a stripper, operating at the same pressure as the reactor, using steam and the feed CO_2 as stripping agent. Here most of the unreacted NH_3 and CO_2 are recovered decomposing the carbamate. About one third of the unreacted NH_3 and CO_2 recovered in the stripper is sent directly to the reactor, while the remaining two thirds are recycled back to the reactor through the HP carbamate condenser (HPCC) to which the ammonia feed is directed. The HPCC is practically a total condenser of the submerged type. The stream of inerts leaving the HP carbamate condenser is then sent straight to the HP scrubber, bypassing the reactor.

The HP scrubber recovers NH_3 and CO_2 from the inerts streams leaving the HPCC and the reactor using the carbamate flow coming form the LP recovery section. The carbamate flow coming from the HP scrubber is sent to the HPCC, to enhance the condensation, using an ejector driven by the ammonia feed, which is also sent to the HPCC.

From the stripper, the urea solution, still containing a certain amount of unreacted NH_3 and CO_2 in the form of carbamate, is sent to a low-pressure single decomposition/condensation stage where practically all the remaining unreacted NH_3 and CO_2 is recovered in the form of a carbamate solution. The urea-water solution, containing only small quantities of NH_3 and CO_2, is then further treated in a two-stage vacuum evaporation section to obtain a urea melt for the prilling tower.

The process condensate, obtained from the vacuum condensers is purified in two stripping columns and one hydrolyser to eliminate all of its urea, NH_3 and CO_2 content.

The carbamate solution obtained in the LP section is sent to the HP scrubber where the inerts leaving the HP loop are washed.

The object of the Split Flow Loop™ process concept is to exclude as far as possible the inert contaminants present in the CO_2 feedstock from the synthesis reactor in order to minimise their adverse effect on CO_2 conversion. As described above, this is accomplished by splitting the gas flow from the HP stripper so that only a minor portion is sent directly to the reactor, which thus operates with the lowest possible concentration of inerts. The remainder is routed to the HP carbamate condenser, where its NH_3 and CO_2 content is separated from the inerts as ammonium carbamate solution, which is recycled to the reactor. A high-efficiency submerged condenser is used to cope with this duty.

The advantages of operating the synthesis section with very low inerts content are:

- high CO_2 conversion in the reactor (up to 63-64%);
- high stripping efficiency;
- high condensation efficiency.

Split Flow Loop™ process performance

The Split Flow Loop™ process can achieve the following performance:

- 63.5% CO_2 conversion in the reactor;
- 82% stripping efficiency;
- production of LP steam up to 5 bara;
- 450 kg/t specific carbamate recycle rate;
- 770 kg/t MP steam consumption (22 bar, superheated);
- Almost stoichiometric raw material consumption.

A Split Flow Loop™ urea plant has been operating in Ukraine since 2003 and is producing 1,500 t/d of urea. In the last couple of years two more Split Flow Loop™ urea process plants have come into operation, producing up to 2,300 t/d. Casale has also recently designed one grass-roots Split Flow Loop™ urea plant process that has been built in France.

Casale-Lurgi mega-ammonia process

Several years ago, engineers from Lurgi and Ammonia Casale analysed the conventional ammonia process with a view to doubling the size of ammonia plants on offer. They concluded that conventional technology suffers certain limitations when capacities in the range of 4,000 t/d or larger are contemplated. As a result, a new process was proposed that was considered to be both economically attractive and bankable. The new process was named MEGAMMONIA® and is now offered by Casale, it is based on the combined experience of both companies. Interest in the process is growing as larger capacity plants are being considered by the market.

The MEGAMMONIA® process comprises five principal units (see Fig. 2):

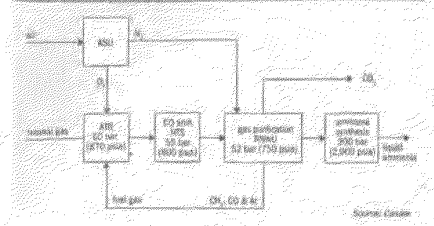
- air separation unit (ASU);
- catalytic partial oxidation unit (ATR);
- CO-Shift unit;
- gas purification unit;
- ammonia synthesis unit.

The separation of air into its components, oxygen and nitrogen, is a well known, and widely practised process. For the MEGAMMONIA® process an ASU produces a gaseous stream of 95% pure oxygen for use in the autothermal reformer, and a stream of 99.99% pure nitrogen for use in the gas purification unit.

In the catalytic partial oxidation unit feedstock, natural gas is preheated and desulphurised in the conventional manner over a cobalt molybdenum catalyst followed by zinc oxide. The desulphurised gas is then saturated using condensate recycled from the CO shift unit, preheated in a fired heater and pre-reformed over



Fig. 1: Block diagram of the KRES AMMONIA process



Source: Casale

a nickel oxide catalyst so as to convert all higher hydrocarbons to hydrogen and methane. Steam is added to the pre-reformed gas to adjust the steam to carbon ratio, the gas is further preheated in the fired heater, and then reformed to CO, H_2 and CO_2 in the ATR by partial oxidation with oxygen. A nickel oxide catalyst located in the ATR vessel further assists reforming. The resulting hot reformed gas is cooled to a temperature to suit the downstream CO shift unit in a process gas boiler raising high-pressure steam for use in driving the major rotating machines. The absence of a pressure limiting steam reformer makes it feasible to raise the pressure of the ATR to 60 bar (870 psia).

Within the CO shift unit, the reformed gas is passed over two beds in series of conventional HT catalyst to convert the remaining CO to H_2 and CO_2. As the volume of catalyst required is considerable, each bed is arranged in axial-radial configuration so as to minimise catalyst volume, pressure drop and vessel diameter. The gas is then cooled to ambient temperature. The condensate arising is separated from the gas and recycled to the saturator in the ATR.

Gas purification is accomplished in two wash columns, the first removing CO_2 and the second removing the remaining impurities, namely CO, CH_4 and Ar. CO_2 is removed by absorption in cold methanol by the well known Rectisol® process. CO, CH_4 and Ar are removed by washing the gas with liquid. The CO_2 is recovered from the cold methanol by reducing the pressure to near atmospheric, and the recovered gas is sufficiently pure for use in the synthesis of urea. The recovered impurities, CO, CH_4 and Ar are recycled to the ATR for use as fuel in the fired heater. Refrigeration for the Rectisol® process is provided by ammonia supplied from the ammonia synthesis unit. Pure synthesis gas, comprising H_2 and N_2 in the correct stoichiometric proportion, is passed to the ammonia synthesis unit.

The ammonia synthesis unit is of conventional design. The synthesis of ammonia from H_2 and N_2 is carried out over an iron based catalyst at high pressure provided by a syngas compressor. The ammonia converter is of the most advanced axial-radial design by Ammonia Casale. Synthesis is carried out by passing the gas over three inter-cooled adiabatic beds of catalyst in series. The heat of reaction is recovered by a loop boiler, and by a boiler feed water pre-heater. Heat is conserved by heat exchange between feed and effluent streams to and from the converter. Synthesised ammonia is removed from the synthesis loop, in the conventional manner, by condensing the ammonia against low pressure boiling ammonia and by separating the argon from the unreacted synthesis gas. The pressure of the liquid is reduced in several stages and unreacted gases are recycled to the syngas compressor. The extremely high purity of the ammonia syngas results in higher conversion of gas per pass, lower circulator duty, lower refrigeration duty, and generally smaller equipment throughout the loop.

A refrigeration compressor in the ammonia synthesis unit raises the pressure of gaseous ammonia to a level at which it can be liquefied against cooling water, thereby providing a means of refrigerating the synthesis loop and the Rectisol® process.

Owing to the absence of impurities from the ammonia syngas, the synthesis loop needs no purge, nor purge gas treatment system. Pure ammonia is stored as a liquid in atmospheric pressure storage tanks.

Energy consumption for this process is estimated to be 6.5-6.7 Gcal/t ammonia, based on the lower heating value of a representative natural gas. The range given covers the supply of warm ammonia to a downstream urea plant, or the storage of cold ammonia in an atmospheric pressure tank. This energy consumption includes the power required for the process, the ASU, and all its utilities, inclusive of natural gas compressor, steam water and sea water cooling systems, and a water treatment plant. The import of electricity is not required other than to start the plant.

Advantages of the MEGAMMONIA® process include:

- Lower investment cost compared to a scaled up version of conventional technology at a size of 4,000 t/d;
- Reduced operating cost due to fewer unit operations and fewer catalyst steps;
- Lower CO_2 and NO_x emissions;
- Increased urea production – the recycle enable CO_2 from MEGAMMONIA® will be sufficient to convert all of the ammonia produced to urea, compared to the conventional ammonia process, which uses a steam reformer and is always short of CO_2.

New technologies from Haldor Topsoe

Haldor Topsoe offers several new features to improve the energy savings and flexibility of ammonia plants including:

- New developments that enable production at lowered low S/C ratios – resulting in lower specific energy consumption with no additional investment cost;
- HTER, revamp of existing plants, steam balance optimisation, smaller SMR reformer.
- Post ammonia converter as revamp feature.
- Reformer refractory coating for increased efficiency and capacity.

Significant energy savings

A common understanding of how steam to carbon (S/C) ratio is related to energy consumption in an ammonia plant, is the higher the S/C ratio, the higher the energy consumption. In modern ammonia plants, the limiting factor determining how low the S/C can be designed is the existing high temperature CO shift (HTS) catalyst. The normal S/C ratio in today's ammonia plants is approximately 3.0. New developments within the area of HTS conversion enables Topsoe to design with S/C at 2.4 while still keeping the required heat input to the CO_2 removal section. This makes it possible to achieve an energy saving of close to 0.1 Gcal/t ammonia. Normally, energy consumption in the ammonia plant is reduced by lowering the losses, which requires larger and/or more equipment such as reactors and heat exchangers which will typically increase the plant cost. For new plant designs, the latest developments enable reduction of the energy consumption without additional investment cost.

HTER

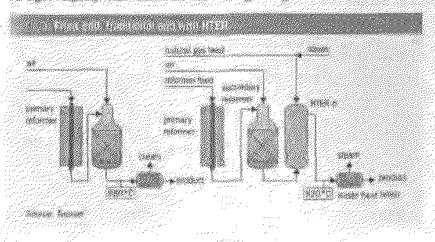
Various options are available for a capacity increase in the front-end of an ammonia complex. Of these, convective gas heated reforming, stands out, as an attractive option from both a technical as well as a cost effective perspective. The Haldor Topsoe Exchange Reformer (HTER) technology is a proven revamp option where a capacity increase of 20-25% can easily be achieved, while the methane leakage is retained at a low level (Fig. 3).

The obvious advantage of HTER for ammonia, besides the reduction in primary reforming duty, is that it offers a very high reforming temperature. A high reforming temperature results in a low methane slippage even with a S/C ratio at the same level as used in a traditional primary reformer for ammonia. The overall S/C ratio used in the front-end with HTER is the same as in the traditional front-end for ammonia. The outlet temperature from the primary reformer is not higher than in the traditional case. For a given capacity, HTER reduces the size of primary reformer for two reasons: firstly, because part of the reforming duty is transferred to the HTER and secondly, because the secondary reformer will perform better, as the total amount of process air, which is determined by the ammonia capacity, is fed to the secondary reformer and only part of the feedstock passes the secondary reformer. When the secondary reformer operates with a higher ratio of process air to process gas, the exit temperature will increase and the methane slip decrease. Another important feature of revamping with HTER is the steam generation system which can be reused without modification, even with 20% higher plant capacity.

Post ammonia converter

In many vintage plants, the ammonia synthesis loop is designed for high inert level and normally also high loop pressure. One simple and interesting revamp feature is to employ a purge gas converter to increase capacity and save energy. Having a purge gas converter permits the inert level in the synthesis loop to be decreased by increasing the purge gas flow rate, without sacrificing hydrogen recovery. The main converter will have much better performance with a lower inert level, resulting in lower loop pressure, energy savings and higher capacity. The purge gas converter can also be installed without modifying the plant to simply increase the ammonia production. Having more plants with one common purge gas converter will be even more favourable. Compared to the Topsoe S-50 post converter located downstream of the main converter, the purge gas converter will be much smaller, installation will be much simpler and the cost will be much lower. However, the S-50 will improve performance of the synthesis in terms of capacity increase and energy savings.

Fig. 3: From conventional and with HTER



Source: Topsoe

Reformer refractory coating

The furnace walls in a side-fired (tubular) reformer are lined with refractory, bricks and fibre materials and a relative low emissivity. By applying a "high emissivity coating" on the surface of the furnace walls it is possible to increase the emissivity and thereby improve the thermal efficiency of the furnace box significantly. The enhanced efficiency of the furnace box can be utilised to alleviate excessive temperatures in the convection section, increase the capacity of the reformer or prolong the lifetime of the catalyst tubes. The lifetime of the catalyst tubes may be further prolonged if the heat releases in the bottom row burners can be reduced to half the heat release of the upper row burners. At least six Topsoe licensed plants have applied high emissivity coating of the furnace walls in the tubular reformer with satisfactory results.

KBR revamp technology

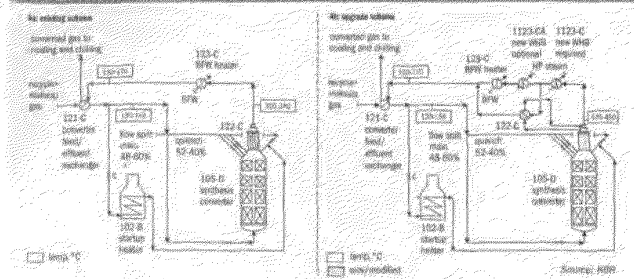
KBR have done several studies recently for clients that are interested in utilising KBR's new proprietary revamp technology to upgrade the ammonia synthesis loops of KBR ammonia plants built in the 1960s to 1980s. The technology can also be applied to relocated MW Kellogg plants. By implementing a simple modification in the existing ammonia converter and incorporating a HP steam raising boiler in the synthesis loop a high grade heat recovery synthesis loop can be achieved.

Over the years, ammonia plant owners have incorporated various energy saving features in their existing plants to reduce energy costs. However, in spite of retrofitting the latest technology features, the energy consumption of those plants built decades ago still remain higher than that of the latest generation plants.

KBR has looked in depth for the key inherent factors that cause the plants of the 1960s to 1980s to be higher energy consumers and has identified that one inherent factor preventing these older plants from achieving low energy consumption is their inability to recover the waste heat in their synthesis loop by raising HP steam. KBR recognised that there is a benefit to recovering waste heat as HP steam in these older synthesis loops without replacing the existing ammonia converter. The converter outlet stream should be made available at above 425°C for economic heat recovery to raise HP steam.

Topsoe, Inc. – EX1003
Page 832 of 1210

Revamp scheme for existing KBR synloops having converter 105-D



Source: KBR

To enable the plant owners to accomplish this objective, KBR offers a technology to upgrade the existing synthesis loop to make the waste heat available at higher thermodynamic grade and enable its recovery as HP steam. The upgrade technology requires that the existing internal heat exchanger bundle inside the top of the converter is removed and a new specially engineered external feed/effluent heat exchanger is incorporated in the scheme outside the ammonia converter. The existing pressure vessel shell of the converter still has a cold wall in operation as before but the product syngas exits the converter at a very high temperature. Two specific examples of the high grade heat recovery technology applications are given below for a typical existing KBR plant with synthesis loop at 150 kg/cm² pressure. In both examples, the ammonia converter is already retrofitted with axial-radial baskets but the bed temperature control is still of by-pass mechanism. This upgrade technology will also apply to other plants with different existing retrofits. The fundamentals will remain the same but optimised parameters and details outside the ammonia converter may be somewhat different.

Post revamp, the main syngas cooling feed stream (48-55% of total) will continue to flow into the converter at the bottom through the annular space of the converter, and will continue to maintain temperature of the pressure vessel shell unchanged. This stream will exit the converter separately, without mixing with the quench flow streams (52-45%), through a new nozzle, and without flowing to the catalyst bed baskets. This cold gas stream will be preheated in a new "external feed/effluent exchanger" and fed back to the converter through a new nozzle to flow to catalyst bed No 1 without any further pre-heating inside the converter. The final converted syngas from the last catalyst bed will flow through the existing centre pipe and be collected through a new nozzle on the converter top. This very hot effluent gas stream will be fed to a new waste heat boiler, added downstream of the converter, that will raise HP steam. The existing system of gas quench will remain unchanged.

Process schemes for two typical application scenarios of this upgrade technology are shown in Figs 4a and 5a.

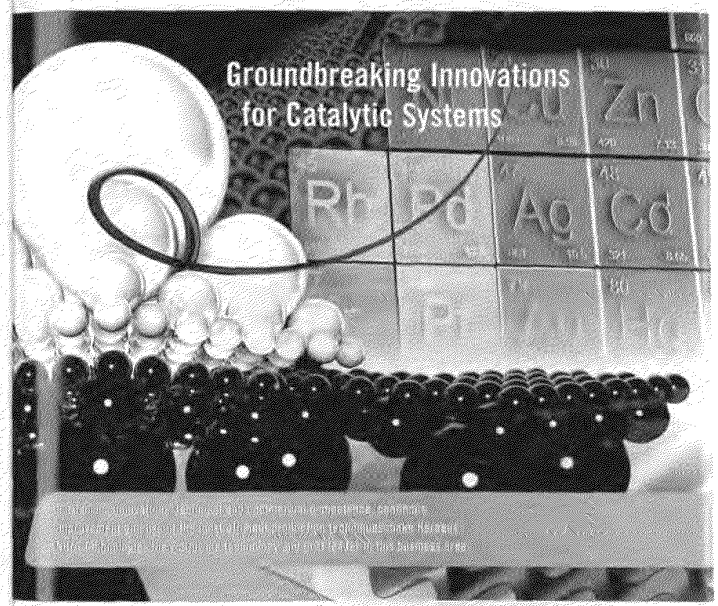
The following modifications are needed to the existing synthesis loop as shown in the Figs 4b and 5b:

- The existing internal heat exchanger 122-C is removed and discarded from inside of 105-D.
- The upper portion of 105-D is modified by bolting a proprietary engineered cap at the top of 105-D.
- No hot work is needed on the 105-D pressure vessel; there is a hot work on the upper portion of the internals which is easily accommodated and executed in a planned shutdown. This proprietary modification of 105-D is simple, low cost and easy to execute.
- The hot syngas exit 105-D at about 445-455°C is cooled to 335 to 385°C in a new waste heat boiler (112-B) where HP steam at 105 to 127 kg/cm²g is raised. If the existing synthesis loop has a separate second ammonia converter in series then depending upon its design, this temperature is 335 to 370°C, otherwise a higher temperature 380-385°C is used.
- A new external 122-C is provided to preheat the 105-D bed-1 feed gas. The syngas flow stream exit the 1123-C in Fig. 4b (or alternatively exit the second existing converter in Fig 5b) is split into two parts. About 48-55% of the flow is cooled in the existing BFW preheater 123-C. Remaining gas is cooled by preheating the 105-D shell cooling gas in the new "external 122-C". These two streams are combined and cooled by preheating 105-D feed gas in the existing 121-C which remains unchanged.

Energy saving by heat integration

Total heat recovery from the synthesis loop to the steam system for generating HP steam does not change after implementing the upgrade scheme described above. What changes is the temperature level at which heat is available for recovering into the steam system. In the existing scheme, this heat is typically recovered all by preheating the cold deaerated boiler feed water which is ultimately used for producing HP steam. In some plants that have already modified the synloop by adding a second ammonia converter, some of the waste heat may be recovered as MP steam. In the KBR's upgraded scheme

Heraeus



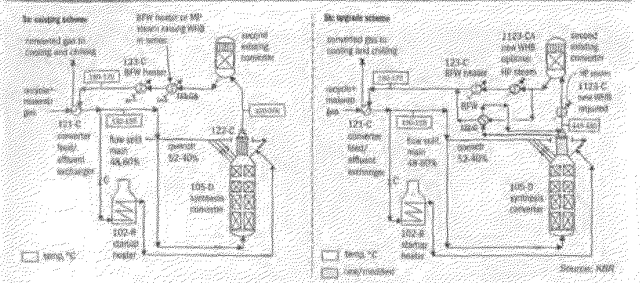
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Fig 1. Revamp scheme for existing KBR Ammonia Plant with 3050 and 2 existing converter



after revamping, up to 60% of the total waste heat in the syngas is used for directly raising HP steam. This heat is now available at a temperature well above the boiling temperature of the high pressure BFW. The remaining heat in the syngas is still used for preheating the BFW.

As heat recovery at lower temperature in the syngas is reduced drastically, the deaerated cold boiler feed water is now available for recovering waste heat available at low grade (i.e. at lower temperature) in the other sections of the ammonia flowsheet which could not be recovered earlier to HP steam system. Additional amount of lower grade heat is now recovered in the one or more (but not limited to) of the following locations:

- LT shift converter outlet for preheating BFW or demin water;
- CO_2 removal unit from hot solvent or stripper overhead;
- methanator outlet (exit feed/effluent exchanger);
- primary reformer flue duct;
- other sources made available by reducing duty on (or eliminating) an existing user of low grade heat (example reboiler heat for CO_2 removal unit).

Thus, the upgrade technology scheme enables generation of increased quantity of high pressure steam as additional low grade heat is recovered into the HP steam system. First, the syngas is upgraded to produce more HP steam directly. Second, the cold BFW not required as a heat sink by syngas is used in other areas of the ammonia plant to bring additional low grade heat into the HP steam system by heat integration. Total HP steam production inside the ammonia plant is thus increased. If possible, either the firing to the auxiliary boiler is reduced or the steam can be exported to OSBL which will save fuel on the OSBL package boiler. Thus, energy efficiency of the ammonia plant is improved significantly.

Energy efficiency of the ISBL ammonia plant can be improved by 0.18 to 0.30 Gcal/tonne by revamping the existing plant using KBR's high grade heat recovery synthesis loop technology. Exact energy saving of a plant will depend on its current base conditions.

Application to existing plants

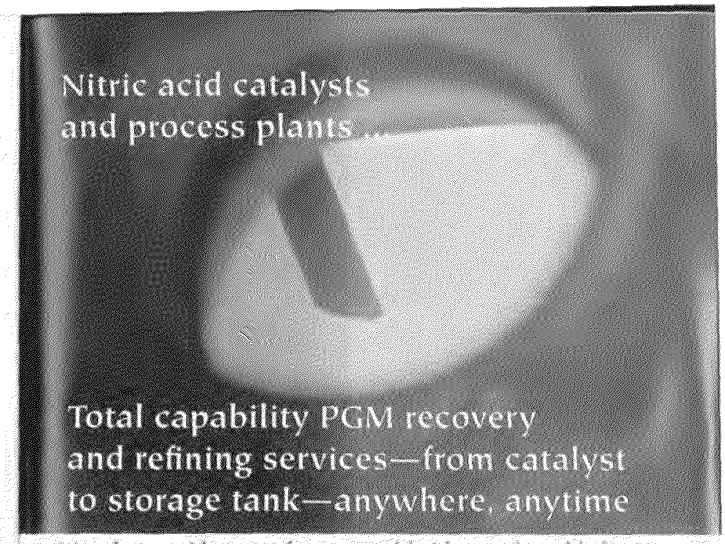
If implemented, this upgrade technology will produce HP steam in all KBR plants that still have the original KBR vertical ammonia converter pressure vessel. In principle, subsequent basket retrofits, no matter what type, do not reduce potential of raising HP steam using this upgrade technology. Similarly, subsequent addition of a second ammonia converter, irrespective of its details, does not reduce potential of raising HP steam. It is the original converter design that prevents possibility of raising HP steam; the above described technology makes it now possible with only a minor change to the top of the existing converter.

KBR is unaware of an existing ammonia plant of the design being discussed that has HP steam producing waste heat boiler in the synthesis loop. Depending upon its specific existing retrofits, the plant will have less energy saving if a HP steam raising boiler has already been incorporated in such an existing plant. However the specific plant with an existing HP steam boiler may also benefit by using this revamp technology, as production of HP steam is increased and the plant energy efficiency is improved by utilising the existing boiler after rating it for the new conditions.

It is expected that through mutual cooperation with the plant owners, this upgrade technology can also be applied to numerous CIAP ammonia plants in Russia and other FSU countries. ■

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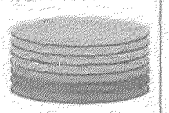


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Ammonia catalysts show continuous improvement

The performance of ammonia catalysts continues to improve with the growing demand for this key chemical. **S. Gebert, Y. Cai, and B. Kniep** of Süd-Chemie AG discuss the high performance of the wustite-based ammonia synthesis catalyst AmoMax®-10 that offers much improved performance compared to conventional systems.

Ammonia is one of the world's most valuable industrial and agricultural chemicals. It serves as the basis for the production of fertilizers that are in high demand to meet the global food production needs. Süd-Chemie is actively engaged in addressing the process demands for this product.

The very heart of the ammonia process is the iron synthesis catalyst, which enables the fixation of nitrogen from air with hydrogen. The industrial success of commercial ammonia production would not have been possible without the appropriate catalyst choice. Though different catalysts were tested during the early stages of the process nothing has approximated the advantages of iron (magnetite) for industrial ammonia production. For more than 90 years iron catalyst has supported this industry with very few significant changes[1-3].

Table 1. Chemical formulae of wustite and magnetite

	Wustite	Magnetite
Chemical formula	$Fe_{1-x}O$ (Fe^{2+})	Fe_3O_4 (Fe^{2+}/Fe^{3+})
Oxygen content	22.3%	27.7%

AmoMax®-10, the long-awaited innovation

In 1986, Prof. Ruyu Xu, Wang Suzheng, and Lu Peilin from the Zhejiang University of Technology (ZUT) were working on the recovery of used ammonia synthesis catalysts. They discovered that they could make a new type of iron oxide material where the iron to oxygen ratio was higher than in the starting magnetite-type material (used ammonia synthesis catalyst). Also, X-ray diffraction (XRD) patterns showed a different diffraction from the typical Fe_3O_4 structure. The main phase of the newly discovered material was wustite, a non-stoichiometric ferrous oxide $Fe_{1-x}O$. This was the first time that a species other than magnetite was recorded as the main phase of an ammonia synthesis catalyst. To their surprise, this new catalyst showed better performance.

After further improvement studies, the catalyst was successfully produced in 1991 at a larger industrial scale. This product, A301, was tested in small and medium ammonia plants. The results were very encouraging showing high low-temperature activity (requiring also low pressure), easy regeneration (quick reduction rate) and easy dehydration (rapid water-loss). Pernicone *et al* confirmed that the catalyst proved to be more active, especially at lower temperatures[4].

However, the catalyst also displayed rapid deactivation and poor thermal stability, which limited its application in large-scale ammonia plants. ZUT set up a significant interdisciplinary co-operation project from 1992 to 1994 to address the drawbacks of the new catalyst and make it successful for the market. Major parameters targeted by the effort were the main phase manufacturing process and the promoters, including their size, form and distribution. Finally, in 1996 Professors Ruyu Xu, Yaning Kao, and others published breakthrough results, reporting the development of a novel catalyst based on $Fe_{1-x}O$ (wustite) for ammonia synthesis[5]. In 1999 a technology transfer agreement between ZUT and Laiche Huachin Chemical Group (LHCG) was signed based on the original catalyst patent. During 2001-2002 a successful commercial-scale production of the improved catalyst was completed in LHCG's catalyst plant in Panjin, China.

In 2003 Süd-Chemie formed a 60/40 joint venture with Laiche Huachin Chemical Group, called Panjin Süd-Chemie Laiche Catalyst Company. Subsequently the optimised and industrially tested catalyst was named AmoMax®10. This catalyst is also available in a reduced and stabilised form called AmoMax®10RS.

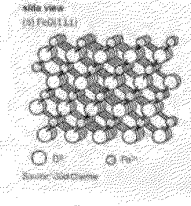
Building from laboratory research to an industrial testing, Süd-Chemie and independent laboratories have extensively investigated AmoMax®10 compared to the magnetite catalyst. Some data provide an indication about its superior performance, but detailed scientific explanations have not yet been determined.

The wustite precursor of AmoMax®10 is a non-stoichiometric ferrous oxide ($Fe_{1-x}O$, with $x = 0.03$ to 0.15), which has a significantly lower oxygen content than magnetite (Fe_3O_4), the precursor of the traditional catalyst (Table 1).

Since it is the reduced form of the iron precursor which is the active catalyst (particularly the alpha-iron atoms), the lower oxygen content is already the first benefit offered by wustite, allowing users to shorten the reduction time by typically one day. This translates into energy savings and increased ammonia production.

It is well known for the iron catalysts that the (111) planes of the crystal structure are most active for ammonia synthesis[6]. It was reported that AmoMax®10, at least theoretically, offers an improvement in the (111) planes (Fig. 1) and thus it is reasoned to be more active[6]. The (111) crystal lattice plane is maintained for AmoMax®10 in the reduced form, resulting in the most active iron surface for ammonia synthesis (structure-sensitive reaction).

Fig. 1. Schematic representation of the plane (111) in Wüstite crystal.



The heart of this innovation lies in the selection of optimal structural and electronic promoters for AmoMax®, which are different in nature and quantity than those used for traditional magnetite catalysts. Previous literature had discussed poor thermal stability[7,8], which can be explained by the lack of an appropriate promoter system and an optimised preparation route. It is important to note that wustite itself, without promotive stabilising, the defect-rich crystal structure of the oxide, does not result in appropriate ammonia synthesis catalysts.

AmoMax®10 has a unique promoter system, which uses the classical "magnetite promoters" potassium, alumina and calcium and also several other confidential promoters like e.g. certain transition metal oxides. A SEM image of a reduced AmoMax®10 particle is depicted in Fig. 2.

Figures 3 and 4 show, for example, that aluminium and potassium, like most other promoters, are located in the intergranular spaces of the reduced AmoMax®10. However, there are also promoters that are incorporated in the Fe crystals after reduction (Fig. 5). The combination of all promoters leads to the proven high activity and thermal stability of AmoMax®10.

Unique benefits of AmoMax®-10

As shown in the Arrhenius plot in Figure 6, AmoMax®10 is not only more active than traditional magnetite catalysts, but it also

Fig. 2. SEM image of a reduced AmoMax®-10 particle



Fig. 3. SEM-EDX mapping of aluminium in reduced AmoMax®-10

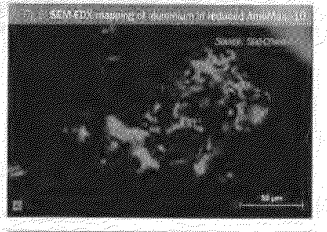


Fig. 4. SEM-EDX mapping of potassium in reduced AmoMax®-10

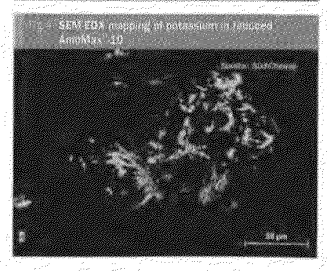
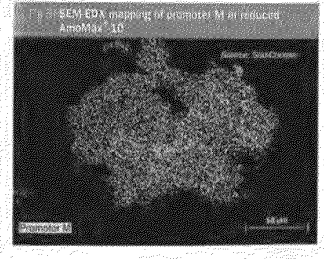


Fig. 5. SEM-EDX mapping of promoter M in reduced AmoMax®-10



Topsoe, Inc. – EX1003
Page 835 of 1210

provides a much higher activity at lower temperature. This allows operation at lower inlet temperatures while providing more conversion per pass because of a more favorable thermodynamic equilibrium at the lower temperature.

Thermal stability is very important for a long catalyst life of the catalyst due to the elevated temperature and pressure of typical operations. Lab tests were conducted at temperatures exceeding normal operating conditions (550°C) comparing the performance of a commercially available magnetite catalysts with AmoMax®-10. As shown in the life test in Fig. 7, AmoMax®-10 not only provides higher initial activity, but it also undergoes less deactivation with time on stream. Comparatively, it behaves much better than the magnetite based catalyst. This has been confirmed by stable commercial operation at several references that have been on-stream for several years; the oldest charge has been on-stream for more than eight years.

The considerable lower light-up temperature of AmoMax®-10, as shown in Fig. 8, allows faster start-up of the loop (saving energy and time) and results in less potential for loss of reaction during an upset, which adds a safety margin to ammonia plant operation. Also, pressure drop across the catalyst bed has proven to be extremely stable, implying a long life of the catalyst.

Commercial performance of AmoMax®-10

AmoMax®-10 has nearly 70 references globally in eight years (Fig. 9).

Examples of the commercial success of AmoMax®-10 include the first commercial application at Liaohe Huachin Chemical Group in Panjin, China, where the catalyst was installed in December 2003. This unit is a KBR design from 1976 that was revamped in 1988 by Casale to a 3-bed axial-radial design. The capacity of the unit is 1,070 t/d but production is often limited by incoming gas supply. Despite the variable operations, the catalyst activity and pressure drop continue to remain stable throughout its ongoing operations.

Another reference from Western Europe verifies the high activity of AmoMax®-10. This Casale revamped unit with a nameplate capacity of 1,050 t/d began using this catalyst in March 2011 and even exceeds slightly the optimistic plant design as shown in Table 2.

Fig. 7 Stability of AmoMax®-10 compared to magnetite-based catalysts

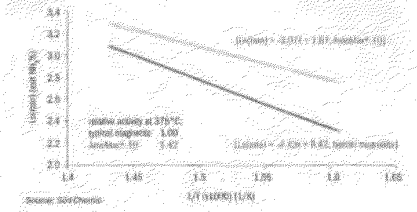


Fig. 8 Temperature profile of AmoMax®-10 compared to magnetite-based catalysts

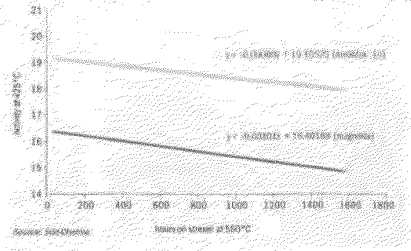
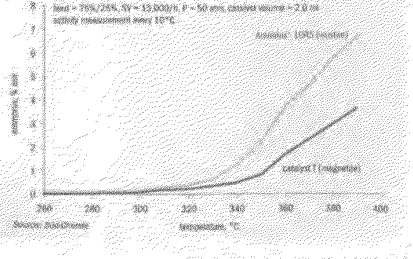


Fig. 9 Lower ignition temperature of AmoMax®-10RR compared to a traditional magnetite-based catalyst



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Fig. 10 Worldwide success of AmoMax®-10

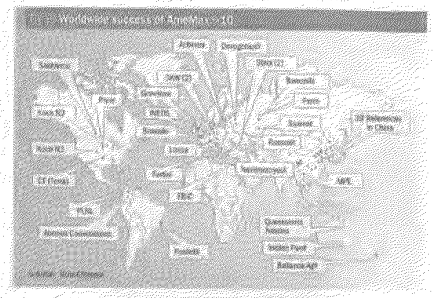
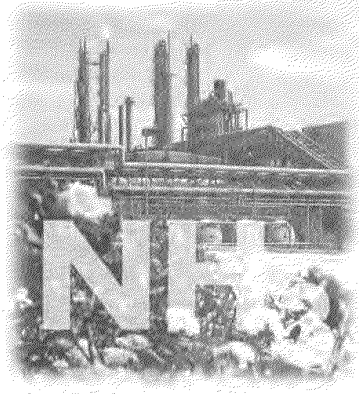


Table 2 Performance of AmoMax®-10 in a European ammonia plant

	Design	AmoMax®-10, 5 months on stream
NH_3 concentration at reactor outlet, %	20.6	20.8
Operating pressure, bar	170	163



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Page 836 of 1210

Process condensate stripper performance in ammonia plants

A project was recently completed on the development of an alternative process route for the removal of methanol, ammonia and carbon dioxide from process condensate in an ammonia fertilizer plant. As part of this project, a performance analysis study on three representative process condensate strippers operating under different conditions in Indian fertilizer plants was initiated and results compared. Steady state simulation runs on these stripper variants using CHEMCAD simulation software were carried out. The effect of stripper operating pressure and temperature and steam tonnage on the stripper performance is reported by **S. Krishnaswamy, S. M. Nazir, P.V.R. Srikonth** and **K. Ponnani** of BITS, Pilani – Goa Campus.

In the ammonia manufacturing process, when syngas is cooled after the low temperature shift (LTS) step, the unreacted steam (used in reforming and shift conversion) forms a condensate stream which contains impurities, the major ones being ammonia (NH_3), methanol (CH_3OH) and carbon dioxide (CO_2). The syngas from this step goes to a CO_2 separation step where another stream containing mostly water and an equilibrium amount of CO_2 is formed. This stream normally known as "Benfield" condensate is subsequently pressurised and added to the condensate stream obtained at the end of the LTS step. The resultant stream called "process" condensate[1] typically contains ammonia, methanol and carbon dioxide, each in the range of 300 to 2000 ppm by weight, depending on the variations in process and operating conditions in a plant. A comprehensive analysis and characterisation of process condensate has been carried out by the investigators earlier and reported.[2]

The current method of treating process condensate involves steam stripping to reduce the ammonia, methanol and carbon dioxide content to below 5 ppm by weight for each and reuse the purified condensate as boiler feed water (BFW). The stripper has to operate under severe operating conditions where a large amount of superheated steam is consumed making it a highly energy intensive operation. Even then, the BFW specifications for recycle are hard to achieve. This can result in degradation of condensate to lower duty or rejection and increase of stripper steam.

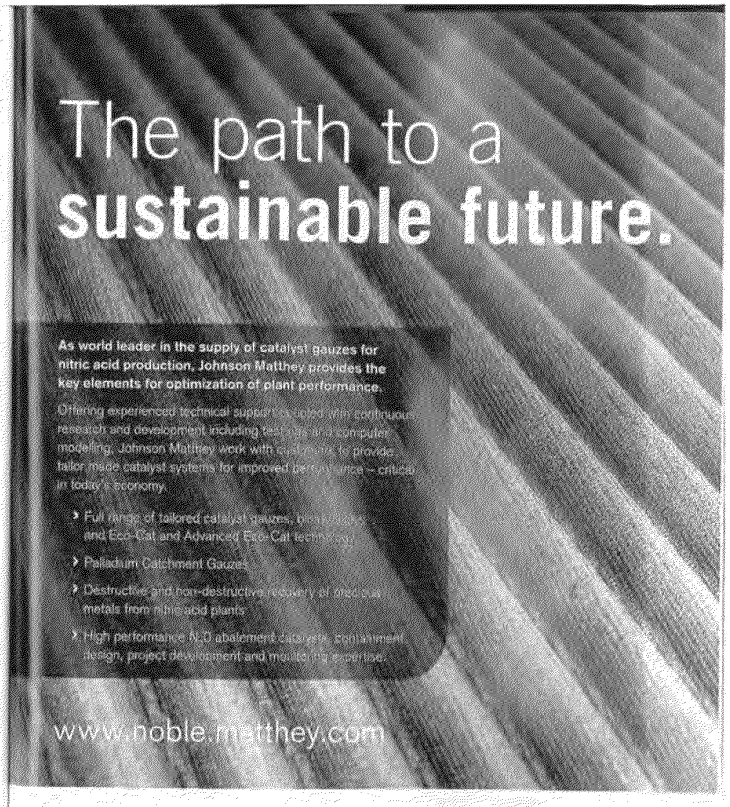
In typical large sized old and new generation ammonia plants, where the process condensate flows are in the region of 40 t/h, the quantity of superheated stripper steam used is typically 10 t/h to 14 t/h. Any attempt to reduce the quantity of steam results in larger impurity concentrations in the condensate (>10 ppm) leaving the stripper. In the case of older generation plants, this recovered condensate sometimes cannot be directed back to the boiler and is instead downgraded to cooling tower water (CTW), where methanol accentuates the growth of algae and other micro-organisms resulting in high cooling tower treatment costs.

In recent years, continuous improvements have been made to the process condensate stripping operation. However, no effort seems to have been made to eliminate the use of superheated steam for stripping. Some of the accumulated impurities are also released as objectionable emissions from process vents causing environmental pollution. This formed the genesis of a recently completed project Birla Institute of Technology and Science (BITS), Pilani – K K Birla Goa Campus (Grants-in-Aid Bill No: 18061/2/2008, Department of Fertilizers, Ministry of Chemicals and Fertilizers) on the development of an alternative route for treatment of process condensate.

As part of this project, it was proposed to conduct a comparative performance study using CHEMCAD simulation on three stripper variants (based on varying operating conditions) generally used for process condensate treatment in existing fertilizer plants across India of different vintages and using different technologies. This study provided an insight into better understanding of process condensate stripper operations prior to development of an alternative energy efficient and cost effective process route for process condensate treatment.

Process description

A typical flow sheet of a stripper used for treating process condensate in existing



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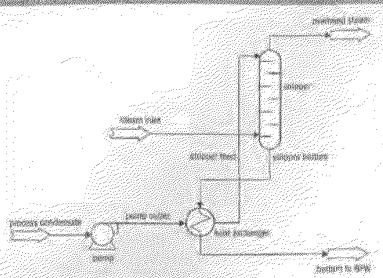
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Fig. 1 Typical flowsheet for process condensate treatment in fertilizer units



* Slight variation in operating conditions possible, may vary from plant to plant

Table 1 Stripper operating conditions in different fertilizer units

Stripper variants	LP stripper	MP stripper	HP stripper
Operating pressure, MPa	0.35	1.1	3.8
Steam inlet temperature, °C	130	200	275
Steam flow rate, t/h	18	8	15
Process condensate flow rate, t/h	90	90	42

* Slight variation in operating conditions possible, may vary from plant to plant

ammonia plants is shown in Fig. 1. The process condensate is pumped to the stripper where it comes in direct contact with superheated steam which strips the condensate of ammonia, methanol and carbon dioxide. The bottom stream from the stripper exchanges energy with the condensate feed stream before being directed to the boiler feed water (BFW) section. The overhead steam from the stripper containing impurities (depending on its operating conditions) is appropriately integrated with the ammonia manufacturing process. The operating conditions of three stripper variants practiced in Indian fertilizer industries and used in the present study are given in Table 1.

CHEMCAD process simulation

The stripper shown in Fig. 1 was simulated using CHEMCAD process simulation software. The VLE in the water-NH_3-CO_2-CH_3OH system is highly complex since the liquid phase is ionic. Several thermodynamic models were chosen and investigated to describe the VLE of the proposed system. The electrolyte NRTL or E-NRTL[3] was found suitable as it considers electrolyte interactions, which are predominant in the process condensate because of the presence of ammonia and carbon dioxide. Tables 2 and 3 show the overhead and bottom stream process conditions obtained from simulation in comparison with plant data for all three stripper variants under consideration. Good agreement is observed confirming once again the choice of thermodynamic model used.

Effect of steam operating conditions

A CHEMCAD sensitivity analysis was subsequently carried out to study the effect of steam temperature, pressure and flow rate on removal of ammonia, methanol and carbon dioxide from process condensate. Representative results are presented on a 40 t/h process condensate basis and discussed herewith.

Table 4 shows the effect of steam inlet temperature on the removal of CO_2, NH_3 and CH_3OH from process condensate in the case of high pressure stripper variant. It is seen that increasing steam temperature i.e. additional superheat has practically no effect on stripping of carbon dioxide, ammonia and methanol. A similar effect was observed in the case of the low and medium pressure stripper variants. It was also observed that an increase in degree of superheat resulted in increased carryover of process condensate in the stripper overhead stream.

Table 5 shows the effect of steam inlet pressure on the removal of CO_2, NH_3 and CH_3OH from process condensate in the case of higher pressure stripper variant. It is seen that increasing steam pressure has no effect on stripping of methanol and carbon dioxide, but the ammonia concentration in the stripper bottom stream increases. A similar effect was observed in the case of the low and medium pressure stripper variants. An increase in steam pressure directly results in an increase in ammonia solubility in process condensate, thereby making it difficult to separate. In addition, increasing inlet steam pressure for a particular temperature reduces the degree of superheat resulting in decreased carryover of process condensate in the stripper overhead stream.

Tables 6, 7 and 8 show the effect of increase in superheated steam tonnage on the removal of CO_2, CH_3OH and NH_3 from process condensate in the case of high, medium and low pressure stripper variants. An increase in steam tonnage has no effect, whatsoever on the stripping of carbon dioxide. In Table 6 (which shows the analysis of high pressure stripper variant), methanol concentration reduces below 5 ppm at a steam inlet flowrate of 12 t/h. However for the same stripper, the steam requirement is to the tune of 42 MT/hr to bring ammonia concentration in process condensate to below the desired concentration of 5 ppm. In the medium and low stripper variant, it is seen that the concentration levels of carbon dioxide, methanol and ammonia drop below 5 ppm if 9 t/h and 7 t/h of stripping steam is used respectively. It is clear from the above results that operating the stripper under low pressure conditions results in less usage of steam. The low pressure stripper operates under these conditions (refer Table 1). Operating the stripper at higher pressures, results in increased usage of steam which touches the effect

Table 2 Comparison of simulation results with plant data (stripper overhead)

Stripper pressure (MPa)	Plant data T (°C)	Plant data P (MPa)	Plant data Flow rate (t/h)	Simulation data T (°C)	Simulation data P (MPa)	Simulation data Flow rate (t/h)
0.35	142	0.3	18	137	0.3	19
1.1	175	0.8	8	170	0.8	8
3.8	248	3.7	16	245.6	3.7	15

Table 3 Comparison of simulation results with plant data (stripper bottom)

Stripper pressure (MPa)	Plant data T (°C)	Plant data P (MPa)	Plant data Flow rate (t/h)	Simulation data T (°C)	Simulation data P (MPa)	Simulation data Flow rate (t/h)
0.35	143	0.4	90	137	0.3	94
1.1	175	0.8	40	170	0.8	39
3.8	248	3.7	41	246	3.7	42

Table 4 Effect of steam inlet temperature on stripping of CO_2, NH_3 and CH_3OH

Steam T (°C)	Stream composition (ppm) CO_2	CH_3OH	NH_3	Condensate carryover (t/h)* H_2O
250	0	0.05	1728	
300	0	0.03	1691	
350	0	0.00	1651	
400	0	0.00	1610	0.52
450	0	0.00	1566	1.41

* Condensate carryover in overhead stream (t/h)

Table 5 Effect of steam inlet pressure on stripping of CO_2, NH_3 and CH_3OH

Steam P (MPa)	Stream composition (ppm) CO_2	CH_3OH	NH_3	Condensate carryover (t/h)* H_2O
3.0	0	0	1164	1.91
3.5	0	0	1497	0.86
4.0	0	0	1721	
4.5	0	0	1890	

* Condensate carryover in overhead stream (t/h)

of ammonia solubility at these pressures. Existing high pressure stripper variants in fertilizer plants in India consume 14 t/h of steam as against 42 t/h required for stripping ammonia from process condensate. It is clear that by compromising on steam usage, the stripper variant does not strip ammonia completely and is utilised only to direct the overhead steam with impurities mainly methanol and carbon dioxide back to the reforming process. It is observed again that increasing steam tonnage results in condensate carryover in the stripper overhead stream, the effect being prominent when the degree of superheat is higher (in the high pressure stripper).

It is also observed that the steam inlet temperature increases with an increase in operating pressure, i.e. stripping conditions become more severe. It is evident that ammonia and carbon dioxide must exist in strippable form as free ammonia and carbon dioxide for separation to take place. However under prevalent pH conditions of process condensate of around 9.2[4], these two impurities cannot exist in free form and combine to form ammonium bicarbonate salt which cannot be stripped using steam. It thus becomes obvious that a significant part of high enthalpy of steam is used to decompose ammonium bicarbonate. The decomposed ammonia is then difficult to strip due to its equilibrium solubility in water/steam.

This idea was further tested using a Gibbs reactor module in CHEMCAD using which the ammonium bicarbonate decomposition reaction was studied. The effect of pressure on decomposition temperature of ammonium bicarbonate is shown in Fig. 2. Pressure is observed to have an adverse effect on the decomposition of ammonium bicarbonate raising its decomposition temperature, even in the lower range of pressures. It is clear that stripper operating temperatures need to be maintained above the decomposition temperature of ammonium bicarbonate and subsequently explains the severity of stripping operation conditions for treatment of process condensate in existing ammonia plants.

The ammonium bicarbonate decomposition was further studied using the Gibbs reactor module. The temperature was varied at a constant pressure of 0.1 MPa (g) and the bicarbonate ion concentration as a NH_4HCO_3 feed concentration of 2300 ppm by weight was tracked in the simulation. This is presented in Fig. 3. It can be seen that at low pressures, even at 105 to 110°C, complete decomposition of ammonium bicarbonate occurs easily even with such high concentration. This supports the idea of operating strippers at lower pressures, thereby reducing severity of operation with maximum separation.

The simulation studies suggest that it is better to use a low pressure stripper with lower degree of superheat. Steam usage and degree of superheat can be optimised in existing strippers, more so in the case of low and medium stripper operation. However, operating conditions must be chosen above an optimum level in all three stripper variants so as not to have contaminant breakthrough in the recovered process condensate at the bottom of the stripper.

Conclusion

A comprehensive study on three stripper variants prevalent in existing fertilizer units indicated that operating the process condensate stripper at low pressures is a better option in terms of energy usage and would give complete separation of CO_2, CH_3OH and NH_3 from process condensate. Steam flow rate is found to have a strong influence on the separation of ammonia and methanol. With an increase in stripper operating pressure, the solubility of

Topsoe, Inc. – EX1003
Page 838 of 1210

Table 3. Effect of steam inlet flow rate on stripping of CO_2, NH_3 and CH_3OH (stripper pressure 0.3 MPa)

Steam flow rate (t/h)	Steam composition (ppm) CO_2	CH_3OH	NH_3	Condensate carryover (t/h) H_2O
6	0	97.0	2422	*
12	0	0.2	1882	*
18	0	0	1318	0.58
24	0	0	732	1.48
30	0	0	208	2.38
36	0	0	21	3.28
42	0	0	1.4	4.17

* Condensate carryover in overhead stream (t/h)

Table 4. Effect of steam inlet flow rate on stripping of CO_2, NH_3 and CH_3OH (stripper pressure 0.4 MPa)

Steam flow rate (t/h)	Steam composition (ppm) CO_2	CH_3OH	NH_3	Condensate carryover (t/h) H_2O
3	0	162	1929	
6	0	53	348	
9	0	1	2	
12	0	0	0	
15	0	0	0	

* Condensate carryover in overhead stream (t/h)

Table 5. Effect of steam inlet flow rate on stripping of CO_2, NH_3 and CH_3OH (stripper pressure 0.5 MPa)

Steam flow rate (t/h)	Steam composition (ppm) CO_2	CH_3OH	NH_3	Condensate carryover (t/h) H_2O
3	0	117	59	
5	0	36	0	
7	0	1	0	0.01
9	0	0	0	0.15
11	0	0	0	0.30

* Condensate carryover in overhead stream (t/h)

Fig. 2. Effect of pressure on decomposition temperature of ammonium bicarbonate

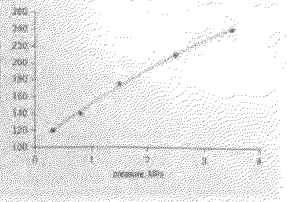
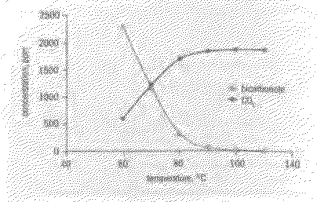


Fig. 3. Effect of temperature on bicarbonate ion concentration at 0.1 MPa pressure



ammonia in process condensate increases resulting in higher steam usage to counter the effect of solubility. Process condensate strippers can operate at any pressure provided the superheated steam inlet temperature is sufficient to decompose ammonium bicarbonate. The formation of ammonium bicarbonate in the process condensate under the prevailing pH conditions has implications on operating conditions of the stripper. There is a strong case for having a relook at high pressure steam stripping operation for treatment of process condensate.

Acknowledgements

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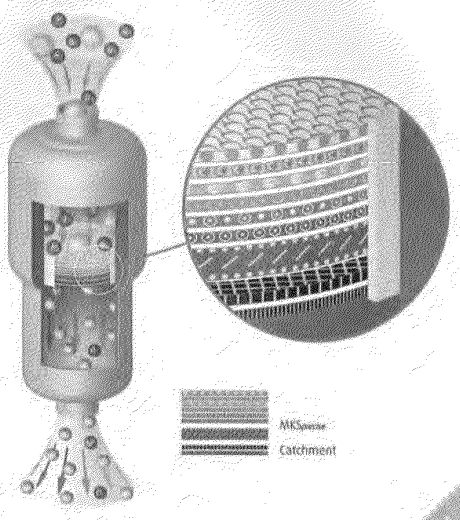
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New approach to secondary catalyst installation

Secondary N_2O abatement in nitric acid plants with high nitrogen loading can be challenging. **S.P. Roe** of Johnson Matthey Noble Metals reports on the development of a new design approach to secondary catalyst installation utilising axial radial technology. Following extensive development and testing a new system design is being fabricated for installation in 2012.

Industrial production of nitric acid uses the Ostwald process. The first stage of this process is the production of nitric oxide by oxidation of ammonia by reaction 1.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad (1)$$

This process is carried out in the presence of a catalyst (most commonly Pt based) with a range of temperatures and pressures according to plant design. The combination of reaction conditions and catalyst design can give a range of selectivity's for the oxidation process which is usually between 92 and 98%. The non-selective products are nitrogen and nitrous oxide according to the reactions 2-4 below:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \quad (2)$$

$$2NH_3 + 4O_2 \rightarrow N_2O + 3H_2O \quad (3)$$

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O \quad (4)$$

The extent of formation of these undesirable side reactions is dependent on the selectivity of the reaction. Yields of 93-98% are possible with good catalyst pack and plant designs.

Kyoto Protocol

The adoption of the Kyoto protocol in 1997 was seen as the first step towards a global reduction of world emissions and since the protocol came into effect in 2005 there have been developments to reduce "greenhouse gas" emissions driven either by trading opportunities or by local legislation.

Reaction 3 shows the formation of nitrous oxide (N_2O) which is recognised as a greenhouse gas with a global warming potential (GWP) of 310 when compared to CO_2. N_2O represents approximately 6% of the greenhouse gases that contribute to the worldwide anthropogenic climate change and N_2O emissions from nitric acid plants represents the largest single source of N_2O in the chemical industry contributing approximately 1.25 million tonnes of CO_2e per year. This has resulted in the development of technologies for the reduction of N_2O emissions from nitric acid plants.

N_2O abatement technology

The technologies for reducing the N_2O emitted as a result of nitric acid production is generally considered as one of three categories:

- **Primary** – development of the ammonia oxidation catalyst to minimise selectivity for the N_2O producing reaction.
- **Secondary** – decomposition of N_2O directly under the ammonia oxidation catalyst either catalytically or by increasing residence time at high temperature (>750°C) by increasing the volume of the vessel before gas cooling.
- **Tertiary** – removal of the N_2O in the tail gas train downstream of the absorption column.

This article focuses on developments in secondary catalytic decomposition.

Secondary abatement system

Johnson Matthey has been the market leader in development and supply of primary catalysts for the nitric acid industry and, through the acquisition of the former ICI Synetix business in 2002, experience in the design and operation of nitric acid plants. By virtue of this knowledge and experience it was realised that there would be a requirement for a range of catalyst forms to meet the demands of the diverse designs of nitric acid plants in existence. Development of an N_2O abatement catalyst for use in the "secondary" position was started in 1998 and led to the existing range of Amoxie products. In 2006 this range was expanded when Johnson Matthey signed an exclusive marketing agreement with Yara International ASA for the supply of their SK-Y1 series of catalysts.

System design

A secondary N_2O abatement installation as a retrofit to an existing plant needs consideration of both the process and the mechanical circumstances for the plant in question. Experiences in the development of the abatement catalysts highlighted that the parameters which can most significantly influence the performance of the system are the nitrogen loading and the burner design.

Whilst the impact of the loading on performance is obvious with respect to contact time with the catalyst, it has often been overlooked that the loading is proportional to the gas throughput and hence higher loading plants will result in a higher pressure drop across the abatement catalyst bed. This increased pressure drop results in increased risk of by-pass of the abatement catalyst bed. This can result in significant impacts on the N_2O abatement performance achieved either due to low residence times or localised increases in N_2O production from the oxidation catalyst due to flow effects.

The design of the reactor can also impact on the performance of the abatement system is several ways. Apart from the obvious restrictions that may be placed on the quantity of catalyst which can be installed, the design can also increase (or decrease) the risk of gas by-pass around the perimeter of the catalyst bed. The increased pressure drop from the abatement catalyst will exaggerate any minor issues caused by poor design, poor manufacturing or use of inappropriate or inferior materials for basket construction and installation (Fig. 1).

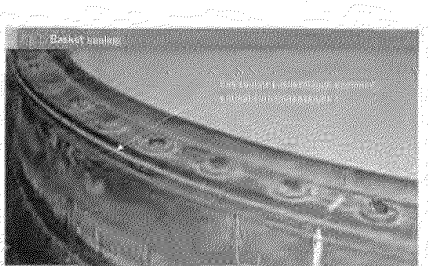


Fig. 1. Basket sealing



Fig. 2. Basket design with space for abatement catalyst bed



Fig. 3. No basket, severe space restriction

Modification of plant designs

Johnson Matthey has found that classification of plants by their loading followed by generic design typing allows ready assessment of the ease and potential cost of installing an abatement catalyst which will deliver optimum performance.

Low loading plants (typically <30 tN/m²/d).

These usually fall into one of three categories:

- **Category 1:** These are plants which will require little or no modification to allow the addition of adequate abatement catalyst to achieve the desired performance.
- **Category 2:** These are plants which have a generally sound basket design and allow space for an adequate bed to be installed (see Fig. 2).
- **Category 3:** These plants have no "basket" and as such no means of easily containing an abatement catalyst bed (see Fig. 3).

High loading plants (typically >30 tN/m²/d)

These plants typically pose two significant problems:

- the high pressure drop generated;
- severe restrictions on the space available for installing catalyst.

Johnson Matthey has a proprietary design of containment system which gives the optimum balance between the requirements for prevention of by-pass whilst also creating a space for the abatement catalyst bed which does not compromise the burner or heat exchanger design.

This system is not ideal as it requires detailed fine tuning to match each plants design in order to maximise the abatement performance which can be achieved.

Performance

Johnson Matthey and its partners have installed secondary catalyst in more than 60 plants worldwide. In low loading plants the performance is routinely >90% abatement (where there was space for adequate volumes of catalyst). The high loading plants are more challenging with abatement levels between 50% and 80% being achieved with only one plant operating >90%.

The data from these projects can be reviewed on the UNFCCC website: http://unfccc.int/.

Topsoe, Inc. – EX1003
Page 840 of 1210

stone to survive thermal expansion cycles during start-up and shutdown where the temperature rise can be >200°C/min, at times and the existence of temperature gradients in the region of 100°C per centimeter during start-up.

Axial-radial technology (ART)

The first design project to apply the established principles was a reactor producing 1320 t/d. The pivot design was such that the maximum allowable pressure drop for the abatement catalyst was 350 mbar in order to leave room for additional capacity.

Using the Topsoe approach, the worst flow maldistribution of ~30 % at exit and the expected abatement performance would be ~20%.

A 45° draft ART design was created based on a single annular ring. The height of the ring was limited by the space of the vessel below the ammonia oxidation catalyst and the required catalyst volume to be added at 80kg/ m² thus weight the bed was found to be the optimum design. The "acceleration" was such that the pressure drop reached the point first. This design would be expected to give an abatement performance of approximately 50%.

New design

Due to the issues on high loading plants, a new design approach was required.

The basic approach to secondary catalyst installation was to a flat bed in the reactor with the bed diameter being defined by the vessel and the bed depth by the height available for required catalyst bed depth is available height was greater than that required) as shown in Fig. 4.

To achieve the contact times required for high abatement levels in high loading plants, the depth of the catalyst bed is often such that it would cause severe operational difficulties (in some designs the pressure drop can exceed 1 bar). In order to reduce the pressure drop the contact bed area for the catalyst bed needed to be increased. It was realised that all current systems were applying an axial flow of gas through the catalyst bed and that the application of radial flow technology, as used in many ammonia processes, to this usually abatement process could provide a solution as indicated in Fig. 5.

The challenge was to develop such a system which could be retrofitted to existing economically and which could operate with a pressure drop not exceeding 1 bar. In addition it was required that all current plants were designed for axial flow and that the catalyst bed depth was limited by the vessel diameter. The basic approach to secondary catalyst installation was to a flat bed in the reactor with the bed diameter being defined by the vessel and the bed depth by the height available for required catalyst bed depth is available height was greater than that required) as shown in Fig. 4.

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removing the catalyst rings.

The original design used wire mesh baskets supported on a support ring welded to the vessel wall. A metal gasket was designed to support the load from the catalyst bed and the pressure drop.

However, the material properties of the wire mesh, combined with effects from absorbing the wire mesh to the ammonia oxidation catalyst, the stark-up and shut-down thermal expansion and contraction. This resulted in mechanical damage to the mesh of the containment and to the edges of the catalyst rings.

These issues have been resolve by changing the design to use "V" wire across the wide. This across also to the system. In addition the number of rings for this design has been increased to 5 ft. 9i. Three changes have allowed the weight of material to be increased to 250 kg/ meter (~15lb/in). Gas system was installed in Decem- ber 2011 and the initial performance was ~305% abatement. However, after several thermal cycles, deficiencies were revealed in the mechanical containment of the rings.

It was then declared that the design would require the installation of multiple rings to allow the catalyst bed surface area and volume to be maintained to allow high abatement performance and achieve the desired pressure drop.

The use of a three ring system (Fig. 6) allowed the installation of 200 kg of cata- lyst whilst reducing the pressure drop from the abatement catalyst to 150 mbar.

CFD modelling was used to check the distribution of gas flow through the rings. (Figs 7 and 8) the relative gas flow through the rings and the flow impact on the removal oxidation the flow impact on the removal oxidation catalyst above.

These studies showed that the flow pattern through the ammonia oxidation catalyst was influenced minimally provided there was an appropriate gap between the top of the abatement catalyst rings and the bottom of the oxidation catalyst (typically ~15mm).

Gas system was installed in Decem- ber 2011 and the initial performance was ~305% abatement. However, after several thermal cycles, deficiencies were revealed in the mechanical containment of the rings.

This system is being fabricated and installation is expected in the first half of 2012.

Topsoe, Inc. – EX1003
Page 841 of 1210

Combating corrosion in cooler condensers

The tube-sheet and the inlet of the tubes of the cooler condenser in nitric acid plants are often subject to corrosion. As the bulk gas temperature is much higher than the surface temperature of the tube-sheet and the inlet of the tubes, condensation and reboiling of acid takes place resulting in corrosion. Even when using special materials the lifetime of the cooler condenser is often limited. In this article, Sandvik Materials Technology, ATI Wah Chang and Yara report on their experiences and solutions to this common corrosion problem in nitric acid plants.

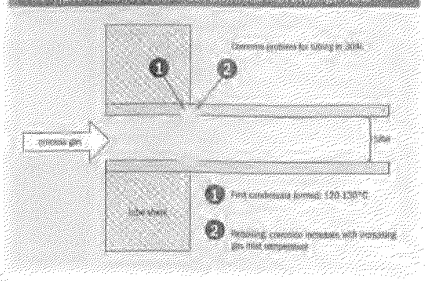
Most of the nitric acid produced worldwide is manufactured by the oxidation of ammonia over a platinum catalyst (gauze) to form nitric acid and water. During the production of nitric acid, conditions in the cooler condensers generally range in the 50-60% concentration range at temperatures exceeding the boiling point.

Nitric acid is a strong mineral acid and is highly corrosive to stainless steel if the temperature or concentration is sufficiently high. Fortunately, the inexpensive stainless steel 304L has very good general corrosion properties in weak nitric acid production. However, in heat exchangers like cooler/condensers, tail gas preheaters and boiler feed water heaters 304L has a tendency towards corrosion. When hot NO_2 gas condenses local corrosion on 304L is very common.

The following case describes the problem when the hot gas is on the tube side and cooling water (typically 20-30°C) is on the shell side. When the hot NO_2 gases hits the cool tube wall, the gas condenses and causes localised intergranular corrosion. The corrosion pattern is very typical and easy to identify once the tube has been removed (Fig 1).

In some condensers the hot gas is in the shell side and the cooling water is on the tube side, in this case localised corrosion appears on the shell side of the tubing. The corrosion attack is not localised as in Figs 1 and 2, but spread out over a larger area. Again, the inlet area is where the corrosion rate is highest.

Fig 1 Typical location of localised corrosion inside hot exchanger tubes



Materials for nitric acid

Sometimes it is sufficient to replace the upper rows of tubing with a stainless steel alloy, such as Sandvik 2RE10 (UNS 31002), to increase the service life of the heat exchanger. Sandvik 2RE10 has been developed for use in hot nitric acid. The iso corrosion diagram in Fig. 3 shows that at 65% concentration Sandvik 2RE10 can be used at about 25°C higher temperature than 304L (Sandvik 3R12).

In most cases the tube sheets in 304L have not corroded, which means that the heat exchanger can be simply re-tubed with new tubes in 2RE10. This is a cost saving solution as it can be done on site to minimise down time. Tubesheets in 2RE10 are available, however an alternative, Sandvik 2RE69 UNS 31050, is more readily available. 2RE69 is very similar to 2RE10 except it contains 2.1 % Mo, which is normally regarded as reducing the corrosion resistance. As the same corrosion rate in the ASTM 262 C (huey testing) maximum 0.12 mm/year is also guaranteed for both 2RE10 and 2RE69 the difference is not great. This test is carried out in boiling (120°C) nitric acid at 65%, which means it a good test for applications in nitric acid. When a German customer insisted on 15 times 48 hours testing cycles instead of the normal 5 x 48 hours, despite the extended testing period, test results showed no increased corrosion rate on 2RE10. This was a clear demonstration of the strong performance of 2RE10 in nitric acid.

Welding and all types of heating procedures increase the risk of intergrandular corrosion when the material is exposed to acids like nitric acid. In Fig. 4 samples of 304L and 2RE10 have been heat at 675°C for up to 100 hours before testing in nitric acid. The corrosion rate for 2RE10 is barely affected by the heating. This means corrosion properties are excellent for 2RE10. Matching welding electrodes Sandvik 25.22.L are available to produce a good quality weld with best possible corrosion properties.

There are several cases where 304L tubing has had a service life shorter than 1-2 years and the change to Sandvik 2RE10 has resulted in a service life well over 7 years. If the service condition is too severe for 2RE10, then it might be better to use Zirconium 702, which can handle nitric acid up 70% up to 200°C. The cost is substantially higher for zirconium, especially in a market with tight supply of zirconium.

Duplex stainless steel is often seen as very cost effective material but nearly all duplex grades have been developed for best possible resistance to pitting corrosion due to presence of chlorides. This is an environment that is far apart from the production of nitric acid. SAF2304 with 23%Cr and low Mo performs better than 304L but the corrosion resistance can't match 2RE10. For concentrations above 90% silicon alloyed stainless steel materials should be used like Sandvik 5X.

Alloys referred to as 310L should not be mixed up with 2RE10, as 310L is not a ASTM designation and 310 designation means a high temperature material with a high carbon content. Instead UNS S31002 can be specified, since it is based on 2RE10 composition for service in nitric acid.

Zirconium in nitric acid cooler condensers

Zirconium has been used in nitric acid service for over 30 years. Zirconium can be used in nitric acid from the lowest concentrations to those concentrations approaching 99% at temperatures well over the boiling point.

When zirconium was being considered for use in nitric acid cooler condensers, a series of laboratory tests were conducted by the ATI Wah Chang corrosion laboratory. These tests were conducted at the 50% and 65% nitric acid concentrations at temperatures from 120°C to 204°C. The common stainless alloys currently used in nitric acid cooler condenser tubing were compared with zirconium grade 702 in both the welded and non-welded condition. Table 1 shows the results of this testing.

Since the late 1990s, Zirconium has been specified as a material of construction for use in the cooler condenser equipment by Weatherly, Inc of Atlanta, Georgia, a subsidiary of Chematur International. The cooler condenser conditions were found to be extremely corrosive to the available stainless steels and titanium in the Weatherly mono-pressure nitric acid process.

Weatherly, Inc. has designed and built nitric acid plants since 1959. The process design for the production of nitric acid was developed with the philosophy of low capital cost, high ammonia conversion, low catalyst cost, low maintenance cost, and with high efficiency. This high pressure, mono-pressure design is cost competitive with the dual pressure process.

Over the years, Weatherly has, in stages, increased the operating pressure of the nitric acid plant to improve the efficiency and help to minimise the capital investment. Although other construction materials, such as 430SS, 329SS, 310L SS and titanium, have been used in the Weatherly process, Zircadyne® zirconium grade 702 tubing has shown excellent corrosion resistance to this nitric acid environment. Many of the zirconium heat exchangers have exceeded a service life of over 20 years. Since Weatherly specified zirconium for the cooler condenser equipment in 1987, over 20 new plant sites have utilised zirconium for their nitric acid production process and many Weatherly nitric acid plants built before 1987 have retrofitted zirconium cooler condensers.

Elliott Industries of Port Coquitlam, BC, Canada is a fabricator that has been involved in many of these cooler condenser fabrications. Elliott Industries has been fabricating heat exchangers for the nitric acid industry for over 20 years, beginning with a cooler condenser that was built for Esso Chemical of Redwater, Alberta, Canada

Fig 2 Intergranular corrosion attack has penetrated the tube wall

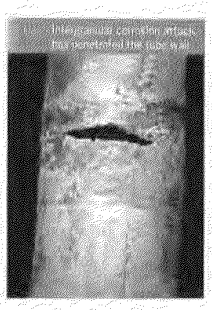
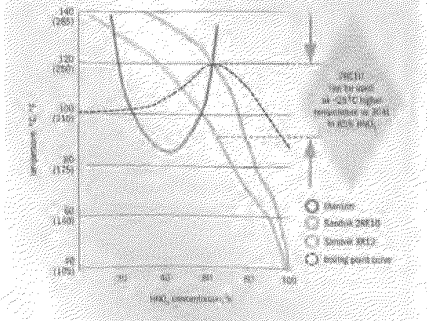


Fig 4 Nitric Acid corrosion rate: 0.2 mm/long line lines



Topsoe, Inc. – EX1003
Page 842 of 1210

in 1989. This nitric acid plant is now the Agrium Redwater Nitrogen operation. This particular cooler condenser was 88" in diameter and contained almost 2500 tubes, 18ft in length. This heat exchanger utilised zirconium clad stainless steel tube sheets. At the time these were the largest Zr/stainless steel tubesheets ever produced. Since then, Elliott Industries has fabricated a further 27 cooler condensers from zirconium materials for the nitric acid industry.

Fabrication of heat exchangers

The initial step in the fabrication of heat exchangers is the design process. Most heat exchangers utilise ASME Section VIII, Div. 1 construction and TEMA standards. It is essential that all process conditions be known during the initial design to ensure optimum operation of the vessel. Factors to consider when designing a zirconium heat exchanger include the design fluid flow rates, imposed mechanical external loads and thermal design/rating requirements. Thin wall zirconium tubes have a higher propensity to vibrate than stainless steel tubes used in similar applications. Thorough vibration analysis is critical. Zirconium's low modulus of elasticity will also require that enhanced baffle support be utilized as compared to higher modulus materials such as the stainless steel alloys. These heat exchangers must also use an expansion element to accommodate the low thermal expansion coefficient of Zr702 tubes as compared to the carbon or stainless steel shell. During this initial design other considerations that must be taken into account are the tube to tubesheet joint design, welder qualifications and procedures, cleaning procedures, and non-destructive testing of the tube joints.

Because zirconium is soft and contamination is very detrimental to weld quality and corrosion resistance, every effort should be made to protect zirconium surfaces from embedded foreign particles and surface damage during the fabrication process. The later steps in the heat exchanger fabrication process will include the final cleaning, inspection and non-destructive testing. The heat exchanger will then be packaged and supported for transportation to the chemical plant. Due to zirconium's low modulus if elasticity, it is critical that all zirconium nozzles, bleeds, drains, vents, branch connections, etc. be well supported during transportation to help ensure that cracking does not occur.

Fig. 1. Corrosion test in HNO_3 samples heated at 675°C (1pt) to 100 hours

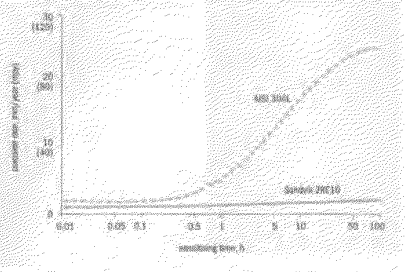


Table 1. Results of corrosion testing in nitric acid

Material	Acid conc. %	Temperature °C	Average corrosion rate mm/yr
Carpenter 7-Mo[1]	65	120	0.31
Carpenter 7-Mo[1]	65	149	12.2
Carpenter 7-Mo[1]	65	204	92.4
Carpenter 7-Mo[1] Plus	65	120	0.23
Sandvik RE10[2]	50	220	62.7
Sandvik RE10[2]	65	120	0.2
Sandvik RE10[2]	65	149	2.2
Sandvik RE10[2]	65	204	27
VDM 2521 LC[3]	65	120	1.7
VDM 2521 LC[3]	65	149	10.4
VDM 2521 LC[3]	65	204	193
VDM 2522 LCN[3]	65	120	1.78
VDM 2522 LCN[3]	65	149	17.7
VDM 2522 LCN[3]	65	204	318.5
Zircadyne® 702[4]	65	120	0
Zircadyne® 702[4] (welded)	65	120	0
Zircadyne® 702[4]	65	204	0
Zircadyne® 702[4] (welded)	65	204	0

[1]Trademark of Carpenter, [2]Trademark of Sandvik, [3]Trademark of VDM, [4]Trademark of ATI Properties, Inc.

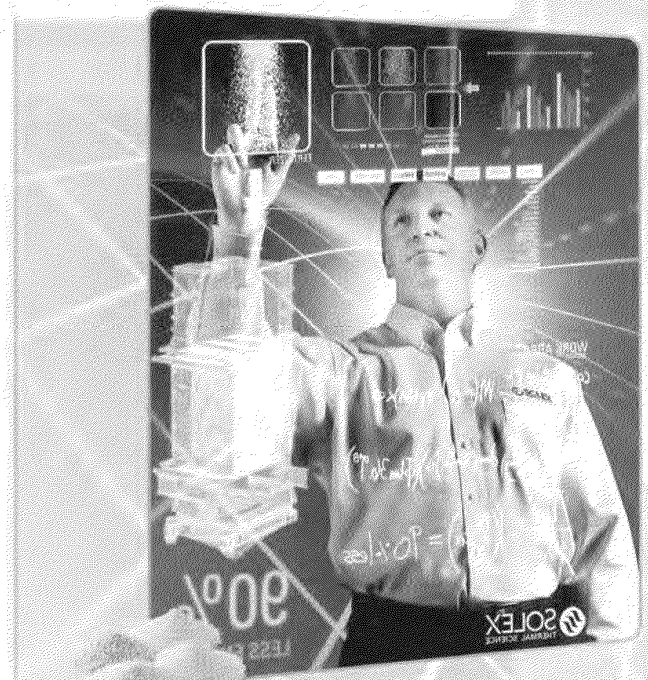
New cooler condenser design from Yara

Without the use of expensive materials, the lifetime of the cooler condenser in nitric acid plants is often limited. As the bulk gas temperature is much higher than the surface temperature of the tubesheet and the first part of the tubes, condensation and reboiling of acid takes place resulting in corrosion. Yara has investigated this problem and found that by keeping the temperature of the tubesheet and the tubes at the inlet above the dew-point of the NOx gases and taking care that the temperature difference between the bulk gas and the metal surface remains relatively low, excessive reboiling can be avoided and consequently the corrosion will be significantly reduced, resulting in a significantly longer life time. A possible advantage may be the use of lower alloyed materials for the tubes and the tubesheets.

To keep the metal surface temperature of the tubesheet at the gas inlet of the cooler condenser above the dew-point it is necessary to increase the cooling water temperature at that point. This can be done by splitting the cooling water streams of the cooler condenser to get a hot part and a cold part on the cooling water side.

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Fig. 5: New low pressure cooler condenser design at Sluiskil NA7

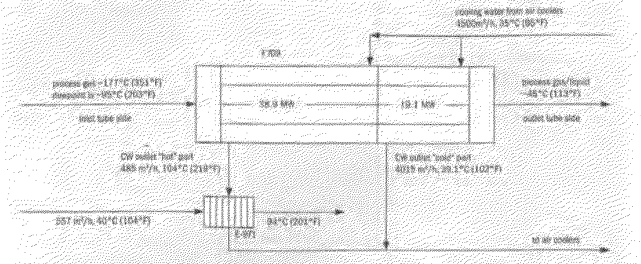
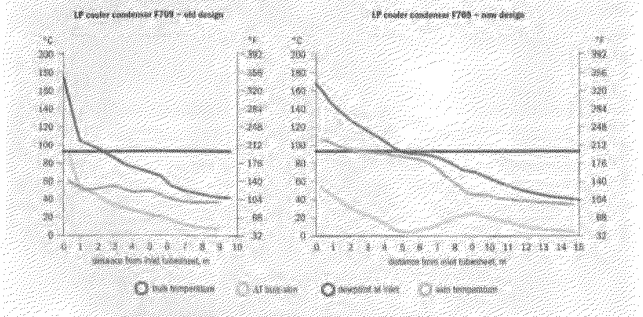


Fig. 6: F709 old and current operating conditions



Cooling water is introduced counter-current with the process gas in the cooler-condenser. The main part of the cooling water leaves the cooler-condenser at lower temperature in the middle of the shell. A small stream of cooling-water flows further to the tubesheet at the outlet end is heated to a temperature above the dew-point of the incoming process gas. This design is currently being developed for the high pressure condenser in Sluiskil NA6.

Another way to split the cooler condenser into a hot and cold part is by installing an intermediate tubesheet and by having two separate cooling water compartments where the cooling water enters both compartments separately and leaves the compartments separately. The cooling water at the outlet of the hot part can be used as a heating source for e.g. district heating or greenhouses. This is already in place and is proven technology within Yara for the low pressure condenser in Sluiskil NA7. First inspections have shown no corrosion whatsoever (101 tubes have been checked with eddy current).

Both designs can be applied for low pressure and high pressure in horizontal and vertical position.

Sluiskil NA7

Yara Sluiskil nitric acid plant 7 (Sluiskil NA7) is a Grande Paroisse dual pressure plant with a nameplate capacity of 1,500 t/d and a current capacity ~2,200 t/d that started up in 1986. The original low pressure cooler condenser F709 at Sluiskil NA7 was a horizontal tube-side cooler condenser with disc and donut baffles. The cooler condenser had 3,200 titanium tubes, 10 m in length, 0.9 mm thick and a titanium cladded AISI304L tubesheet.

Leakages of the low pressure cooler condenser F709 were first discovered at the beginning of 2000. All tubes showed an internal ring of corrosion at the back of the tubesheet, several tubes were plugged, 0.5 mm corrosion was discovered along with problems of cladding and corrosion of the Ti / AISI304L connection.

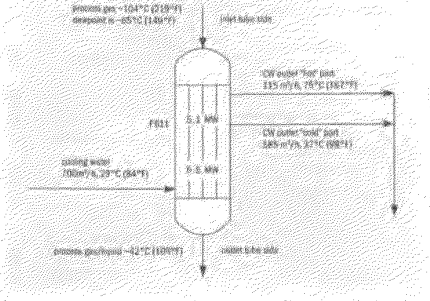
During a longer outage in 2009, F709 was sent to the workshop, tubes were shortened by 1.5 m, the tubesheet was relocated and the cladding restored. The exchanger lasted for another nine years before thinning tubes made replacement necessary.

In 2006 the site decided to participate in the delivery of heat and CO_2 to a greenhouse project.

Low temperature heat is a suitable source and a study was carried out in 2006 to investigate whether heat could be supplied to greenhouses from the cooler condenser. Heat duty of 58 MW from the low pressure cooler condenser was being dissipated to air via air coolers. The study revealed that 30 MW of heat from the cooler condenser could be sent to the greenhouses by using sensible and latent heat up to a certain point. The initial idea was to use one new cooler condenser plus the existing F709 cooler condenser in series. The challenge was to remove the formed weak acid between both exchangers.

The final design for cooler condenser F709 was a shell divided by an intermediate tube sheet in the hot and cold part. The hot part has a small flow of cooling water and the cold part has a large flow of cooling water. The diameter of the exchanger is 2.8 m and comprises 3,770 tubes, tube length 15 m, tube material 2RE10, diameter and thickness 25.8 x 1.65 mm, tubesheet at inlet AISI304L (1.4307) with weld overlay. The cooler condenser was installed in 2009 (see Fig. 5). Operating conditions for the old and new cooler condenser are shown in Fig. 6.

Fig. 7: New design for a high pressure cooler condenser at Sluiskil NA6



The recovery of waste heat for district heating or heating greenhouses increases the energy efficiency significantly and lowers the carbon footprint of nitric acid plants. In new nitric acid plant designs, this heat could also be used for (pre-)heating boiler feed water and/or tail gas and boost energy efficiency.

Sluiskil NA6

Yara Sluiskil nitric acid plant 6 (Sluiskil NA6), is a Grande Paroisse dual pressure plant with a nameplate capacity of 1,250 t/d and a current capacity of ~1,900 t/d that started up in 1977. The original high pressure cooler condenser F611 at Sluiskil NA6 was a vertical tube side cooler condenser with disc and donut baffles. The cooler condenser had 1,605 tubes, 4,225 m length, diameter and thickness 25 x 1.5 mm, material 304L (1.4306). The tubesheet material was 304L (1.4306).

In 1992 the cooler condenser was turned by 180° because of corrosion of the inlet tubesheet along the outer diameter and 69 tubes were plugged. F611 was partly retubed in the workshop in 2001 and was subsequently replaced with a new one in 2002. The new cooler condenser had 1,885 tubes, 5.182 m length, diameter and thickness 25 x 1.5 mm, material A213/Tp304L, tubesheet material A240/Tp304L. In 2009 the thickness of the tubes just behind the tubesheet had reduced by 0.7 mm. The exchanger was turned by 180°C and several tubes were plugged.

Discussions took place with a mechanical engineer about how to prevent reboiling of acid at the tube sheet. Inspired by F709 design from 2009, a design was developed that was simpler and with no need for a separated cooling water loop. The current operating conditions are:

- Process gas inlet 95°C, outlet 47°C.
- Dew point at inlet ~ 65°C
- CW inlet 29°C, outlet ±2°C

The final design has a hot and cold part without an intermediate tube sheet. No reboiling is expected. Tube characteristics are: tube length 7.6 m, tube material AISI 304L (2RE10 was evaluated, but operational conditions allow 304L), number of tubes increased to compensate for pressure drop. Support on the absorption tower is reinforced. The new design cooler condenser (see Fig. 7) is under construction with installation expected after 2011. Despite the bigger exchanger and piping, modifications the cost is lower for AISI 304L compared to the replacement of the current exchanger in 2RE10.

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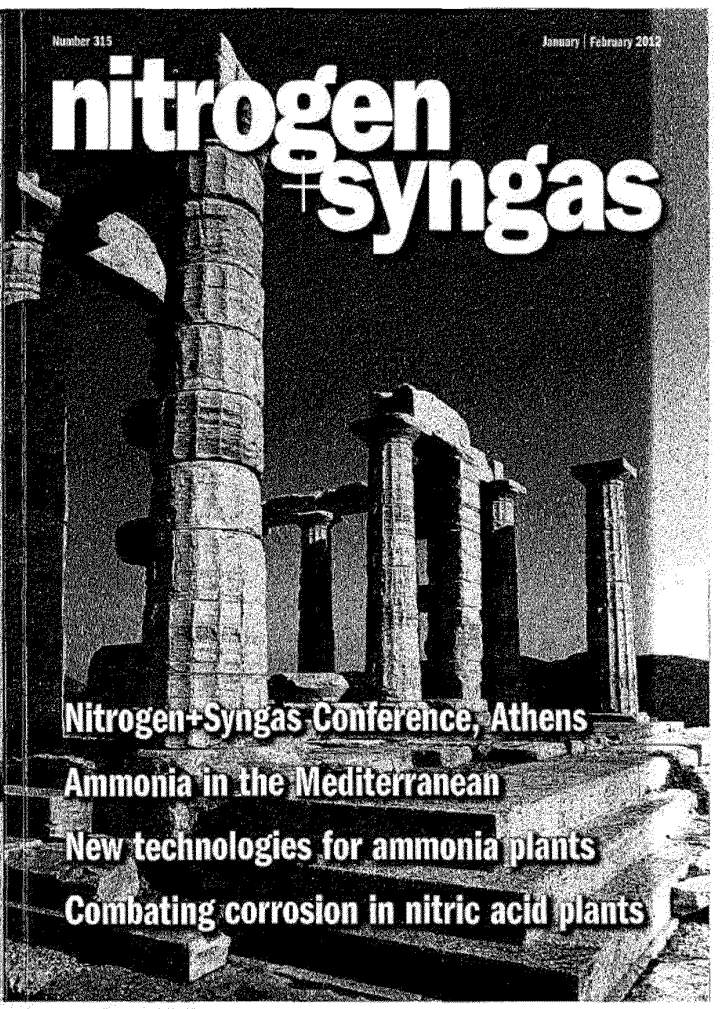
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New technologies for ammonia plants

Research and development continues to yield novel concepts for ammonia production and some of these are now ready for their first commercial application. In this article, we report on new technologies and process enhancements from Ammonia Casale, Haldor Topsøe and KBR.

Casale ammonia plant design

Casale's policy has long been based upon the development and application of new advanced technologies to get the best improvements in ammonia plant performance in terms of energy consumption, capacity, or a combination of the two.

Many articles have been written on Casale technologies for plant revamping, whose application can lead to a capacity increase of 50% or more, and a significant energy saving. For this reason, this article presents the new technologies developed by Casale for new ammonia plants only.

Casale advanced ammonia-urea process

Through the continuous development of its technologies, Casale has developed innovative processes for world-scale ammonia and urea grass-roots plants at conventional capacities and is now in the unique position of owning proprietary technologies for the design of ammonia-urea grass-roots plants.

Having designed and built two grass-roots ammonia plants according to the Casale advanced ammonia process and one grass roots urea plant according to the Split Flow Loop™ urea process, Casale is ready to offer the Casale advanced ammonia-urea process for the design of a combined and fully integrated ammonia-urea fertilizer complex featuring very low energy consumption.

The ammonia and urea plants are designed to be best integrated, with optimised exchanges of energy and materials. In practice this translates in an overall consumption per tonne of urea of only 4.6 Gcal/tonne, including feed and fuel, electricity and utilities (Fig. 1). This result has been obtained by integrating the steam balance of the two plants in such a way that there is no export of steam from the ammonia-urea complex and the import of electric power is 0.025 kW/tonne urea.

Steam consumption of the urea plant is completely fulfilled by export of HP and MP steam (HP for the CO_2 compressor and MP as process steam) from the ammonia plant, while there is no back export of LP steam from urea to ammonia. The CO_2 production is balanced with ammonia production with a slight excess of air in the secondary reformer and by burning a small amount of synthesis gas as fuel upstream of the methanator. Necessary electric power is produced in two expanders in the ammonia plant.

The high efficiency of the Casale ammonia-urea advanced process, makes it possible to reduce, for a given capacity, the size of the equipment and, therefore, to build a plant with lower investment costs.

In addition, the Casale ammonia-urea process has been designed to minimise the environmental impact. In fact, the only liquid wastes are the boiler blow down, the air compressor inter stage coolers condensate and the urea process condensate.

The boiler blow down, after flashing and cooling, is used as cooling water make-up for the cooling water loop. The same for the air compressor inter stage condensate, which is returned to the cooling water return header. The process condensate from the urea plant is, as described above returned clean as boiler feed water.

The only gaseous wastes are the flue gas from the primary reformer, the inerts from the urea plant and the air exhaust from the prilling tower. The flue gas from the primary reformer contains less than 110 mg/Nm³ of NOx. The guaranteed figure of NOx is lower than the figure required by the European Community for new plants (140 mg/Nm³ calculated at 3% oxygen excess). The ammonia content in the other gaseous waste can be kept below the allowable emission levels.

Casale advanced ammonia process

The main features of the Casale advanced ammonia process are:

- high efficiency design for the secondary reformer;
- axial-radial technology for the shift conversion;
- ejector ammonia wash process;
- axial-radial technology for the ammonia converter;
- advanced waste heat boiler design in the synthesis loop;
- coupling of converter and downstream exchangers;
- low temperature heat recovery;
- hydrogen recovery unit.

Most of this equipment and these technologies were first applied in revamping projects, allowing performance improvement, before being installed in Casale grass-roots plants.

Ammonia process performance and implementation

Thanks to the features listed above, the Casale ammonia process offers:

- Steam to carbon ratio (referred to NG stream only): 2.9
- CO slip from LTS: less than 0.3% vol. (dry base, EOR)
- CO_2 slip from absorber: less than 900 ppm vol.
- Ammonia loop pressure: 140-180 bar
- Ammonia conversion: about 21 %
- Very low total energy consumptions (evaluated as feeds + fuel + electricity and steam export to urea) of less than 6.5 GCal/tonne of produced ammonia.

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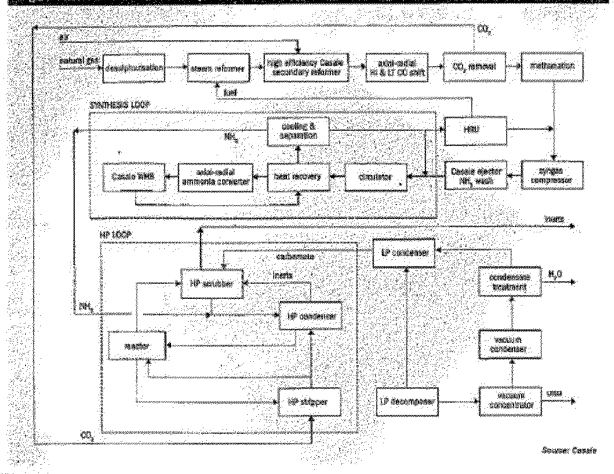
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Fig 1: Casale advanced ammonia-urea process



Source: Casale

The Casale advanced ammonia process is currently operating in a 2,050 t/d plant in Iran operated by Razi Petrochemical Company. The new plant, which was designed by Casale and built by the Iranian contractor Pidec, has been in operation since the beginning of 2008.

A second 2,050 t/d ammonia plant is under advanced implementation in Iran to be built for Shiraz Petrochemical Company. More recently, Casale has been awarded with three more contracts for the design of three new 2,050 t/d ammonia plants in various locations in Iran.

Casale Split Flow Loop™ urea process

The Casale Split Flow Loop™ process for grass-roots urea plants is an improved CO_2 stripping process in which urea is formed in a reactor fitted with high efficiency trays. The solution from the reactor is first treated in a stripper, operating at the same pressure as the reactor, using steam and the feed CO_2 as stripping agent. Here most of the unreacted NH_3 and CO_2 are recovered decomposing the carbamate. About one third of the unreacted NH_3 and CO_2 recovered in the stripper is sent directly to the reactor, while the remaining two thirds are recycled back to the reactor through the HP carbamate condenser (HPCC) to which the ammonia feed is directed. The HPCC is practically a total condenser of the submerged type. The stream of inerts leaving the HP carbamate condenser is then sent straight to the HP scrubber, bypassing the reactor.

The HP scrubber recovers NH_3 and CO_2 from the inerts streams leaving the HPCC and the reactor using the carbamate flow coming form the LP recovery section. The carbamate flow coming from the HP scrubber is sent to the HPCC, to enhance the condensation, using an ejector driven by the ammonia feed, which is also sent to the HPCC.

From the stripper, the urea solution, still containing a certain amount of unreacted NH_3 and CO_2 in the form of carbamate, is sent to a low-pressure single decomposition/condensation stage where practically all the remaining unreacted NH_3 and CO_2 is recovered in the form of a carbamate solution. The urea-water solution, containing only small quantities of NH_3 and CO_2, is then further treated in a two-stage vacuum evaporation section to obtain a urea melt for the prilling tower.

The process condensate, obtained from the vacuum condensers is purified in two stripping columns and one hydrolyser to eliminate all of its urea, NH_3 and CO_2 content.

The carbamate solution obtained in the LP section is sent to the HP scrubber where the inerts leaving the HP loop are washed.

The object of the Split Flow Loop™ process concept is to exclude as far as possible the inert contaminants present in the CO_2 feedstock from the synthesis reactor in order to minimise their adverse effect on CO_2 conversion. As described above, this is accomplished by splitting the gas flow from the HP stripper so that only a minor portion is sent directly to the reactor, which thus operates with the lowest possible concentration of inerts. The remainder is routed to the HP carbamate condenser, where its NH_3 and CO_2 content is separated from the inerts as ammonium carbamate solution, which is recycled to the reactor. A high-efficiency submerged condenser is used to cope with this duty.

The advantages of operating the synthesis section with very low inerts content are:

- high CO_2 conversion in the reactor (up to 63-64%);
- high stripping efficiency;
- high condensation efficiency.

Split Flow Loop™ process performance

The Split Flow Loop™ process can achieve the following performance:

- 63.5% CO_2 conversion in the reactor;
- 82% stripping efficiency;
- production of LP steam up to 5 bars;
- 450 kg/t specific carbamate recycle rate;
- 770 kg/t MP steam consumption (22 bar, superheated);
- Almost stoichiometric raw material consumption.

A Split-Flow-Loop™ urea plant has been operating in Ukraine since 2003 and is producing 1,500 t/d of urea. In the last couple of years two more Split Flow Loop™ urea process plants have come into operation, producing up to 2,300 t/d. Casale has also recently designed one grass-roots Split Flow Loop™ urea plant process that has been built in France.

Casale-Lurgi mega-ammonia process

Several years ago, engineers from Lurgi and Ammonia Casale analysed the conventional ammonia process with a view to doubling the size of ammonia plants on offer. They concluded that conventional technology suffers certain limitations when capacities in the range of 4,000 t/d or larger are contemplated. As a result, a new process was proposed that was considered to be both economically attractive and bankable. The new process was named MEGAMMONIA® and is now offered by Casale. It is based on the combined experience of both companies. Interest in the process is growing as larger capacity plants are being considered by the market.

The MEGAMMONIA® process comprises five principal units (see Fig. 2):

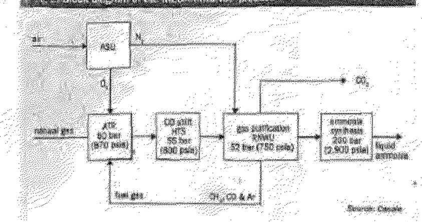
- air separation unit (ASU);
- catalytic partial oxidation unit (ATR);
- CO-Shift unit;
- gas purification unit;
- ammonia synthesis unit.

The separation of air into its components, oxygen and nitrogen, is a well known, and widely practised process. For the MEGAMMONIA® process an ASU produces a gaseous stream of 95% pure oxygen for use in the autothermal reformer, and a stream of 99.99% pure nitrogen for use in the gas purification unit.

In the catalytic partial oxidation unit feedstock, natural gas is preheated and desulphurised in the conventional manner over a cobalt molybdenum catalyst followed by zinc oxide. The desulphurised gas is then saturated using condensate recycled from the CO shift unit, preheated in a fired heater and pre-reformed over

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Fig 2: Block diagram of the MEGAMMONIA® process



Source: Casale

a nickel oxide catalyst so as to convert all higher hydrocarbons to hydrogen and methane. Steam is added to the pre-reformed gas to adjust the steam to carbon ratio, the gas is further preheated in the fired heater, and then reformed to CO, H_2 and CO_2 in the ATR by partial oxidation with oxygen. A nickel oxide catalyst located in the ATR vessel further assists reforming. The resulting hot reformed gas is cooled to a temperature to suit the downstream CO shift unit in a process gas boiler raising high-pressure steam for use in driving the major rotating machines. The absence of a pressure limiting steam reformer makes it feasible to raise the pressure of the ATR to 60 bar (870 psia).

Within the CO shift unit, the reformed gas is passed over two beds in series of conventional HT catalyst to convert the remaining CO to H_2 and CO_2. As the volume of catalyst required is considerable, each bed is arranged in axial-radial configuration so as to minimise catalyst volume, pressure drop and vessel diameter. The gas is then cooled to ambient temperature. The condensate arising is separated from the gas and recycled to the saturator in the ATR.

Gas purification is accomplished in two wash columns, the first removing CO_2 and the second removing the remaining impurities; namely CO, CH_4 and Ar. CO_2 is removed by absorption in cold methanol by the well known Rectisol® process. CO, CH_4 and Ar are removed by washing the gas with liquid. The CO_2 is recovered from the cold methanol by reducing the pressure to near atmospheric, and the recovered gas is sufficiently pure for use in the synthesis of urea. The recovered impurities, CO, CH_4 and Ar are recycled to the ATR for use as fuel in the fired heater. Refrigeration for the Rectisol® process is provided by ammonia supplied from the ammonia synthesis unit. Pure synthesis gas, comprising H_2 and N_2 in the correct stoichiometric proportion, is passed to the ammonia synthesis unit.

The ammonia synthesis unit is of conventional design. The synthesis of ammonia from H_2 and N_2 is carried out over an iron based catalyst at high pressure provided by a syngas compressor. The ammonia converter is of the most advanced axial-radial design by Ammonia Casale. Synthesis is carried out by passing the gas over three inter-cooled adiabatic beds of catalyst in series. The heat of reaction is recovered by a loop boiler, and by a boiler feed water pre-heater. Heat is conserved by heat exchange between feed and effluent streams to and from the converter. Synthesised ammonia is removed from the synthesis loop, in the conventional manner, by condensing the ammonia against low pressure boiling ammonia and by separating the liquid from the unreacted synthesis gas. The pressure of the liquid is reduced in several stages and unreacted gases are recycled to the syngas compressor. The extremely high purity of the ammonia syngas results in higher conversion of gas per pass, lower circulator duty, lower refrigeration duty, and generally smaller equipment throughout the loop.

A refrigeration compressor in the ammonia synthesis unit raises the pressure of gaseous ammonia to a level at which it can be liquefied against cooling water, thereby providing a means of refrigerating the synthesis loop and the Rectisol® process.

Owing to the absence of impurities from the ammonia syngas, the synthesis loop needs no purge, nor purge gas treatment system. Pure ammonia is stored as a liquid in atmospheric pressure storage tanks.

Energy consumption for this process is estimated to be 6.5-6.7 Gcal/t ammonia, based on the lower heating value of a representative natural gas. The range given covers the supply of warm ammonia to a downstream urea plant, or the storage of cold ammonia in an atmospheric pressure tank. This energy consumption includes the power required for the process, the ASU, and all its utilities, inclusive of natural gas compressor, sweet water and sea water cooling systems, and a water treatment plant. The import of electricity is not required other than to start the plant.

Advantages of the MEGAMMONIA® process include:

- Lower investment cost compared to a scaled up version of conventional technology at a size of 4,000 t/d;
- Reduced operating cost due to fewer unit operations and fewer catalytic steps;
- Lower CO_2 and NO_x emissions;
- Increased urea production – the recoverable CO_2 from MEGAMMONIA® will be sufficient to convert all of the ammonia produced to urea, compared to the conventional ammonia process, which uses a steam reformer and is always short of CO_2.

New technologies from Haldor Topsøe

Haldor Topsøe offers several new features to improve the energy savings and flexibility of ammonia plants including:

- New developments that enable production at unheard low S/C ratios – resulting in lower specific energy consumption with no additional investment cost;
- HTER, revamp of existing plants, steam balance optimisation, smaller SMR reformer;
- Post ammonia converter as revamp feature;
- Reformer refractory coating for increased efficiency and capacity.

Significant energy savings

A common understanding of how steam to carbon (S/C) ratio is related to energy consumption in an ammonia plant, is the higher the S/C ratio, the higher the energy consumption. In modern ammonia plants, the limiting factor determining how low the S/C can be designed is the existing high temperature CO shift (HTS) catalyst. The normal S/C ratio in todays ammonia plants is approximately 3.0. New developments within the area of HTS conversion enables Topsøe to design with S/C at 2.4 while still keeping the required heat input to the CO_2 removal section. This makes it possible to achieve an energy saving of close to 0.1 Gcal/t ammonia. Normally, energy consumption in the ammonia plant is reduced by lowering the losses, which requires larger and/or more equipment such as reactors and heat exchangers which will typically increase the plant cost. For new plant designs, the latest developments enable reduction of the energy consumption without additional investment cost.

HTER

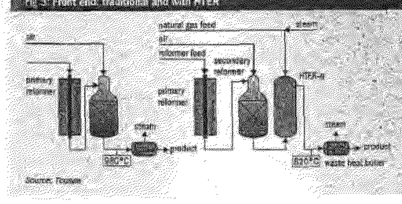
Various options are available for a capacity increase in the front-end of an ammonia complex. Of these, convective gas heated reforming stands out as an attractive option from both a technical as well as a cost effective perspective. The Haldor Topsøe Exchange Reformer (HTER) technology is a proven revamp option where a capacity increase of 20-25% can easily be achieved, while the methane leakage is retained at a low level (Fig. 3).

The obvious advantage of HTER for ammonia, besides the reduction in primary reforming duty, is that it offers a very high reforming temperature. A high reforming temperature results in a low methane slippage even with a S/C ratio at the same level as used in a traditional primary reformer for ammonia. The overall S/C ratio used in the front-end with HTER is the same as in the traditional front-end for ammonia. The outlet temperature from the primary reformer is not higher than in the traditional case. For a given capacity, HTER reduces the size of primary reformer for two reasons: firstly, because part of the reforming duty is transferred to the HTER and secondly, because the secondary reformer will perform better, as the total amount of process air, which is determined by the ammonia capacity, is fed to the secondary reformer and only part of the feedstock passes the secondary reformer. When the secondary reformer operates with a higher ratio of process air to process gas, the exit temperature will increase and the methane slip decrease. Another important feature of revamping with HTER is the steam generation system which can be reused without modification, even with 20% higher plant capacity.

Post ammonia converter

In many vintage plants, the ammonia synthesis loop is designed for high inert level and normally also high loop pressure. One simple and interesting revamp feature is to employ a purge gas converter to increase capacity and save energy. Having a purge gas converter permits the inert level in the synthesis loop to be decreased by increasing the purge gas flow rate, without sacrificing hydrogen recovery. The main converter will have much better performance with a lower inert level, resulting in lower loop pressure, energy savings and higher capacity. The purge gas converter can also be installed without modifying the plant to simply increase the ammonia production. Having more plants with one common purge gas converter will be even more favourable. Compared to the Topsøe S-50 post converter located downstream of the main converter, the purge gas converter will be much smaller, installation will be much simpler and the cost will be much lower. However, the S-50 will improve performance of the synthesis in terms of capacity increase and energy savings.

Fig 3: Front end: traditional and with HTER



Source: Topsoe

Reformer refractory coating

The furnace walls in a side-fired tubular reformer are lined with refractory, bricks and fibre materials and a relative low emissivity. By applying a "high emissivity coating" on the surface of the furnace walls it is possible to increase the emissivity and thereby improve the thermal efficiency of the furnace box significantly. The enhanced efficiency of the furnace box can be utilised to alleviate excessive temperatures in the convection section, increase the capacity of the reformer or prolong the lifetime of the catalyst tubes. The lifetime of the catalyst tubes may be further prolonged if the heat releases in the bottom row burners can be reduced to half the heat release of the upper row burners. At least six Topsøe licensed plants have applied high emissivity coating of the furnace walls in the tubular reformer with satisfactory results.

KBR revamp technology

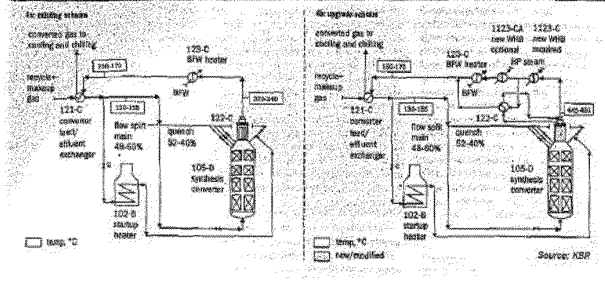
KBR have done several studies recently for clients that are interested in utilising KBR's new proprietary revamp technology to upgrade the ammonia synthesis loops of KBR ammonia plants built in the 1960s to 1980s. The technology can also be applied to relocated MW Kellogg plants. By implementing a simple modification in the existing ammonia converter and incorporating a HP steam raising boiler in the synthesis loop a high grade heat recovery synthesis loop can be achieved.

Over the years, ammonia plant owners have incorporated various energy saving features in their existing plants to reduce energy costs. However, in spite of retrofitting the latest technology features, the energy consumption of those plants built decades ago still remain higher than that of the latest generation plants.

KBR has looked in depth for the key inherent factors that cause the plants of the 1960s to 1980s to be higher energy consumers and has identified that one inherent factor preventing these older plants from achieving low energy consumption is their inability to recover the waste heat in their synthesis loop by raising HP steam. KBR recognised that there is a benefit to recovering waste heat as HP steam in these older synthesis loops without replacing the existing ammonia converter. The converter outlet stream should be made available at above 425°C for economic heat recovery to raise HP steam.

Topsoe, Inc. – EX1003
Page 849 of 1210

Fig 4: Revamp scheme for existing KBR synloops having converter only



Source: KBR

To enable the plant owners to accomplish this objective, KBR offers a technology to upgrade the existing synthesis loop to make the waste heat available at higher thermodynamic grade and enable its recovery as HP steam. The upgrade technology requires that the existing internal heat exchanger bundle inside the top of the converter is removed and a new specially engineered external feed/effluent heat exchanger is incorporated in the scheme outside the ammonia converter. The existing pressure vessel shell of the converter still has a cold wall in operation as before but the product syngas exits the converter at a very high temperature. Two specific examples of the high grade heat recovery technology applications are given below for a typical existing KBR plant with synthesis loop at 150 kg/cm² pressure. In both examples, the ammonia converter is already retrofitted with axial-radial baskets but the bed temperature control is still all by quench mechanism. This upgrade technology will also apply to other plants with different existing retrofits. The fundamentals will remain the same but optimised perimeters and details outside the ammonia converter may be somewhat different.

Post revamp, the main syngas cooling feed stream (48-56% of total) will continue to flow into the converter at the bottom through the annular space of the converter, and will continue to maintain temperature of the pressure vessel shell unchanged. This stream will exit the converter separately, without mixing with the quench flow streams (52-45%), through a new nozzle, and without flowing to the catalyst bed baskets. This cold gas stream will be preheated in a new "external feed/effluent exchanger" and fed back to the converter through a new nozzle to flow to catalyst bed No.1 without any further pre-heating inside the converter. The final converted syngas from the last catalyst bed will flow through the existing central pipe and be collected through a new nozzle on the converter top. This very hot effluent gas stream will be fed to a new waste heat boiler, added downstream of the converter, that will raise HP steam. The existing system of gas quench will remain unchanged.

Process schemes for two typical application scenarios of this upgrade technology are shown in Figs 4b and 5b.

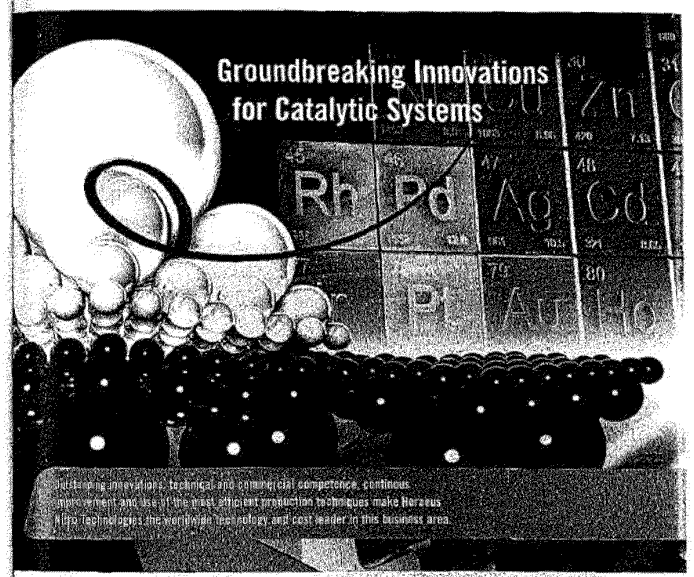
The following modifications are needed in the existing synthesis loop as shown in the Figs 4b and 5b:

- The existing internal heat exchanger 122-C is removed and discarded from inside of 105-D.
- The upper portion of 105-D is modified by bolting a proprietary engineered cap at the top of 105-D.
- No hot work is needed on the 105-D pressure vessel; there is a hot work on the upper portion of the internals which is easily accommodated and executed in a planned shutdown. This proprietary modification of 105-D is simple, low cost and easy to execute.
- The hot syngas exit 105-D at about 445-455°C is cooled to 335 to 385°C in a new waste heat boiler (123-C) where HP steam at 105 to 127 kg/cm²g is raised. If the existing synthesis loop has a separate second ammonia converter in series then depending upon its design, this temperature is 335 to 370°C, otherwise a higher temperature 360-385°C is used.
- A new external 122-C is provided to preheat the 105-D bed-1 feed gas. The syngas flow stream exit the 123-C in Fig. 4b (or alternatively exit the second existing converter in Fig 5b) is split into two parts. About 45-55% of the flow is cooled in the existing BFW preheater 123-C. Remaining gas is cooled by preheating the 105-D shell cooling gas in the new "external 122-C". These two streams are combined and cooled by preheating 105-D feed gas in the existing 121-C which remains unchanged.

Energy saving by heat integration

Total heat recovery from the synthesis loop to the steam system for generating HP steam does not change after implementing the upgrade scheme described above. What changes is the temperature level at which heat is available for recovering into the steam system. In the existing scheme, this heat is typically recovered all by preheating the cold deaerated boiler feed water which is ultimately used for producing HP steam. In some plants that have already modified the synloop by adding a second ammonia converter, some of the waste heat may be recovered as MP steam. In the KBR's upgraded scheme

Heraeus



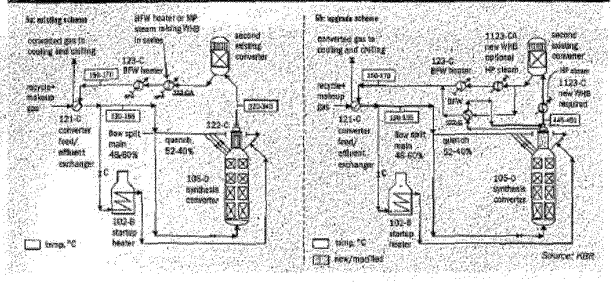
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Fig 5: Revamp scheme for existing KBR synloops having 105-D and a second converter



after revamping, up to 60% of the total waste heat in the synloop is used for directly raising HP steam. This heat is now available at a temperature well above the boiling temperature of the high pressure BFW. The remaining heat in the synloop is still used for preheating the BFW.

As heat recovery at lower temperature in the synloop is reduced drastically, the generated cold boiler feed water is now available for recovering waste heat available at low grade (i.e. at lower temperature) in the other sections of the ammonia flow-sheet which could not be recovered earlier to HP steam system. Additional amount of lower grade heat is now recovered at the one or more (but not limited to) of the following locations:

- LT shift converter outlet for preheating BFW or demin water;
- CO_2 removal unit from hot solvent or stripper overhead;
- methanator outlet (exit feed/effluent exchanger);
- primary reformer flue duct;
- other sources made available by reducing duty on (or eliminating) an existing user of low grade heat (example reboiler heat for CO_2 removal unit).

Thus, the upgrade technology scheme enables generation of increased quantity of high pressure steam as additional low grade heat is recovered into the HP steam system. First, the synloop is upgraded to produce more HP steam directly. Second, the cold BFW not required as a heat sink by synloop is used in other areas of the ammonia plant to bring additional low grade heat into the HP steam system by heat integration. Total HP steam production inside the ammonia plant is thus increased. If possible, either the firing to the auxiliary boiler is reduced or the steam can be exported to OSBL which will save fuel on the OSBL package boiler. Thus, energy efficiency of the ammonia plant is improved significantly.

Energy efficiency of the ISBL ammonia plant can be improved by 0.18 to 0.30 Gcal/tonne by revamping the existing plant using KBR's high grade heat recovery synthesis loop technology. Exact energy saving of a plant will depend on its current base conditions.

It is expected that through mutual cooperation with the plant owners, this upgrade technology can also be applied to numerous GIAP ammonia plants in Russia and other FSU countries. ■

Application to existing plants

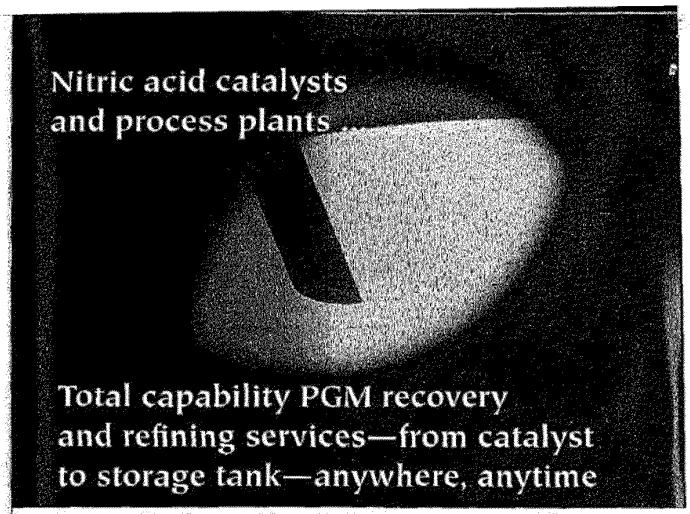
If implemented, this upgrade technology will produce HP steam in all KBR plants that still have the original KBR vertical ammonia converter pressure vessel. In principle, subsequent basket retrofits, no matter what type, do not reduce potential of raising HP steam using this upgrade technology. Similarly, subsequent addition of a second ammonia converter, irrespective of its details, does not reduce potential of raising HP steam. It is the original converter design that prevents possibility of raising HP steam; the above described technology makes it now possible with only a minor change to the top of the existing converter.

KBR is unaware of an existing ammonia plant of the design being discussed that has HP steam producing waste heat boiler in the synthesis loop. Depending upon its specific existing retrofits, the plant will have less energy saving if a HP steam raising boiler has already been incorporated in such an existing plant. However the specific plant with an existing HP steam boiler may also benefit by using this revamp technology, as production of HP steam is increased and the plant energy efficiency is improved by utilising the existing boiler after rating it for the new conditions.

It is expected that through mutual cooperation with the plant owners, this upgrade technology can also be applied to numerous GIAP ammonia plants in Russia and other FSU countries. ■

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United States District Court
Southern District of Texas, Galveston Division

Topsoe, Inc. Plaintiff, vs. **Casale US, Inc.** **Casale SA** Defendants.	Case No.: 3:24-cv-00033 Jury Trial Demanded

FIRST AMENDED COMPLAINT

INTRODUCTION

1. This action arises out of Defendants' bad faith, fraudulent conduct aimed at procuring a patent on technology that they did not invent and then wielding that patent, and making false and misleading statements, to unfairly compete against Plaintiff Topsoe, Inc. ("Topsoe").

2. Topsoe is the U.S. subsidiary of Danish company Topsoe A/S, which has been one of the world's leading suppliers of chemical processing solutions and related technology for over 80 years. It supplies high-performance, proprietary technologies, engineering, and services to the chemical and oil and gas industries. Topsoe helps these industries to get the most out of their process and products using the least possible energy and resources and is at the forefront of developing sustainable technologies.

3. One of Topsoe's key environmentally sustainable technologies is its ammonia processes, currently also referred to as blue or low carbon ammonia processes, which are used to reduce greenhouse gases that are emitted during the process of creating ammonia. Ammonia (NH_3) is critical in the manufacturing of fertilizers and is one of the largest volume synthetic chemicals produced in the world. It is produced through a chemical reaction between hydrogen and nitrogen

at high pressure and temperatures. The process is highly energy-intensive, accounting for up to 2% of energy consumption and 3% of carbon emissions worldwide.

4. Topsoe is a pioneer in the field of ammonia technology, particularly targeting strategies for lowering carbon emissions, and began commercially selling and installing its ammonia technology in manufacturing facilities over 30 years ago. During that time Topsoe has extensively presented and published on its low carbon ammonia process and has obtained multiple patents protecting the technology in the United States and abroad.

5. Defendants Casale US, Inc. and Casale SA (collectively, "Casale") are direct competitors with Topsoe, and market and sell their own ammonia process. As described in more detail below, in 2019 Casale filed for a U.S. patent application claiming to have "invented" features of a low carbon ammonia process that had been used in Topsoe's own process for decades. Casale was well aware of this because, among other things, over the previous four years it had received extensive exposure and access to Topsoe's commercially installed ammonia process while working on revamping a factory in India that utilized the Topsoe process. Casale has also attended presentations where Topsoe had described these features of its ammonia process, including a presentation in 2009, *ten years earlier*. Casale received the pre-print of the Topsoe paper relating to the presentation, and the records from the conference confirm that Casale attended the Topsoe presentation. Casale misued Topsoe's information by including it in a patent application and misrepresenting that it had been developed by Casale.

6. Casale procured the U.S. patent through deception. During prosecution of the patent application Casale failed to disclose as prior art Topsoe's commercial process or the publications describing it, which were clearly material to the process Casale was trying to patent. Casale even failed to disclose its own material prior art disclosures from many years earlier which

publicly disclosed the key feature it impermissibly was trying to patent and therefore precluded Casale from trying to patent the technology.

7. After improperly obtaining the patent, Casale set out to deliberately disrupt Topsoe's customer relationships, falsely claiming that it owns technology that was developed by Topsoe, that Topsoe infringes its patents, and that any customer employing Topsoe's technology would be infringing its patents as well. When Topsoe asked Casale point blank whether it had contacted any of Topsoe's customers, Casale falsely claimed that it had not. Casale has also been wrongfully asserting that Topsoe infringes the patent.

8. Topsoe accordingly brings this action to have the Court declare that Casale's patent is unenforceable because of the fraud Casale committed in procuring the patent from the U.S. Patent and Trademark Office ("US PTO"). More specifically, Topsoe asks the Court to declare that Casale's U.S. Patent No. 11,286,168 (the "'168 Patent") and all related patents and applications of its family (collectively, the "Disputed Patents") are unenforceable, and to enjoin Casale from asserting the Disputed Patents any further. Topsoe further seeks to recover damages and hold Casale accountable for its wrongful acts in asserting the unenforceable patents, making false statements, and engaging in unfair competitive practices.

THE PARTIES

9. Topsoe, Inc. is a Texas corporation, with its principal place of business at 18050 Saturn Lane, Suite 400, Houston, Texas 77058.

10. Defendant Casale US, Inc. is a Texas corporation with a principal place of business at 2925 Richmond Ave, Suite 1218, Houston, Texas 77098.

11. Casale US, Inc. resides in the Southern District of Texas at least because it is incorporated in Texas and its principal place of business is in the Southern District of Texas.

12. Casale US, Inc. is a wholly owned subsidiary of Casale SA.

13. Casale SA is a privately owned Swiss company with headquarters in Lugano, Switzerland.

JURISDICTION AND VENUE

14. This is an action arising under the Lanham Act, 15 U.S.C. § 1125(a) and the patent laws of the United States, 35 U.S.C. §§ 271, *et seq*, and the Declaratory Judgement Act 18 U.S.C. §§ 2202 and 2202. Accordingly, this Court has subject matter jurisdiction pursuant to 28 U.S.C. §§ 1331 and 1338(a).

15. Topsoe's unfair competition claim arises under Texas state law. This Court has subject matter jurisdiction over that claim pursuant to 28 U.S.C. § 1367, because it is so related to other claims in the action within the Court's original jurisdiction that it forms part of the same case or controversy. This Court also has jurisdiction under 28 U.S.C. § 1338(b) because Topsoe's unfair competition claim derives from a common nucleus of operative facts.

16. This Court has general personal jurisdiction over Casale US, Inc. due to its incorporation in Texas, and its principal place of business being located in the Southern District of Texas.

17. This Court has specific personal jurisdiction over Casale SA because this lawsuit arises out of and relates to Casale SA's affirmative acts in the Southern District of Texas. Among other things, Casale SA contacted representatives of Topsoe located in the Southern District of Texas repeatedly through its attorneys in an attempt to enforce its improperly obtained and unenforceable U.S. patent, insisting that Topsoe's ammonia process cannot be used without its written consent. Casale SA also purposefully directed its wrongful activities, including its false advertising and misleading statements, to at least one potential Topsoe customer to dissuade that

customer from installing Topsoe's ammonia technology at its facilities in Texas. Given the facilities location in Texas, Casale US would have been aware of and involved in the pursuit of potential Topsoe customers and would have been aware of and participated in these wrongful activities. Casale SA, in collaboration with Casale US, is actively and forcefully using its U.S. patent in a competitive context within the form of this suit. Casale SA purposefully directed its unlawful conduct to this district, has substantial business conducted in this district, and published false advertising and misleading statements and other unlawful acts in this district or affecting residents of this district.

18. Moreover, Casale SA controls the day to day activity of its wholly owned subsidiary, Casale US, Inc., which it holds out as its agent. Both share a website (https://www.casale.ch/contacts/casale-in-the-world) and share email domains (casale.ch). Casale's website includes no mention of specific activities or individuals associated with Casale US only.

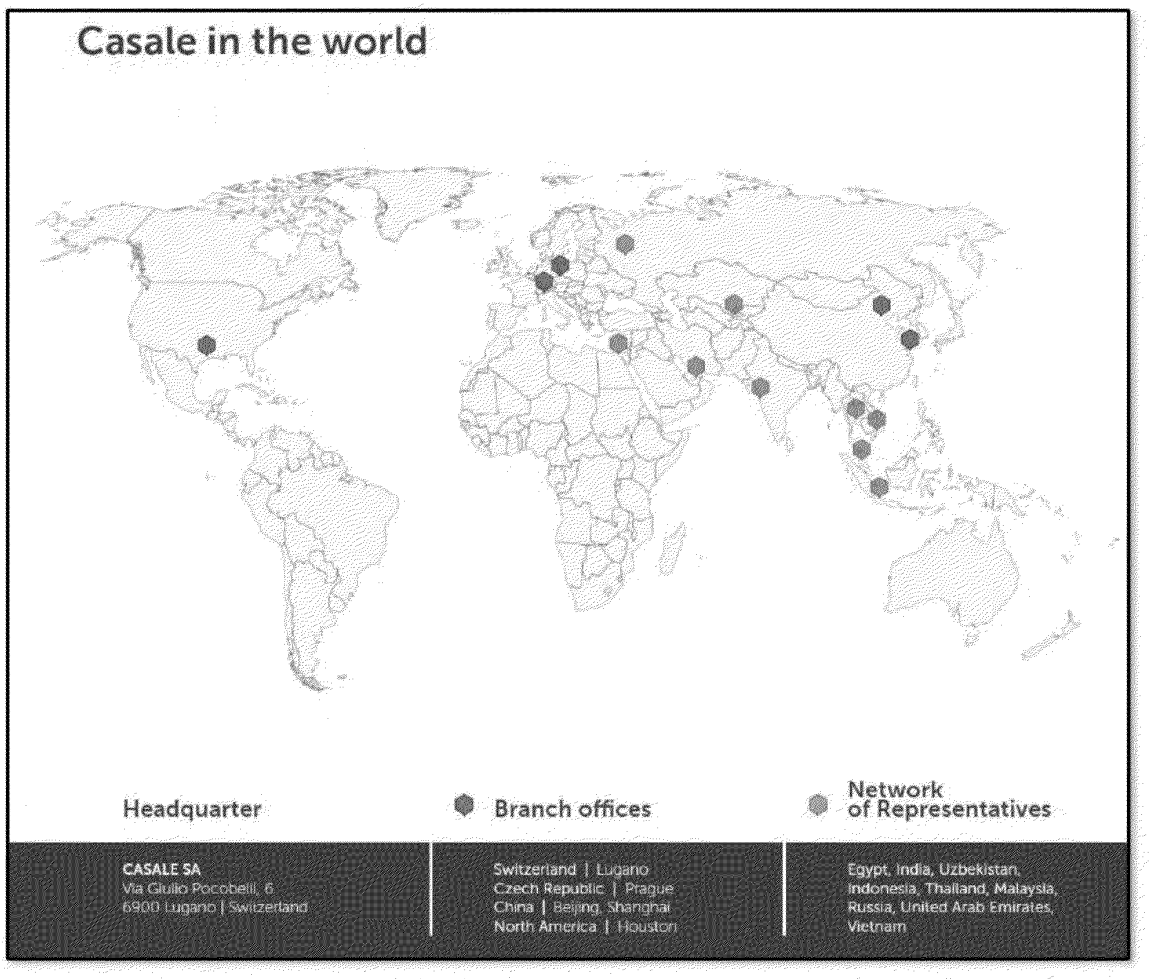
19. Consistent with this, Topsoe can find no reference to Casale US business activity online and can find no individuals online holding themselves out as employees of Casale US. Rather, employees of Casale US, including its sole officer, hold themselves out as employees of Casale SA. The current President of Casale US is Mr. Chris Mancinelli who is employed "full time" by Casale SA as "Sales Manager - Americas at Casale SA" and located in Houston. *See* https://www.linkedin.com/in/chris-mancinelli-922b82/. Casale US thus appears to have no significant employees of its own.

20. Upon information and belief, Casale US appears to be undercapitalized, and does not have operations separate from Casale SA. Casale US's certificate of formation shows that it has authority to issue 10,000 shares with no value., Casale US has no separate website and is

indistinguishable from Casale SA in public press releases and announcements. Casale US appears to exist for purposes of marketing, promoting, and selling Casale SA technology in the US.

21. On information and belief, Casale SA uses Casale US's property as its own. For at least these reasons, Casale US and Casale SA have failed to observe corporate formalities and, accordingly, Casale US's jurisdictional contacts may be imputed to Casale SA.

22. Additionally, Casale SA holds itself out as a global company with "a network of representative offices and agents all over the world." *See* https://www.linkedin.com/company/casale-sa/about/. One of Casale SA's global offices is located in Houston, Texas, and Casale SA has at least one managing agent based out of Houston, Texas.In fact, in promotion materials for blue ammonia Casale SA represents that it has a branch office located in Houston.



23. Defendants, via themselves and/or their subsidiaries or affiliates, regularly conduct and transact business throughout the United States, in the State of Texas, and within the Southern District of Texas. In addition, Casale SA is the assignee of the '168 Patent and Casale prosecuted the '168 Patent before the USPTO through its attorney representatives as described below.

24. Casale SA has also filed a lawsuit asserting claims in the Southern District of Texas in at least one prior litigation: *Ammonia Casale S.A. v M/V Skanderborg, et al.* No. 4:00-cv-2121 (S. D. Tex.).[1]

25. Casale SA's website (https://casale.ch/about/) states: "Casale is a private Group with over 400 professionals, headquartered in Switzerland and present in the Czech Republic, China, and the United States. Casale Holding is the sole owner of the Group Casale."

26. Casale SA has employees that work in Houston, Texas. These employees include at least one senior process engineer currently working in Houston. https://www.linkedin.com/in/robertfsmithpe/. Casale SA also advertises to hire employees in Houston. *See* https://casale.ch/people-careers/job-opportunities/?_sft_job_locations=houston-texas-united-states.

27. Casale SA has imported ammonia process equipment into the U.S. and into this district through the Port of Houston.

28. In addition, Casale SA has licensed low-carbon ammonia technology (Flexiblue®) for use at a facility located in this district, including, on information and belief, the '168 patent technology, which impose enforcement obligations with a party residing in Texas. https://www.casale.ch/news/casale-8-rivers-capital-on-the-forefront-of-chemical-industrys-energy-transition.

29. In the alternative, this Court has personal jurisdiction over Casale SA under Federal Rule of Civil Procedure 4(k)(2)(A) because: (a) Topsoe's claims arise under federal law; (b) Casale

[1] Ammonia Casale SA is predecessor to Casale SA. *See* June 19, 2014 press release https://casale.ch/harmonized-skills-to-serve-you-best/#:~:text=We%20are%20pleased%20to%20announce,the%20name%20of%20Casale%20SA ("We are pleased to announce that, Ammonia Casale, Urea Casale, Methanol Casale and Casale Chemicals have merged into a single entity, which will trade under the name of Casale SA.").

SA is a foreign defendant not subject to personal jurisdiction in the courts of any State; and (c) Casale SA has sufficient contacts with the United States as a whole, including, but not limited to, filing lawsuits in the United States and licensing and designing plants located within the United States, such that this Court's exercise of jurisdiction over Casale SA satisfies due process and comports with the Constitution and laws of the United States.

30. Additionally, Casale SA has sought patent protection in the U.S. and filed the '168 patent application at the U.S. PTO. Similarly, Casale SA has registered a trademark at the U.S. PTO for its low-carbon blue ammonia technology, Flexiblue®, which Casale SA has described as covering goods/services directed to "Licensing of patents; legal services, namely, licensing of trademarks; licensing of intellectual property rights."

31. Venue is proper in the Southern District of Texas pursuant to 28 U.S.C. §§ 1391, at least because Casale US is incorporated in the State of Texas, has its principal place of business in the Southern District of Texas and at least because Defendants have committed acts of false advertising and unfair competition in the Southern District of Texas and attempted to enforce their unenforceable patent in the Southern District of Texas. Venue is also proper in the Southern District of Texas pursuant to 28 U.S.C. § 1391(c)(3), as Casale SA is not a resident of the United States and, accordingly, they may be sued in any judicial district.

FACTUAL ALLEGATIONS

Topsoe's Contributions to the Field of Low Carbon Ammonia Technology

32. Topsoe Inc. was incorporated in 1961 and is a wholly owned subsidiary of Topsoe A/S. Topsoe A/S was founded in 1940 by chemical engineer Dr. Haldor Topsoe and is headquartered in Ravnholm, Kgs. Lyngby, Denmark. It has been a provider of industry-leading chemical processing solutions and related technologies in the over 80 years since its founding.

33. Topsoe, Inc. employs approximately 220 full time employees, including 128 at its catalyst manufacturing facilities located at Pasadena, Texas, and approximately 90 at its principal corporate offices in Houston, Texas.

34. Topsoe has long been a leader in the development and commercial implementation processes to produce ammonia. Topsoe has worked to develop ammonia processes, particularly targeting low carbon emissions, which it currently markets commercially under the name SynCOR™ ammonia, low carbon, or blue ammonia, to reduce CO_2 emissions for more than two decades.

35. Topsoe A/S owns numerous United States patents in the field of low carbon ammonia technology, and Topsoe, Inc. is the exclusive licensee (with rights to license to its clients) of those patent rights in the United States.

36. Apart from its patents, Topsoe's low carbon ammonia technology has been presented at industry conferences and implemented commercially in ammonia plants around the world.

37. An example is the 2009 Fertilizer Association of India (FAI) Annual Seminar where Topsoe described aspects of its low carbon ammonia process in a presentation and companion paper both titled "Energy efficiency and CO_2 reduction potential in ammonia plants based on lean gas." Of particular relevance here, the presentation and paper both describe as part of Topsoe's process splitting the synthesis gas stream into two streams one of which is used as fuel—a key feature that Casale would claim to have invented a decade later.

38. Another, much more recent example, is Topsoe's presentation and publication about its blue ammonia process at the AICHE Ammonia Safety Conference on September 13, 2022. Topsoe's paper entitled "Decarbonize with blue ammonia," and authored by Ameet Kakoti

and Per Juul Dahl, noted that "[m]ore than 20 years ago, i.e. before the decarbonization took off, Topsoe introduced the foundations for the SynCOR™ concept."

39. Topsoe's ammonia technology also has been used in commercial ammonia plants. Topsoe designed an ammonia plant for the Indian Farmers Fertilizer Cooperative Ltd. (IFFCO), Aonla, India. The first unit at IFFCO was commissioned in May 1988 and the second unit in December 1996. Both units are based on Topsoe's low carbon ammonia technology, including the splitting of a synthesis gas stream into two streams of the same composition in which one of the streams is used as fuel.

Casale's Knowledge of and Access to Topsoe Technology

40. Casale has long been aware of Topsoe's low carbon ammonia technology.

41. Casale is a regular attendee and presenter at Fertilizer Association of India ("FAI") meetings, attended the 2009 FAI meeting, and received preprints of the seminar papers, including the ammonia paper authored by Topsoe. Materials from the conference show that Casale attended the Topsoe presentation.

42. Casale circulated information from industry meetings and events within the company. For example, US 7,465,324, which lists Ermanno Filippi as sole inventor, refers to prior art processes of competitors that were presented at an industry meeting. US 7,465,324 col. 1, ll. 58-63. ("Processes of this type have been described for example in the following papers: "Synetix's advanced gas heated reformer, P. W. Farnell" and "New Kellogg Brown & Root ammonia process, Jim Gosnell"; both expounded at the "44th AIChE Annual meeting on safety in ammonia plants and related facilities", Seattle, USA, 27-30 Sep. 1999."). Another example is US 2002/0151749, which lists as a co-inventor Federico Zardi, and refers to "AIChE Ammonia Safety Symposium, Boston September 1996." US 2002/0151749 ¶ 9.

43. Additionally, Ermanno Filippi, Francesco Baratto, and Raffaele Ostuni regularly present at industry events, including events in the United States. For example, Ostuni presented on blue ammonia at the 2022 Ammonia Energy Association meeting in Phoenix, Arizona, Baratto presented on blue ammonia at the 2021 Arab Fertilizer Association, and Filippi was a panelist for low-carbon ammonia plants at the 2023 Ammonia Energy Association Annual Conference in Atlanta (for which Casale was a sponsor).

44. On information and belief, Filippi, Baratto and Ostuni maintain a close working relationship in which technical information is shared between them. For example, they are listed as co-inventors in US 2019/0023565. Indeed, in this application Filippi, Baratto and Ostuni attempted to claim "a method for revamping of an ammonia plant" and Casale's work on the IFFCO plant in India described above was a revamp.

45. Casale also gained access to the IFFCO plant in which Topsoe's low carbon ammonia technology had been installed. Casale gained detailed information about Topsoe's ammonia technology as part of a revamp project at IFFCO in 2014. Casale was responsible for the design and supply of equipment for the revamp.

46. As part of Casale's work on the IFFCO ammonia units, it was given access to Topsoe's design for the ammonia units and learned—similar to what had been described in Topsoe's 2009 paper—that Topsoe's design included splitting a synthesis gas stream into two streams of the same composition so one stream could be used as a fuel.

47. Casale's knowledge of Topsoe's work in ammonia synthesis is further evidenced by Casale's citation to Topsoe processes in prior patent applications, including citation by Casale's Chief Technology Officer, Ermanno Filippi. *See, e.g.*, US2012/0279033 (referring to and providing a diagram of a Topsoe ammonia synthesis loop); US2019/0023565 (naming as inventors

Ermanno Filippi, Francesco Baratto, and Raffaele Ostuni, based upon a PCT application filed by Marco Zardi, and rejected by the PTO over Topsoe prior art references including a PCT application entitled "Process for the production of ammonia").

48. Accordingly, Casale has had access to, and detailed information about, Topsoe's low carbon ammonia process since as early as 2009, if not earlier.

Casale's Application for and Prosecution of the '168 Patent

49. Casale filed the application for the '168 Patent with the US PTO on August 13, 2019, shortly after completing its work on revamping the IFFCO plant where Topsoe's technology had been installed.

50. The '168 Patent issued on March 29, 2022.

51. The '168 Patent is related to EP 3,583,067 (the "'067 Patent"), filed on January 31, 2018. Both the '168 Patent and the '067 Patent are related to EP 3,363,770 (the "'770 Patent"), filed on October 6, 2017.

52. Attorneys of Dorsey & Whitney LLP, including Marcus S. Simon (Reg. No. 50,258) represented Casale in the prosecution of the '168 patent.

53. The claims of the '168 patent require, among other things, splitting a synthesis gas stream into two streams of the same composition so one stream could be used as a fuel, just as was done by Topsoe's technology that had been in use at the IFFCO plant. Specifically, claim 1 of the '168 patent requires "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." *See* claim 1.

54. All patent applicants and persons involved with the substantive preparation of a patent application have a duty of candor to disclose to the US PTO all known prior art or other information that may be material to the patentability of the invention. This prior art information is disclosed in the form of an Information Disclosure Statement ("IDS") Casale filed one IDS during prosecution of the '168 Patent on August 13, 2019. In this IDS, Casale disclosed only a limited number of prior art references.[2] Casale did not disclose any prior art references, including prior uses, that were attributed to Topsoe, despite being aware of Topsoe's low carbon ammonia technology since at least as early as 2009 and having been extensively exposed to it as part of its work at the IFFCO plant.

55. Casale's inclusion in its claims of the requirement of splitting the synthesis gas into two streams having the same composition so one stream could be used as fuel—the concept which it knew Topsoe was already using and had repeatedly published—played a crucial part in Casale's ability to procure the patent. To overcome a rejection by the US PTO of its claim, Casale argued to the Examiner that the "distinguishing feature of the 'first and second streams having the same composition,'…plays a substantial role in the solution of the technical problem underlying the claimed subject matter. Due to the fact that a stream of CO2-depleted synthesis gas (i.e., a gas very poor in CO2 and rich in nitrogen and hydrogen) is used as a fuel in the furnace, instead of a methane rich stream as suggested by [the prior art] it is advantageously possible to reduce the CO2 emissions of the process if compared to [the prior art]." Reply to Office Action dated April 28, 2021.

[2] Casale disclosed only the following prior art references: (1) U.S. Pub. No. 2004/0234426; (2) U.S. Pub. No. 2014/0248205; (3) U.S. Pub. No. 2015/0031916; (4)WIPO Pub. No. 2010/018550; (5) International Preliminary Report on Patentability for International Application No. PCT/EP2018/052358 completed May 10, 2019; and (6) International Search Report from International Application No. PCT/EP2018/052358 mailed July 31, 2018.

56. At the time Casale and its lawyers made these statements, Casale knew that the Topsoe ammonia technology included this same "same distinguishing feature" but intentionally hid this information from the Examiner in order to secure allowance of the patent.

57. Casale's strategy worked, and the Examiner withdrew the rejection. The Examiner's reason for allowing the claims was the "distinguishing feature of the first and second streams having the same composition." Notice of Allowance dated Nov. 18, 2021.

Casale's European Patent

58. As noted above, the European counterpart to the '168 Patent, is the '067 Patent.

59. European Patent Office ("EPO") procedure allows for any member of the public to file an opposition to any patent granted by the EPO within the first nine months after the patent issues. Almost immediately after it was granted, Casale's '067 Patent was in jeopardy. An opposition to the '067 Patent was filed by Linde AG and Thyssenkrupp Industrial Solutions AG (the "European Opposition"), bringing to the attention of the EPO additional prior art that Casale had not put before the EPO that called the viability of Casale's patent into serious question.

60. Casale recognized the severity of the challenge to its patent from the prior art included in the European Opposition. Casale had not disclosed this prior art to the US PTO either. As discussed in more detail below, Casale filed a "supplemental examination" in the US PTO and submitted the prior art from the European Opposition to the US PTO.

61. Both the '067 Patent and the related '770 patent were prosecuted on behalf of Casale by European law firm M. Zardi & Co. SA ("Zardi").

62. Zardi was founded in 1999 by Marco Zardi and is a Swiss law firm specializing in intellectual property.

63. Both the US and European patents are based on the same PCT application filed by Zardi, and specifically, Marco Zardi.

64. Zardi also is representing Casale in the European Opposition.

65. Zardi, including Marco Zardi and Riccardo Biazzi, also were substantively involved in the prosecution of the '168 Patent.

66. The current Chief Executive Officer of Casale is Frederico Zardi.

67. On information and belief, Marco Zardi and Federico Zardi (CEO of Casale) are blood relatives.

68. On information and belief, Casale engaged Zardi, rather than a law firm with no affiliation with Casale or its officers, to assist it in its wrongful scheme to prosecute the U.S. patent without disclosing the material prior art, and to attempt to improperly enforce it by corresponding directly with Topsoe to demand a license, and to assist with correspondence to at least one Topsoe potential customer.

Casale's Communications with Topsoe Customers

69. Unbeknownst to Topsoe at the time, Casale began communicating with Topsoe customers about the Disputed Patents and Topsoe's low carbon (blue) ammonia technology beginning in the Fall of 2022.

70. Casale raised the Disputed Patents, including the '168 Patent, in a November 2022 letter to at least one Topsoe customer who is planning to develop low carbon (blue) ammonia projects in Texas and Louisiana. The letter was an effort by Casale to license the '168 patent for use in the United States and specifically for use in this forum.

71. Casale's communications to that customer referred to Casale's rights in the Disputed Patents, including the '168 Patent, and expressly represented that the Disputed Patents were enforceable.

72. The one feature of the patented technology that is mentioned in the letter is the technique that, as Casale knew, has been used by Topsoe in its commercial installations and disclosed in its publications since at least 2009 of splitting the synthesis gas stream into two streams one of which is used as fuel. Specifically, Casale stated that the patent concerns "a process for the synthesis of ammonia wherein part of the hydrogen-containing process gas is used as a fuel fraction to reduce the consumption of hydrocarbon fuel and, consequently, to reduce emissions of carbon dioxide." Casale represented that, according to its evaluation, without the use of this technique, "the result would anyway be a higher plant cost and a lower efficiency."

73. Casale's letter to the customer referred to Topsoe's blue ammonia technology and Topsoe's 2022 AICHE paper and presentation and attached a copy of the Topsoe's paper claiming that it fell within the scope of the patent.

74. Casale's communications were made to disparage and malign Topsoe by characterizing Topsoe as an infringer, as well as to threaten customers with patent infringement should they choose to do business with Topsoe. Casale was hoping to scare customers away from doing business with Topsoe now, and in the future.

75. The European Opposition, filed on June 8, 2022, predates Casale's communications to Topsoe's customer. Casale's communications did not include any information related to the European Opposition of the '607 Patent, however, nor did Casale reveal that the prior art raised in those opposition proceedings raised significant concerns about the enforceability and validity of the Disputed Patents.

Topsoe, Inc. – EX1003
Page 868 of 1210

76. The European Opposition, in which the validity of the '607 Patent is being disputed, was relevant to the contents of Casale's communications at the time sent. The prior art references cited in the European Opposition are material to patentability and enforceability of the Disputed Patents.

77. Casale knew that the European Opposition was relevant to the contents of the Casale's communications to customers at the time sent. Casale knew that the prior art references cited in the European Opposition are material to patentability and enforceability of the Disputed Patents at the time Casale sent its communications to Topsoe's customer.

78. In addition, no reference was made in Casale's communications to any of Topsoe's prior art publications to which Casale had access, many of which predate the '168 Patent or to the fact that Topsoe had been using the accused technology many years before the patent was filed. And no reference was made to the fact that Casale had failed to put any of the Topsoe prior art or the prior art raised in the European Opposition when it obtained the patent from the US PTO.

79. Casale knew that its patent was invalid and unenforceable but engaged in these communications regardless. Casale knew that these statements were objectively baseless for the many reasons described above.

80. Casale's statements were also false, misleading and objectively baseless because Casale represented that it was the only legitimate source for low carbon ammonia technology that uses a portion of the synthesis gas stream as fuel. Casale was fully aware that this was not true.

Casale's Communications with Topsoe

81. On February 24, 2023, after Casale began sending its false and misleading communications to customers, Casale, through Riccardo Biazzi of Zardi, sent its first correspondence ("First Letter to Topsoe") to Topsoe.

Topsoe, Inc. – EX1003
Page 869 of 1210

82. The First Letter to Topsoe stated that Casale was "of the opinion that the SynCOR™ process with hydrogen firing includes all the features recited, at least, in the independent claims of the [Disputed Patents]."

83. The First Letter to Topsoe did not include a claim chart or other detailed infringement analysis and instead again emphasized that the synthesis gas is split into two streams, one of which is used as fuel. Specifically, the First Letter to Topsoe states that the Disputed Patents "protect a process for synthesis of ammonia from natural gas comprising the conversion of desulphurized natural gas and steam with oxygen-enriched air or oxygen, and further comprising that a part of CO2-depleted synthesis gas (i.e. hydrogen-rich gas) is fed as fuel to at least one furnace."

84. In a second letter to Topsoe dated June 1, 2023 ("Second Letter to Topsoe") Casale pointed to the Topsoe September 13, 2022 paper that was presented at the AICHE Ammonia Safety Conference, alleging its "opinion that the SynCOR process appears to include features patented by Casale is based on the following diagram from the paper by Kakoti and Dahl." This diagram is as follows:

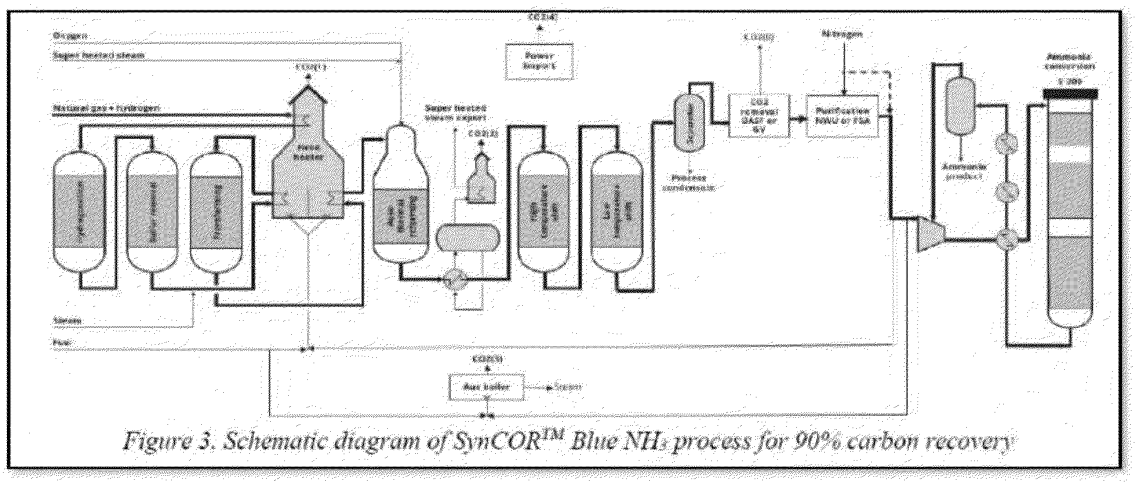


Figure 3. Schematic diagram of SynCOR™ Blue NH_3 process for 90% carbon recovery

85. Casale explained: "If we compare the above diagram with claim 1 of US 11,286,168 we find self-evident that the SynCOR process includes all features of the claim."

86. Neither The First Letter or Second Letter to Topsoe disclosed that Casale already had communicated false, misleading, and disparaging statements to customers. Instead, Casale concealed that information.

87. Topsoe responded to the Second Letter to Topsoe on June 13, 2023 ("Second Letter to Casale"). Topsoe pointed out that the Topsoe's SynCOR™ ammonia process "was using the features purportedly claimed by Casale long before Casale filed its patents" and that a process identical to the one described in the diagram Casale had included in its second letter was described in at least the presentation and accompanying paper at the 2009 FAI meeting that Casale had attended. Topsoe noted that Casale had access to at least the "2009 FAI meeting, and received preprints of the seminar papers, including the paper authored by Topsoe . . . [which] Casale did not disclose . . . to the patent office." Topsoe also noted that that Casale had direct access to Topsoe's technology implemented at the IIFCO plant when "Casale began a revamp of [Topsoe's technology implemented at IFFCO's Aonla Fertilizer plant] in 2014 and completed the revamp in 2018" and that despite this revamp being started and completed before the filing date of the '168 Patent, the technology implemented by Topsoe in the plant was not disclosed to the PTO. Topsoe closed the letter by asking Casale to advise whether it had communicated its infringement allegation to customers and if so, to identify those customers and provide copies of any written communications.

88. On September 15, 2023, representatives from Casale and Topsoe briefly discussed verbally Casale's allegations. Casale's US attorneys and attorneys Marco Zardi and Riccardo Biazzi from Zardi participated on the call, as did officers of Casale, Ermanno Filippi, Chief

Technical Officer, and Raffaele Ostuni, Head of Gas Technologies (who also is named as an inventor on the '168 patent). Topsoe asked whether Casale had communicated to customers its infringement allegations about Topsoe's SynCOR™ ammonia technology. Casale's Chief Technical Officer, Ermanno Filippi, stated unequivocally that it had not done so. This was a lie.

Casale's Request for Supplemental Examination of the '168 Patent

89. On February 16, 2023, shortly before its initial correspondence with Topsoe and significantly after becoming aware of the Oppositions filed in the European counterpart '067 patent, Casale filed a request for supplemental examination of the '168 Patent at the USPTO.

90. Casale's request for supplemental examination presented to the U.S. Patent Office eleven prior art references that were raised in the European Opposition proceedings stating:

> the European counterpart (EP Patent No. 3583067Bl) 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.

Corrected Request for Supplemental Examination dated April 16, 2023.

91. A supplemental examination is a process brought by the patent owner to reconsider a patent that was issued by the US PTO. It is an *ex parte* procedure in which no party other than the patent owner can participate. By raising this prior art in the supplemental examination, Casale precluded Topsoe or any other competitor from filing a petition for Inter Partes Review ("IPR) with the US PTO raising any of the prior art that Casale had omitted. In contrast to the supplemental examination procedure chosen by Casale, in an IPR proceeding, the third party who files the petition is allowed to fully participate. Casale wanted to prevent this from occurring so that it could completely control the dialogue with the US PTO.

Topsoe, Inc. – EX1003
Page 872 of 1210

92. Casale did not include any other prior use or prior art reference in its request for supplemental examination beyond those that had been raised in the European Opposition. Incredibly, in requesting the supplemental examination Casale *still* failed to raise the Topsoe prior art of which it was fully aware. Casale did not include any reference to Topsoe's 2009 FAI presentation or publication in its request for supplemental examination, or any other Topsoe presentation or publication about its low carbon ammonia technology.

93. Nonetheless, even without the Topsoe prior art, and even without an adverse party participating in the proceeding, on May 11, 2023, the US PTO issued the Supplemental Examination Certificate, finding that there was "[a] substantial new question of patentability affecting claims 1-23" of the '168 Patent based on the prior art references that were included by Casale in its request for supplemental examination that Casale had not previously disclosed during prosecution of the '168 Patent.

94. On June 28, 2023, an ex parte reexamination was ordered by the US PTO pursuant to 35 U.S.C. § 257. As the name implies, in a reexamination proceeding the validity of the patent is reexamined by the US PTO. That reexamination proceeding is still ongoing as of the date that this Complaint is being filed.

95. Casale did not include any reference to its revamp of IFFCO's Aonla Fertilizer plant from 2014 to 2018 in its request for supplemental examination or in any subsequently filed papers in the ex parte reexamination.

96. On November 2, 2023, Casale submitted an IDS in the ex parte reexam that included "Response letter from Topsoe counsel dated June 13, 2023" and Topsoe's 2009 FAI paper: "'Fertiliser Policy for Sustainable Agriculture', The Fertiliser Associate of India Annual Seminar 2009, December 3-5, 2009, 10 pages."

Topsoe, Inc. – EX1003
Page 873 of 1210

97. Casale has never retracted any of its statements to Topsoe's customer regarding the Disputed Patents and their enforceability, despite knowing that the US PTO placed the '168 Patent into reexamination because it found "[a] substantial new question of patentability affecting claims 1-23" and that the validity of the '067 European Patent is being seriously challenged in the European Opposition.

FIRST COUNT

(DECLARATORY JUDGMENT OF UNENFORCEABILITY OF U.S. PATENT NO. 11,286,168)

98. Topsoe incorporates by reference the allegations set forth in this Complaint as though fully set forth herein.

99. An actual and justiciable controversy exists between Topsoe and Casale concerning the '168 patent.

100. Due, at least in part, to Casale's repeated letters to Topsoe and to at least one Topsoe customer, there is a substantial controversy between Topsoe and Casale and there is sufficient immediacy and reality that Casale will seek to assert and enforce its patents against Topsoe. Therefore, a declaratory judgment action is appropriate.

101. Topsoe seeks a judgment declaring that the claims of the '168 Patent, and any related U.S. patents, are unenforceable under the doctrine of inequitable conduct.

102. The claims of the '168 Patent are unenforceable due to inequitable conduct committed before the US PTO by Casale, Casale's attorneys (including Zardi attorneys and Marco Zardi), attorney Simon, and Casale's employees' and '168 Patent inventors' Francesco Baratto ("Baratto") and Raffaele Ostuni ("Ostuni"), as well as Casale's Chief Technology Officer, Ermanno Filippi. These individuals deliberately and knowingly withheld and/or omitted material information from Topsoe prior art and Casale's own prior art in connection with the prosecution

Topsoe, Inc. – EX1003
Page 874 of 1210

of the application that matured into the '168 Patent in violation of the duty of candor to the PTO prescribed in 37 C.F.R. § 1.56. The information withheld and omitted was highly material, non-cumulative, and was withheld and omitted with an intent to deceive the PTO and/or '168 patent examiner, as described below.

103. The '168 Patent lists two inventors, Francesco Baratto and Raffaele Ostuni.

104. On information and belief, Casale's Chief Technology Officer, Ermanno Filippi, was associated with and substantively involved in the preparation or prosecution of the patent application. Filippi is highly involved with Casale's research, development, and design related to ammonia production, as well as the design of the revamping and of new ammonia plants. Filippi also is highly involved with Casale's efforts to seek patent protection for its ammonia technology, as shown by the fact his name appears on hundreds of Casale's patents, many of which relate to ammonia processes. *See e.g.* U.S. Patent Nos. 11,155,468, 10,464,818.

105. Casale's attroneys at Zardi (e.g., Marco Zardi) were associated with and substantively involved in the preparation or prosecution of the patent application. The patent application was based on a PCT application filed by Zardi, and specifically, Marco Zardi. On information and belief, Zardi, and specifically, Marco Zardi, was involved in in instructing Casale's U.S. lawyers on the prosecution of the patent application by, for example, providing (and not providing) material prior art references.

106. The '168 Patent was prosecuted by the attorneys of Dorsey & Whitney LLP, including Marcus S. Simon (Reg. No. 50,258) ("Simon"), assisted by Angela Staschke and Holly Morton.

107. As a registered patent attorney for Casale, Simon was aware, or should have been aware, of his duty of candor to the US PTO.

Topsoe, Inc. – EX1003
Page 875 of 1210

108. Each inventor listed on the '168 Patent was made aware of and acknowledged their duty of candor to the US PTO and duty to disclose material information to the USPTO, stating:

> I acknowledge the duty to disclose all information which is material to patentability as defined in 37 C.F.R. § 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

Combined Declaration and Assignment signed August 28, 2019.

109. Additionally, each inventor falsely declared in violation of 37 C.F.R. § 1.63: "I am the original inventor or an original joint inventor of a claimed invention in the above-identified application." Both inventors were fully aware that the invention claimed in the '168 Patent had already been publicly disclosed and in the prior art.

110. Filippi, Ostuni, Zardi, and Simon have been actively involved in communications regarding Casale's assertion of claims of infringement against Topsoe. Filippi, Ostuni, and Simon were each present during the September 15, 2023, call between Casale and Topsoe.

111. The '168 Patent has an effective filing date of January 31, 2018.

112. Prior to the effective filing date of the '168 Patent, Casale, including those individuals involved with prosecution of the '168 patent, had access to and knowledge of Casale's own prior art references as well as several pieces of prior art attributable to Topsoe, including but not limited to the 2009 Fertilizer Association of India Annual Seminar presentation; 2009 FAI Paper; and Topsoe's technology installed in IFFCO's Aonla Fertilizer plant, which Casale was hired to revamp between 2014 and 2018. Topsoe's disclosures predate the '168 Patent.

113. Baratto, one of the two inventors of the '168 Patent, was appointed Deputy Department Head of the Syngas Process Department of Casale in December 2012. His duties associated with this position include coordinating technical proposals and feasibility study

Topsoe, Inc. – EX1003
Page 876 of 1210

activities. On information and belief, due to Baratto's position, and the relatively small size of Casale, he would have worked on or at the very least known of the IFFCO project to revamp the Aonla Fertilizer Plant. Further, Baratto was involved in the design of Casale's ammonia plants, including revamp projects such as the IFFCO revamp of the Aonla Fertilizer Plant. Therefore, prior to, at the time of, and after the effective filing date of the '168 Patent, at least one of the '168 inventors, Baratto, had direct, firsthand knowledge of at least one piece of Topsoe prior art, namely, the low carbon ammonia processes and products embodied in the Aonla Fertilizer Plant that was installed by Topsoe and revamped by Casale from 2014 to 2018.

114. As CTO, Filippi duties associated with this position include revamping activities. Due to Filippi's position, and the relatively small size of Casale, he would have worked on or at the very least known of the IFFCO project to revamp the Aonla Fertilizer Plant. Further, Filippi was involved in the design of Casale's ammonia plants, including revamp projects such as the IFFCO revamp of the Aonla Fertilizer Plant. Therefore, prior to, at the time of, and after the effective filing date of the '168 Patent, at least Filippi, had direct, firsthand knowledge of at least one piece of Topsoe prior art, namely, the low carbon ammonia processes and products embodied in the Aonla Fertilizer Plant that was installed by Topsoe and revamped by Casale from 2014 to 2018.

115. Additionally, Filippi, frequently attends and presents at industry conferences. As just one example, Filippi attended the ESF North America 2022 Conference in Houston, Texas and presented on Casale's technologies for low-carbon ammonia. *See* https://www.linkedin.com/posts/casale-sa_greytogreen-ammonia-greenammonia-activity-6945292014645092352-R-ro/.

116. On information and belief, Filippi, Barrato, and Ostuni also had direct, firsthand knowledge of at least one additional piece of Topsoe prior art. As described above, materials from the 2009 FAI conference show that Casale representatives attended the Topsoe presentation, and Casale received the accompanied paper. Casale regularly participates in FAI meetings, seminars, and conferences and at least Filippi has attended and presented at FAI events.

117. Further, given that Topsoe and Casale are direct competitors in an industry with only a few players, and given that the Topsoe technology at issue had been widely known and used in the industry for decades, it is extremely unlikely that an alleged inventor of ammonia processes at Casale would not have known of Topsoe's technology. This is especially true in light of the frequency at which Topsoe publishes papers and other material on this technology and in light of the fact Topsoe's technology is used commercially in many facilities worldwide. Casale, as one of Topsoe's main competitors, undoubtedly paid attention to Topsoe's activity in the marketplace and at industry events. In fact, Casale has referenced Topsoe's commercial systems in its patents in the past, including in patents prosecuted by the Zardi firm that list Filippi as an inventor. *See e.g.* E.P. 16,168,159.

118. The '168 Patent is directed towards a process for synthesis of ammonia from natural gas. The '168 Patent includes two independent claims.

119. The first independent claim of the '168 Patent is:

> **1**. A process for synthesis of ammonia from natural gas, the process comprising:
>
> conversion of a charge of desulphurized natural gas and steam, with oxygen-enriched air or with oxygen, into a synthesis gas containing hydrogen, CO and CO2, in a conversion section;
>
> treatment of said synthesis gas including at least a shift reaction of the carbon monoxide into CO2, and subsequent separation of CO2 from the gas, thus obtaining a CO2-depleted synthesis gas and a CO2-rich gaseous flow containing the CO2 separated from the gas;
>
> separation of a part of said CO2-depleted synthesis gas as fuel fraction, wherein said fuel fraction is fed as fuel to at least one furnace and wherein said separation of the fuel fraction includes the split of said CO2-depleted synthesis gas into at least a first stream and a second stream, said first and second streams having the same composition, wherein the first stream forms the fuel fraction and the second stream is process gas intended for the synthesis of ammonia.

Dkt. 1-1 at col. 18, ll. 38-57.

120. The second independent claim of the '168 Patent is:

> **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.

Dkt. 1-1 at col. 20, ll. 22-38.

121. As is apparent from the claims above, a key element of both claims is separating out the synthesis gas into two streams, one of which is then used as fuel.

122. During prosecution of the application that eventually issued as the '168 Patent, independent claim 1 was independent claim 19 and independent claim 21 was independent claim 39. The patent Examiner initially rejected both claims as obvious under 35 U.S.C. § 103 in light of Reddy et al (US 2004/0234426) in view of a much earlier filed patent owned by Casale, Ostuni et al (US 2016/0115017 A1). Office Action dated April 28, 2021.

123. In response, Casale argued that "[t]he PTO ha[d] not established a *prima facie* case of obviousness against independent claim [1] because, at a minimum, the PTO ha[d] not demonstrated that the cited references teach or suggest . . . 'separation of a part of said CO2-depleted synthesis gas as fuel fraction . . . 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." Response dated Oct. 22, 2021. (emphasis in original). Casale distinguished Reddy on the basis that Reddy did not split the synthesis gas into two streams having the same composition, but rather into "an hydrogen rich stream and a methane rich stream.". Casale argued that the "distinguishing feature of the 'first and second streams having the same composition,'…plays a substantial role in the solution of the technical problem underlying the claimed subject matter." This is because using the CO2-depleted synthesis gas rather than a methane rich gas (as Casale argued was taught in Reddy), reduces the CO2 emissions of the processes disclosed in the '168 Patent.[3]

[3] Casale did not make a separate argument directed towards the obviousness rejection of independent claim 21, but instead argued that in light of the arguments distinguishing Reddy in view of Ostuni, "the other rejections to the claims [were] moot and [did] not, therefore, need to be addressed individually." While Casale acknowledged that independent claim 21 did not specifically claim that "said first and second streams having the same composition," it claimed this

124. At the time Casale made these statements, it was well aware that the Topsoe low carbon ammonia technology included this same "distinguishing feature" but intentionally concealed this material information from the Examiner in order to secure allowance of the patent.

125. Casale's concealment strategy worked, and the Examiner withdrew the rejection. The reason the Examiner gave for allowing the claims was the "distinguishing feature of the first and second streams having the same composition." Notice of Allowance dated Nov. 18, 2021. As a result, the claims were allowed as originally filed. Independent Claims 1 and 21 in the issued patent are identical to independent claims 19 and 39, respectively, filed in the preliminary amendment on August 13, 2019.

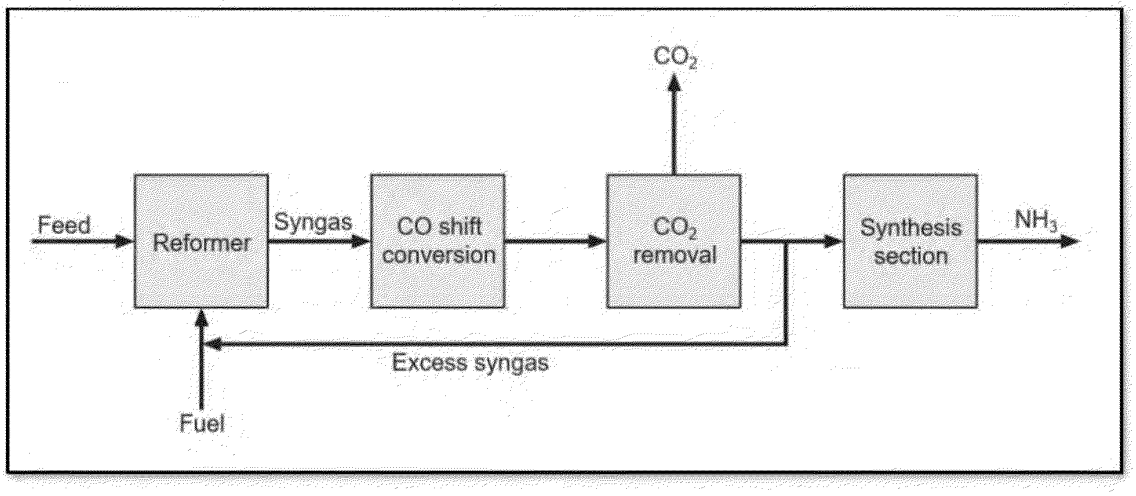
126. The 2009 FAI Paper states that "Various schemes for optimizing the ammonia process in order to minimize the energy consumption as well as the emission of CO_2 will also be discussed in detail." This reference specifically discloses using part of the synthesis gas stream as fuel, stating that: "an excess of synthesis gas is produced, and this excess synthesis gas is used as fuel in the primary reformer." As specified by Casale in distinguishing the Reddy prior art reference, the purpose of separating two streams of synthesis gas, one used as fuel and one used for ammonia production, "plays a substantial role in the solution" provided in the '168 Patent. The 2009 FAI Paper discloses that the excess syngas used for fuel and the gas used to produce ammonia can be from the same source gas (e.g., have the same composition). The reference explains: "excess synthesis gas is produced, and this excess gas is used as fuel in the primary reformer." Therefore,

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limitation was implicit. Casale contended that, in claiming that "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" and incorporating the argument as to claim 1 by reference, it is implicit in the language of independent claim 21 that the synthesis gas is separated into two streams having the same composition.

this reference is highly material to the patentability of the '168 Patent and should have been disclosed during prosecution.

127. The 2009 FAI Annual Seminar presentation discloses substantially the same information as disclosed in the 2009 FAI Paper, and includes the below figure, which shows the excess syngas being recycled back to the primary reformer as fuel. Therefore, for the same reasons as discussed above with respect to the 2009 FAI Paper, this reference is highly material to the patentability of the '168 Patent and should have been disclosed during prosecution.



128. In addition, as part of Casale's work on revamping the IFFCO ammonia units from 2014-2108, it was given extensive access to Topsoe's design for the ammonia units and learned that Topsoe's design included splitting a synthesis gas stream into two streams of the same composition so one stream could be used as a fuel. Therefore, this information is highly material to the claimed subject matter of the '168 Patent and should have been disclosed during prosecution of the '168 Patent.

129. Despite Casale's clear and undeniable knowledge of the numerous material Topsoe disclosures that predated the '168 Patent, no reference was made to any prior art disclosures attributable to Topsoe during prosecution of the '168 Patent.

130. Casale also did not disclose any of the Topsoe prior art references or Topsoe's low carbon ammonia process that was in commercial use when Casale filed a request for supplemental examination of the '168 Patent. Casale further did not disclose its revamp of IFFCO's Aonla Fertilizer plant from 2014 to 2018 after filing or during the pendency of the ex parte reexamination.

131. Casale intentionally omitted and only finally submitted the Second Letter that Topsoe had written to Casale and the 2009 publication referenced in the Second Letter to Casale in an IDS filed on November 2, 2023 in response to the reexamination non-final Office Action. Casale finally did so because it knew that Topsoe was aware of the reexamination and Casale's duty of disclosure to the USPTO.

132. Casale's disclosure during the ex parte reexamination of the Second Letter to Casale and the reference cited in that letter, Topsoe's 2009 publication of "Energy efficiency and CO2 reduction potential in ammonia plants based on lean gas" shows that Casale knows and understands that Topsoe's disclosures of its ammonia technology and the technology used in the IFFCO plant were material to patentability of the '168 Patent and are non-cumulative prior art to the '168 Patent. Therefore, Casale's knowing and intentional nondisclosure of these prior art references, and its access to Topsoe's technology implemented in the IFFCO plant constitutes an intentional and material nondisclosure.

133. Casale knew of the materiality of the Topsoe prior art references before, during, and after prosecution of the '168 Patent, and thus intentionally withheld the art so that it could receive a patent and wield that patent against Topsoe, the real inventor of the technology. The '168 Patent has an effective filing date of January 31, 2018, shortly after Casale completed its revamp of IFFCO's Aonla Fertilizer plant. Casale began sending communications to customers in the Fall of 2022, shortly after the '168 Patent issued on March 29, 2022. Casale's knowledge of the

materiality of Topsoe's prior art reference is also established by the fact Casale argued during prosecution that its invention was novel over the prior art due to the exact feature that Topsoe's concealed prior art has used and disclosed for decades.

134. For this reason, the Topsoe prior art that Casale concealed was necessarily non-cumulative, as Topsoe's prior art papers and implementation clearly include the specific feature that Casale argued was the "distinguishing feature" that made its purported invention patentable over the prior art, and that the patent examiner used as the basis of their notice of allowance of Casale's patent. The fact that Casale itself disclosed the Second Letter to Casale and the 2009 publication referenced in the Second Letter during the reexamination further demonstrates that the Topsoe prior art that Casale concealed was non-cumulative.

135. Casale's disclosure of the Second Letter to Casale and the 2009 publication referenced in the Second Letter during the reexamination does not, however, satisfy its disclosure requirements before the USPTO.

136. In addition to not disclosing the Topsoe prior art references, Casale withheld its own material prior art disclosures during prosecution of the '168 Patent, including at least 2012 MEGAMMONIA® – the Mega-Ammonia Process: the Newest Trend in the ammonia Industry.

137. Ermanno Filippi, Francesco Baratto, Raffaele Ostuni, and Marco Zardi were aware of Casale's own prior art such as 2012 MEGAMMONIA® – the Mega-Ammonia Process: the Newest Trend in the ammonia Industry. Indeed, Filippi has presented and published on the Megammonia.

138. 2012 MEGAMMONIA® – the Mega-Ammonia Process: the Newest Trend in the ammonia Industry discloses a process in which CO_2 is removed from synthesis gas and split into

two streams, one stream intended for synthesis of ammonia and one stream intended for use as fuel.

139. This Casale prior art reference was published prior to the effective filing date of the '168 Patent and is therefore prior art to that patent. The reference is highly material to the claimed subject matter of the '168 Patent and should have been disclosed during prosecution of the '168 Patent.

140. This reference was published by Casale. Therefore, it is undeniable that Casale knew of this prior art reference before, at the time of, and after the filing date of the '168 Patent. And given that Casale knew of this art, and—by its own admission during prosecution of the '168 patent—knew that the stream splitting feature was material to patentability, Casale should have disclosed this art to the examiner as well.

141. Despite Casale's clear and undeniable knowledge of its own material disclosure that predated the '168 Patent's effective filing date, no reference was made to it during prosecution of the '168 Patent.

142. Casale clearly knew that its own prior art references are material prior art to the patentability of the '168 Patent as Ostuni *et al.* (US 2016/0115017 A1), a patent application also owned by Casale and invented by Ostuni, was cited in the obviousness rejection of the '168 Patent.

143. Similarly, in Casale's US2019/0023565 (which names as inventors Ermanno Filippi, Francesco Baratto, and Raffaele Ostuni and originates from a PCT application filed by Marco Zardi) Casale disclosed its own prior art references, and the US PTO cited Topsoe prior art references when rejecting the claims presented by Casale. Thus, Casale knew its own prior art references, as well as Topsoe prior art references were material to patentability of the '168.

Topsoe, Inc. – EX1003
Page 885 of 1210

144. Casale's failure to disclose the Topsoe prior art references and its own prior art disclosure during the initial prosecution of the '168 Patent was done knowingly and intentionally, with the intent to fraudulently obtain the '168 Patent by withholding material prior art references. This therefore constitutes an intentional and material nondisclosure.

145. Intentional nondisclosure of material prior art during prosecution of a patent application constitutes inequitable conduct.

146. Inequitable conduct during prosecution of a patent application renders any resultant patent unenforceable.

147. All non-duplicative relevant prior art must be disclosed and filed during prosecution of a patent application. An explanation for not submitting any relevant prior art must be included during prosecution of a patent application. No such explanation was filed during prosecution of the '168 Patent as to the nondisclosure of the Topsoe references or the Casale references that were known to Casale.

148. At least attorneys Simon and Zardi, inventors Baratto and Ostuni, and CTO Filippi were aware of certain Topsoe and Casale prior art and the materiality of Topsoe and Casale prior art to the claims they were pursuing in the '168 Patent and intentionally withheld that information from the US PTO.

149. Casale's, Casale's attorneys, attorney Simon's, Zardi's and Casale's employees' and '168 Patent inventors' Baratto and Ostuni and Casale's CTO Filippi's failure to disclose material information to the US PTO was done knowingly and intentionally, and with intent to deceive the Examiner and the US PTO into issuing a patent even though the '168 Patent's claims were not patentable or which would be at risk of not being patentable due to material disclosures in at least Topsoe and Casale prior art.

150. Casale, Casale's attorneys, attorney Simon, and Casale's employees and '168 Patent inventors' Baratto and Ostuni engaged in this conduct to avoid the Examiner rejecting claims of the '168 Patent so that Casale could monetize its intellectual property through litigation against other members of the industry, to monetize the intellectual property of Topsoe that Casale derived from its access to Topsoe's processes as well as to recapture technology that already was part of the public domain.

151. As a result of the unenforceability of the '168 Patent and Casale's assertion of the '168 Patent and allegations of infringement of the '168 Patent against Topsoe and its customers, Topsoe has suffered and will continue to suffer harm and seeks declaratory judgment of unenforceability of the '168 Patent, and any related U.S. patents.

SECOND COUNT

(UNFAIR COMPETITION AND FALSE ADVERTISING UNDER THE LANHAM ACT)

152. Topsoe incorporates by reference the allegations set forth in this Complaint as though fully set forth herein.

153. "Any person who, on or in connection with any goods or services, or any container for goods, uses in commerce any word, term, name, symbol, or device, or any combination thereof, or any false designation of origin, false or misleading description of fact, or false or misleading representation of fact, which—is likely to cause confusion, or to cause mistake, or to deceive as to the affiliation, connection, or association of such person with another person, or as to the origin, sponsorship, or approval of his or her goods, services, or commercial activities by another person, or in commercial advertising or promotion, misrepresents the nature, characteristics, qualities, or geographic origin of his or her or another person's goods, services, or commercial activities, shall

be liable in a civil action by any person who believes that he or she is or is likely to be damaged by such act." 15 U.S.C. § 1125(a)(1)(A)-(B).

154. Casale's communications to at least one Topsoe customer in November 2022 compared its blue ammonia technology, which it falsely claimed were covered by the Disputed patents, with Topsoe's blue ammonia technology. Casale's communications falsely claimed that Topsoe's blue ammonia technology infringed the Disputed Patents, including the '168 Patent and that the '168 Patent was valid and enforceable. Further, Casale falsely claimed that Casale was the only legitimate source for low carbon ammonia technologies that uses a portion of the synthesis gas stream as fuel. Casale knew, however that these communications were false and misleading: Casale knew that the '168 Patent was invalid and unenforceable and that it was it not the only legitimate source for this technology. Casale also knew that its '067 Patent, which it specifically referenced in its communications with the customer, was the subject of the European Opposition, which was filed four months earlier in June 2022 and had raised serious prior art invalidity concerns regarding the Disputed Patents. Thus, Casale misrepresented the nature, characteristics, and qualities of both Casale's products and of Topsoe's products, and made objectively baseless claims to Topsoe's customers.

155. Despite Casale's knowledge of its inequitable conduct and the resultant unenforceability of the '168 Patent, it still engaged in a course of conduct in which it asserted its ***unenforceable*** patent rights against Topsoe and notified customers of its patent rights, falsely claiming that its patents were valid and enforceable.

156. Casale, in asserting its unenforceable patent rights and specifically stating that they were "enforceable," despite knowing that the Disputed Patents are unenforceable, if not also invalid, has acted in bad faith and with malice. In so doing, Casale's actions are not guarded from

Topsoe, Inc. – EX1003
Page 888 of 1210

liability under the Lanham Act. Casale has acted with malice and specific intent, as it had knowledge of the falsehood of its baseless statements and/or acted with reckless disregard for the truth and made the statements regardless, with the intent to cause harm to Topsoe's reputation and business.

157. The false statements made by Casale as set forth here, constitute material misrepresentations and/or omissions of the nature, characteristics, and qualities of Casale's and Topsoe's goods, services and/or commercial activities, and are thus in violation the Lanham Act, 15 U.S.C. § 1125(a). The statements were intended to mislead or confuse consumers and direct them to Casale's products instead of Topsoe's products.

158. Casale's communications constitute unfair competition under 15 U.S.C. § 1125(a)(1)(A). Casale's communications included false and misleading descriptions and representations of facts, including the enforceability of the Disputed Patents and their infringement. These false and misleading descriptions and representations of fact were made with knowledge of their falsehood and with the bad faith intent to cause confusion and mistake as to the ability of Topsoe and its customers to make, use, sell, and offer to sell the Topsoe's low carbon (blue) ammonia products and processes and were likely to cause such confusion and mistake.

159. Casale's communication to customers constitutes commercial advertising or promotion as it constitutes commercial speech by a competitor with the intent to influence consumers into buying Casale's services rather than Topsoe's. Casale's communication to customers constitutes sufficient dissemination to the relevant purchasing public to constitute advertising within the relevant industry. Here, the relevant market for purchasers of low carbon ammonia technology is incredibly small, with limited customers offering only a small number of very large projects that will typically take years to install. Therefore, Casale's communication to

customers, even in a vacuum, constitutes commercial advertising and promotion within the scope of the Lanham Act. Casale engaged in a course of conduct specifically to interfere with Topsoe's relationships with its customers by notifying at least one customer of Topsoe's alleged infringement, and creating uncertainty as to Topsoe customers' abilities to do business with Topsoe without liability. This conduct is well within the scope of commercial advertising and promotion.

160. Casale's actions took place in interstate commerce. Casale, which is a foreign corporation, and which has a United States headquarters in Texas, sent a letter to at least one customer with operations in the U.S. and in this District, about use of Topsoe's blue ammonia technology in projects on the Gulf Coast in Texas. Casale also has falsely advertised that its ammonia technology is "patented" at industry events. Additionally, Casale has caused its blue ammonia technology products to enter interstate commerce, including through its proposals to customers in the U.S.

161. Casale's communications deceived and/or had the capacity to deceive customers. As a result of Casale's communications, at least one customer is under the impression that Casale owns valid, enforceable, and exclusive rights to low carbon (blue) ammonia technology, which is not true.

162. Casale's communications are material and likely to influence the purchasing decisions of customers. As Casale well knew, customers for blue ammonia technology would be unwilling to make the large capital expenditures needed to build or revamp an ammonia plant under threat of patent infringement (even when that threat is unfounded). Therefore, the false statements in Casale's communications were likely to influence purchasing decisions.

Topsoe, Inc. – EX1003
Page 890 of 1210

163. As a direct and proximate result of Casale's false and misleading statements in the marketplace, Casale caused economic injury to Topsoe. Casale's false and misleading statements have caused at least one customer to withhold trade from Topsoe.

164. Further, as a direct and proximate result of Casale's false and misleading statements, Topsoe has suffered, and will continue to suffer, monetary damages, and seeks recovery, in an amount to be proven at trial, to compensate for Casale's false advertising and unfair competition. Casale's false advertising and unfair competition will continue to damage Topsoe, causing irreparable harm for which there is no adequate remedy at law, unless enjoined by this Court.

165. Casale acted in bad faith, intentionally, with knowledge of, and in willful and conscious disregard of Topsoe's rights, in misrepresenting the nature, characteristics and qualities of Casale's process and its illicitly obtained '168 Patent and of Topsoe's process. Topsoe is entitled to injunctive relief and to the recovery of all available damages, interest, attorneys' fees, costs, enhanced damages, and Casale's profits.

166. This is an exceptional case within the meaning of Section 35 of the Lanham Act, 15 U.S.C. § 1117.

THIRD COUNT

(COMMON LAW UNFAIR COMPETITION)

167. Topsoe incorporates by reference the allegations set forth in this Complaint as though fully set forth herein.

168. Topsoe alleges herein that the claim for common law unfair competition arises out of the same facts that support Topsoe's causes of actions for the Lanham Act violations. Therefore, Casale's actions give rise to an actionable cause of action for common law unfair competition.

169. As described in Topsoe's Lanham Act claims, Casale has, among other things, knowingly made false and misleading representations to Topsoe's customers regarding the validity and enforceability of the Disputed Patents and their alleged infringement. These false, misleading, and baseless descriptions and representations of fact were made with knowledge of their falsehood and with the bad faith intent to cause confusion and mistake as to the ability of Topsoe and its customers to make, use, sell, and offer to sell Topsoe's low carbon (blue) ammonia products and processes and were likely to cause such confusion and mistake. As a result of Casale's unfair competition, Topsoe has suffered monetary damages, and seeks recovery, in an amount to be proven at trial, adequate to compensate for Casale's false advertising and unfair competition. Casale's unfair competition will continue to damage Topsoe, causing irreparable harm for which there is no adequate remedy at law, unless enjoined by this Court.

170. As a direct and proximate result of Casale's false and misleading statements, Topsoe has suffered, is suffering, and will continue to suffer immediate and continuing irreparable injury for which there is no adequate remedy at law.

171. On information and belief, Casale's false and misleading statements are knowing and willful, flagrant, and/or with intentional disregard as to the true nature of the product it offers. Topsoe is entitled to an award of punitive damages.

PRAYER FOR RELIEF

WHEREFORE, Topsoe prays for judgment and seeks relief against Casale as follows:

A. For declaratory judgment that Casale's '168 Patent, and any related U.S. patents, are unenforceable;

B. for judgment awarding attorneys' fees pursuant to 35 U.S.C. § 285, or otherwise permitted by law;

C. for judgment awarding to Topsoe all gains, profits, and advantages derived by Casale as a result of its wrongful conduct;

D. for judgment awarding monetary damages sufficient to compensate Topsoe for the harm suffered as a result of Casale's wrongful conduct;

E. for a judgment awarding enhanced damages and/or attorneys' fees pursuant to 15 U.S.C. § 1117;

F. for a permanent injunction that: (a) enjoins Casale, its officers, agents, servants, and employees, and all persons in active concert and participation with them, including their affiliates, from further disseminating the false and misleading statements in any form or medium, making the disparaging claims in any form or medium; and (b) requires Casale to withdraw, retract, and/or retrieve all the offending false and misleading statements and disparaging claims;

G. for a judgment awarding punitive damages for Casale's unfair competition;

H. for judgment awarding costs of suit, as well as pre- and post-judgment interest; and

I. for judgment awarding Topsoe such other and further relief as the Court may deem just and proper.

DEMAND FOR JURY TRIAL

Pursuant to Rule 38(b) of the federal Rules of Civil Procedure, Topsoe hereby demands a trial by jury of this action.

Dated: May 2, 2024

Respectfully submitted

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Europäisches Patentamt
European Patent Office
Office européen des brevets

Espacenet

CN103303863A Method for producing ammonia synthesis gas from coke-oven gas

Applicants: HUANG JIAHU

Inventors: HUANG JIAHU

Classifications:
IPC ***C01B3/02; C01B3/34;***

Priorities: CN201310233151A 2013-06-13

Application: CN201310233151A·2013-06-13

Publication: CN103303863A·2013-09-18

Published as: CN103303863A

Method for producing ammonia synthesis gas from coke-oven gas

Abstract

The invention relates to a method for producing ammonia synthesis gas from coke-oven gas. The method comprises the steps of: by taking coke-oven gas subjected to dedusting, decoking and rough desulfurization as a raw material, firstly separating out hydrogen in the coke-oven gas for later use; respectively converting remaining high methane gas with vapor and air, further converting into conversion gas containing hydrogen and carbon dioxide after converting hydrocarbon gas into hydrogen and carbon monoxide; after removing carbon dioxide from the conversion gas, mixing the remaining gas from the separated hydrogen, and finally purifying through a terminal to obtain ammonia synthesis gas, wherein all operation units can be operated by a conventional mode. Compared with the conventional method in which pure oxygen or high oxygen is needed, with the method, the higher water vapor partial pressure and higher conversion rate can be obtained under the conditions of water vapor using the same water-air ratio and water-carbon ratio, the investment can be reduced, the utilization ratio of raw materials can be improved, the energy consumption and gas consumption can be remarkably reduced, and the economic benefits can be obvious.

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CLAIMS CN103303863A

1.

13 The method for preparing ammonia synthesis gas from coke oven gas uses the coke oven gas after dust removal, decoking and rough desulfurization as raw material, and is characterized by the following steps:

1'

18 : Separate the hydrogen from the coke oven gas for subsequent use;

2'

22 : The remaining coke oven gas after hydrogen separation is methane-rich gas, which is successively subjected to heat exchange steam catalytic reforming with water vapor to convert methane and other hydrocarbons into hydrogen and carbon monoxide to obtain reformed gas, and then subjected to autothermal catalytic reforming with air to convert carbon monoxide in the reformed gas into hydrogen and carbon dioxide to obtain converted gas;

3'

30 : After removing carbon dioxide from the shift gas, decarbonized gas is obtained, and the decarbonized gas is mixed with the hydrogen separated in step 1' and purified to obtain the ammonia synthesis gas.

2.

35 The method according to claim 1, characterized in that hydrogen is separated from the feed gas in said step 1' by pressure swing adsorption.

3.

41 The method according to claim 1, characterized in that the yield of hydrogen separated from the raw gas in said step 1' is about 90 (v) %.

4.

46 The method according to claim 1, characterized in that the sulfur content of the methane-rich gas used for mixing with water vapor in said step 2' is less than 0.2 ppm.

5.

51 The method according to claim 1, characterized in that the amount of water vapor introduced in step 2' is such that the molar ratio of the total carbon of hydrocarbons in the methane-rich gas is H₂O/C=2.7-4.0.

6.

57 The method according to claim 1, characterized in that the hydrogen in the ammonia synthesis gas in the step 3' is the total amount of hydrogen contained in the shift gas and separated in the step 1'.

7.

62 The method according to claim 1, characterized in that the amount of air added in said step 2' is 1.25 to 1.35 times the volume of said methane-rich gas.

8.

67 The method according to claim 1, characterized in that the volume content of residual methane in the conversion gas obtained by converting methane into hydrogen and carbon monoxide by the methane-rich gas and water vapor in step 2' is ≤0.5%.

9.

73 The method according to claim 1, characterized in that the process of converting methane into hydrogen and carbon monoxide by methane-rich gas and water vapor in step 2' is carried out in at least the following manner:

76 The methane-rich gas is compressed to 1~4Mpa with a sulfur content of less than 0.2ppm, heated to 250~450℃, and then mixed with water vapor pressurized to 1~4MPa;

78 The mixture of methane-rich gas and water vapor is converted from methane to hydrogen and carbon monoxide in a heat exchange reformer at 400-550° C;

80 After the methane-rich gas and water vapor complete the conversion from methane to hydrogen and carbon

monoxide, they are autothermally converted in a second-stage furnace together with air preheated to a temperature consistent with or close to that of the converted gas to obtain hydrogen and carbon monoxide.

10.

87 The method according to claim 1, characterized in that the total amount of carbon monoxide and carbon dioxide in the synthesis gas obtained after the mixed gas mixed with hydrogen in step 3' is purified is ⩽ 20ppm.

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由焦炉气制取氨合成气的方法

(57)摘要

由焦炉气制取氨合成气的方法。以经除尘、除焦及粗脱硫后的焦炉气为原料，首先分离出焦炉气中的氢气，供后续使用；剩余的富甲烷气依次分别与水蒸汽和空气进行转化，将烃类气体转化为氢和一氧化碳后，再进一步变换为含氢气和二氧化碳的变换气；变换气脱除二氧化碳后，将剩余气体与之前被分离出的氢气混合，最后通过终端净化后得到所说的氨合成气，其中的各步操作单元均可按常规方式进行。该方法无需常规方法需提供纯氧或富氧，在使用相同水气比和水碳比的水蒸汽条件下能获得更高的水蒸汽分压和更高的转化率，减少了投资，提高了原料利用率，显著降低了能耗和气耗，经济效益显著。

CN 103303863 A

1. 由焦炉气制取氨合成气的方法，以经除尘、除焦及粗脱硫后的焦炉气为原料，其特征是按下述步骤进行：

1'：分离出焦炉气中的氢气，供后续使用；

2'：分离氢气后的剩余焦炉气为富甲烷气，依次与水蒸汽进行换热式蒸汽催化转化，将甲烷等烃类转化为氢和一氧化碳得到转化气，接着再与空气进行自热式催化转化，将转化气中的一氧化碳变换为氢气和二氧化碳，得到变换气；

3'：变换气脱除二氧化碳后得到脱碳气，将脱碳气与第 1' 步被分离出的氢气混合，净化后得到所说的氨合成气。

2. 如权利要求 1 所述的方法，其特征是所说第 1' 步的原料气以变压吸附方式分离出氢气。

3. 如权利要求 1 所述的方法，其特征是所说第 1' 步由原料气中分离出的氢气收率为 90(v)% 左右。

4. 如权利要求 1 所述的方法，其特征是所说第 2' 步中用于与水蒸汽混合的富甲烷气的硫含量小于 0.2ppm。

5. 如权利要求 1 所述的方法，其特征是第 2' 步中送入的水蒸汽量为与所说富甲烷气中的烃类总碳摩尔比为 $H_2O/C=2.7 \sim 4.0$。

6. 如权利要求 1 所述的方法，其特征是所说第 3' 步中氨合成气的氢气为来自变换气中所含的和由第 1' 步分离得到的氢气的总量。

7. 如权利要求 1 所述的方法，其特征是所说第 2' 步中加入的空气量为所说富甲烷气体积的 1.25 ～ 1.35 倍。

8. 如权利要求 1 所述的方法，其特征是第 2' 步中所说的富甲烷气与水蒸汽完成由甲烷转化为氢和一氧化碳的转化气中，残余甲烷的体积含量≤ 0.5%。

9. 如权利要求 1 所述的方法，其特征是第 2' 步中所说由富甲烷气与水蒸汽将甲烷转化为氢和一氧化碳的过程至少采用下述方式进行：

将富甲烷气压缩至 1~4Mpa 且硫含量小于 0.2ppm，加热至 250~450℃，再与加压至 1~4MPa 送入的水蒸汽混合；

所说的富甲烷气与水蒸汽的混合物于 400~550℃在换热式转化炉中进行由甲烷转化为氢和一氧化碳；

所说的富甲烷气与水蒸汽完成由甲烷转变为氢和一氧化碳的转化后，与已预热至与该转化气温度一致或接近的空气共同在二段炉中进行自热式转化得到氢和一氧化碳。

10. 如权利要求 1 所述的方法，其特征是所说第 3' 步与氢气混合后的混合气经净化处理后得到的合成气中，一氧化碳和二氧化碳总量≤ 20ppm。

Topsoe, Inc. – EX1003
Page 900 of 1210

由焦炉气制取氨合成气的方法

技术领域

[0001] 本发明涉及一种由焦炉气制取氨合成气的方法。

背景技术

[0002] 合成氨是目前制造化肥和许多化工产品的重要原料之一。其所需的氨合成气的制备已经历了早期多以煤和焦炭为原料生产的水煤气或半水煤气，随后逐步取代为便于管道输送和可降低合成气制备及后继工序运行费用的天然气。以天然气制备氨合成气的工艺流程，是先将天然气脱硫后，加入水蒸汽并配入空气进行催化转化，得到含 H_2、CO、CO_2、N_2 和 H_2O 的混合气后，进一步经过将其中的一氧化碳变换为等量的氢气和二氧化碳的变换及脱碳(脱除二氧化碳)及终端净化(精脱 CO 和 CO_2)等净化过程，得到由氢气和氮气按所需比例组成的氨合成气。目前氨合成气的氢氮比调节方式主要有以下两种，一是分离 H_2 的 H_2 收率，H_2 收率越高则 H_2/N_2 越大；二是脱碳，如在 PSA 脱碳同时可将其中多余的氮气除去。

[0003] 尽管以天然气或油为原料制取氨合成气的工艺技术在过去几十年里取得了长足的进展，但由于在世界能源结构中固体化石燃料的贮藏量远多于液体与气体，因此，今后以煤或煤化工副产物为原料生产合成气的比例仍会明显增加，综合利用煤加工过程中的副产品焦炉气具有巨大的经济效益和社会效益。

[0004] 焦炉气是焦化产业的主要副产品之一。煤在炼焦过程中，约有 80% 转化为焦炭，15% 转化为焦炉气，5% 转化为焦油和苯。焦炉气是煤在隔绝空气下，在高温炼焦过程中经焦化过程回收炉气后得到的富含氢气和甲烷的混合气体。以焦炉气为原料，将其中的甲烷(含 C_2 以上高级烃)转化生成 CO 和 H_2 的转化气，再于催化下使其中的 CO 与水蒸汽反应，变换成等量的 H_2 和 CO_2 的变换气，并脱除氢氮气体外的其余气体，使最终混合气的氢氮比符合要求的氨合成气，这是目前已有许多深入研究报道并在广泛使用的成熟技术。在上述的转化过程中，由于甲烷转化后得到的转化气中的 CO，经变换后最终均可转化为等量的 H_2，即 CO 和 H_2 的总和均为氨合成气中的 H_2 的等效气体，故在转化过程中所称的有效氢通常可视为是 H_2 和 CO 的总和。转化气的核心技术指标包括：一是转化气中残余 CH_4 尽量低(一般残余 $CH_4 \leqslant 0.5(v)\%$)，二是应满足最终氨合成气中的氢 / 氮比($H_2/N_2=3$)。目前对焦炉气中甲烷的转化，主要有非催化部分氧化法、催化部分氧化法、外热式蒸汽催化转化法和换热式催化转化法等几种。

[0005] 1、非催化部分氧化法，如中国专利 CN1446747A 所报道，是一种不使用催化剂，通过烧嘴将焦炉气与纯氧混合，在适宜的燃烧空间中进行部分氧化产生高温促使甲烷转化。与催化部分氧化法相比，非催化部分氧化法可以无需消耗为提高 CH_4 的平衡转化率和防止催化剂发生析碳而加入大量的蒸汽，在 1160~1600℃的温度反应后就能得到相应的转化气。转化气经变换后，最终需通过加入纯 N_2 调节为氨合成气所需的氢氮比。由于转化温度高，耗氧量大且对设备材质要求苛刻，是制约非催化部分氧化法推广应用的重要因素。

[0006] 2、催化部分氧化法，是在催化剂作用下，在较低温度下加入水蒸汽使 CH_4 转化生成 CO 和 H_2。由于催化剂对硫化物非常敏感，且中毒后生成的 NiS 无法再生而使催化剂失活，因

Topsoe, Inc. – EX1003
Page 901 of 1210

此在进入转化装置前的焦炉气中的硫含量须控制为总硫含量≤0.2ppm。催化部分氧化过程中，由于转化温度基本维持在1000℃左右，为了防止转化炉上部燃烧区高温烧结催化剂，催化部分氧化转化炉必须要有足够的燃烧空间，且由于加入大量蒸汽，为了防止水蒸汽冷凝，焦炉煤气和氧气均需加热至蒸汽露点温度以上，因而系统中必须设置各类换热设备和加热炉，导致了催化部分氧化所需的温度高，蒸汽耗量大。最后还需通过控制富氧空气中的氧浓度，使转化出口的混合气经净化处理后达到氨合成气所需的氢氮比。

[0007] 3、外热式蒸汽催化转化法，在《化工进展》1992.5中有详细阐述，外热式蒸汽转化即加压蒸汽转化，是在管外直接火焰加热的一段转化炉中的辐射段内，进行甲烷和水蒸气的转化反应，在对流段中回收烟气的余热。该方法虽投资省、风险小，但是有富裕蒸汽产生，如无法有效利用，则其能耗将明显高于换热式蒸汽催化转化法。

[0008] 4、换热式蒸汽催化转化法，如“小型合成氨厂节气节能工艺评价”（化工进展，1992.7）等文献所报道，是外热式蒸汽催化转化法基础上所做的进一步改进，其转化过程分两段进行，用换热式转化炉代替外热式转化炉，焦炉气和蒸汽的混合气首先进入换热式转化炉列管内，列管内装填转化催化剂，由管程外二段转化炉出口的高温转化气提供热量进行部分 CH_4 和水蒸汽转化，换热式转化后的混合气再与富氧空气混合后在第二段转化炉进行焦炉气的自热式转化，将第二段转化出口高温转化气通过换热式转化炉壳程加热转化炉内的列管，为列管内焦炉气和蒸汽的混合气提供焦炉气和蒸气转化所需的热量。因此，换热式蒸汽催化转化法更加有效地回收利用了转化炉出口高温气体的热量，但热量和蒸汽的消耗量依然较大，转化过程同样也要加入富氧空气，以达到氨合成气所需 $H_2/N_2=3$ 的要求。

[0009] 由目前以焦炉气制备氨合成气的上述几种主要方式和转化过程可以看出，其转化反应的温度都高于1000℃，特别是非催化部分氧化的转化温度甚至高达1400~1600℃，能耗较大，设备要求高，外热式蒸汽催化转化法有富裕蒸汽产生，但能耗较高；换热式蒸汽催化转化法蒸汽基本平衡，能耗低，但为减少氮气的引入量而使氨合成气达到最终所需的合格氢氮比，仍需要在焦炉气中使用纯氧或富氧空气，因而都需要辅以氧气的制取，导致要增加相应的制氧装置，不仅增加了操作的复杂性，也加大了设备投资。

发明内容

[0010] 针对上述情况，本发明在现有换热式蒸汽催化转化法基础上，提供了一种由焦炉气制取氨合成气的进一步改进方法，很好地解决了上述问题，转化勿需加入纯氧或富氧。

[0011] 本发明由焦炉气制取氨合成气的方法，同样是以经除尘、除焦及粗脱硫后的焦炉气为原料，按下述步骤进行：

1’：分离出焦炉气中的氢气，供后续使用；

2’：分离氢气后的剩余焦炉气为富甲烷气，依次与水蒸汽进行换热式蒸汽催化转化，将甲烷等烃类转化为氢和一氧化碳得到转化气，接着再与空气进行自热式催化转化，通过目前常规的变换过程，将转化气中的一氧化碳变换为氢气和二氧化碳，得到变换气；

3’：变换气脱除二氧化碳后得到脱碳气，将脱碳气与第1’步被分离出的氢气混合，净化后得到所说的氨合成气。

[0012] 本发明的上述方法中，相对于目前传统方法的重要和本质的区别是，首先将原料焦炉气中的氢气分离出来后，再按常规方式对剩余的富甲烷气依次进行与水蒸气的换热式

Topsoe, Inc. – EX1003
Page 902 of 1210

催化转化和空气的自热式催化转化，经变换、脱碳后再将之前被分离出的氢气混合，经终端净化后得到相应的氨合成气。因此，除对操作步骤单元的设置外，所涉及的各操作步骤，均可以选择和采用目前已有报道和 / 或使用的相应成熟技术和方式进行。

[0013] 其中，所说第 1' 步中由所说焦炉气原料对氢气的分离，可优选变压吸附（PSA）方式进行。由于对混合气体中氢的分离是变压吸附的典型方法，不仅已有众多深入的研究报道，也是目前已广泛使用的成熟技术。例如，可以参照包括如 CN101343580A 等文献报道的由焦炉气或高炉气分离提取氢气的成熟方式进行。

[0014] 实验显示，第 1' 步对原料气中氢气的分离虽然越彻底越好，但从经济角度考虑，一般情况下，由原料气中分离出氢气的收率约为 90(v)%，即可以取得使转化气中残余 CH_4 ≤ (v)0.5%，并使最终氨合成气氢氮比合格的满意效果，被分离出的氢气可达焦炉气总量的约 50(v)%。

[0015] 所说第 2' 步对分离氢气后的富甲烷气按常规方式与送入的水蒸汽换热式催化转化和空气自热式催化转化，进行将甲烷转化为氢和一氧化碳的转化，和将转化气中的一氧化碳进一步变换为氢气和二氧化碳而得到变换气，可以参照包括前述文献在内的现有各类成熟技术和方式进行。

[0016] 其中，为避免后续转化过程中所使用的催化剂中毒，所说用于与水蒸汽混合的所说富甲烷气中的硫含量优选应小于 0.2ppm。为此，必要时可以对该气体进一步按公开号 CN85103555A 等已有文献报道的方式进行精脱硫处理。

[0017] 所说第 2' 步进行的转化和变换时，送入的水蒸汽量优选为与该富甲烷气中烃类总碳的摩尔比为 $H_2O/C=2.7\sim4.0$。

[0018] 此外，本发明不同于传统方法进一步的显著差别和重要特点是，所说第 2' 步中进行转化所用的空气，被一次性加入；氢气为来自变换气中所含的氢和由第 1' 步分离得到的氢的氢气总量。试验显示，所说送入的空气量一般可优选为待进行转化的富甲烷气体积的 1.25~1.35 倍，以满足转化环境催化剂层温度足够高（通常≥ 860℃），残余 CH_4 才能足够低。

[0019] 所说第 2' 步由富甲烷气与水蒸汽完成由甲烷转化为氢和一氧化碳的转化气中，残余甲烷的体积含量优选应≤ 0.5%。

[0020] 进一步，第 2' 步中由富甲烷气与送入的水蒸汽进行由甲烷转化为氢和一氧化碳，在所说可采用目前已有报道和 / 或使用的相应常规技术和方式中，优先选用下述方式中的一种或任意形式的组合：

a. 将所说的富甲烷气压缩至 1~4Mpa 且硫含量小于 0.2ppm 并加热至 250~450℃，再与加压至 1~4MPa 送入的水蒸汽混合；

b. 所说的富甲烷气与水蒸汽的混合物于 400~550℃在换热式转化炉中进行由甲烷转化为氢和一氧化碳的转化；

c. 所说的富甲烷气与水蒸汽完成由甲烷向氢和一氧化碳的转化后，再与已预热至与其温度接近或一致后的空气共同在二段炉中进行由一氧化碳转化为氢气和一氧化碳的自热式催化转化。

[0021] 根据氨合成气的需要，可以按常规方式，对上述第 3' 步中与返回的氢气混合后的混合气体，进一步进行相应的终端净化处理，如采用甲烷化、铜洗、液氮洗、醇烃化、烷烃化等目前已有报道 / 使用的常规和成熟方法，进一步将其中一氧化碳和二氧化碳的含量降低

Topsoe, Inc. – EX1003
Page 903 of 1210

至允许的范围(通常其总量宜≤ 20ppm),无需再详细描述。

[0022] 以采用常规的二段炉进行焦炉气的转化和变换为例,本发明上述制取方法的一个典型和基本的氨合成气制取过程可如下述:

首先,对焦炉气常规除尘、除焦等预处理后,加压至 0.01~3.0MPa 后进入湿法脱硫,脱除大部分无机硫,常温干法脱除其中大部分有机硫;

脱硫后的焦炉气加压到 1.0~3.0Mpa 后送入 PSA(变压吸附)系统,分离出其中约 90(v)% 的 H_2,直接送入后续脱碳气管道。剩余的约为原焦炉气体积总量的 50(v)% 的富甲烷气体,进入后续转化/变换工序;

分离出 H_2 后的富甲烷气压缩至 1~4Mpa 并加热至 250~450℃,再经精脱硫处理,使其中的硫含量≤ 0.2ppm。然后与在 1~4Mpa 下送入的水蒸汽混合,水碳摩尔比为 $H_2O/C=2.7\sim4.0$。该混合气与二段炉出口经换热式转化炉换热后的转化气预热,升温到 400~550℃后进入换热式转化炉,在换热式转化炉进行甲烷水蒸汽转化。将换热式转化后温度约为 400~700℃的混合气,配入已预热至 500~600℃的工艺空气进入二段炉进行自热式催化转化,出二段转化炉的转化气中的残余甲烷小于 0.3(v)%, $(H_2+CO)/N_2=2$ 左右。约 900℃左右的高温转化气进入换热式转化炉壳程换热后,再预热换热式转化炉入口混合气,最后进入转化气废锅副产中压蒸汽;

经转化气废锅后的转化气经变换,混合气中的 H_2O、CO 生成 H_2、CO_2,经变换后的混合气中 CO 的含量小于 0.3(v)%,降温除水后的混合气脱碳至 CO_2 小于 0.3(v)%,与前述由 PSA 所分离出的 H_2 混合,达到合成氨工艺所需氢氮比的混合气;

上一步脱碳气与由 PSA 分离出的氢气混合后,再经终端净化处理,如用甲烷化处理,使最终氨合成气中的一氧化碳和二氧化碳的总量≤ 20ppm,最终制得杂质气体少,CH_4 ≤ 0.3(v)%, $H_2/N_2=3$ 的氨合成气。

[0023] 由此可以理解,与传统将全部焦炉气直接进行相应的转化、变换、脱碳及终端净化后制备氨合成气的方法相比,本发明采用先将焦炉气中的氢气分离,只需对剩余的富甲烷气进行转化、变换和脱碳,然后再将前期所分离出的氢气混合,经终端净化后最终得到氨合成气,具有不言而喻的显著优越性。首先,本发明方法先期将焦炉气中 90% 左右的氢气分离后,需进行转化、变换和脱碳的剩余富甲烷气较原焦炉气的体积几乎减少了一半,大量的氢气并不进入转化、变换及脱碳系统,不仅可大大减少电力和蒸汽的消耗,而且由于转化和变换过程中气体中的氢气分压的大为减小,在加入相同水气比和水碳比的水蒸汽情况下,可以产生更高的水蒸汽分压,从而能获得更高的转化过程和变换过程的转化率,大大提高了对原料的利用率。本发明另一重要的特点是直接加入为氨合成所需的工艺空气量进行换热式催化转化,通过返回前期所分离出的氢气,即可得到符合氨合成所需氢氮比的氨合成气,从而完全无需加入纯氧或富氧空气,并因此可完全无需相应的制氧装置,减少了投资,显著提高了综合经济效益。

[0024] 以下通过实施例的具体实施方式再对本发明的上述内容作进一步的详细说明。但不应将此理解为本发明上述主题的范围仅限于以下的实例。在不脱离本发明上述技术思想的情况下,根据本领域普通技术知识和惯用手段做出的各种替换或变更,均应包括在本发明的范围内。

Topsoe, Inc. – EX1003
Page 904 of 1210

具体实施方式

[0025] 实施例

焦炉气：气量 24600Nm^3/h，主要参数如表 1 所示：

表 1 焦炉气的参数

成分	CO_2	CO	H_2	CH_4	N_2	C_nH_m	有机硫	H_2S	焦油
V%	2.3	6.5	56.7	26.0	5.0	3.0	≤ 0.05	≤ 0.1	≤ 0.01

按下述步骤制取氨合成气：

1'：由气柜引出的焦炉气经二级 50kv 直流静电除焦器，除去焦炉气中的焦油后，进入 10kv 高压电除尘；

2'：经螺杆压缩机加压至 0.3MPa 后，进入湿法脱硫塔，脱除 H_2S、SO_2、HCl 和 HF 等有害气体成分，湿法脱硫后再进入水分离器分离除去游离水。湿法脱硫后焦炉气的有机硫 ≤ 200ppm，H_2S ≤ 20ppm；

3'：经常温预处理脱除有机硫至≤ 20ppm 后，加压至 2.0MPa，通过变压吸附分离提出焦炉气中 90% 左右的 H_2（约 12400Nm^3/h），直接送入后序 PSA 脱碳后的氢氮混合气管道；

4'：对分离出 H_2 后约剩余原焦炉气总量 50(v)% 的富甲烷气（约 11800Nm^3/h），取出部分（约 1200 Nm^3/h）作为燃料气分别送入原料气－蒸汽加热炉和空气加热炉，其余部分（约 10600Nm^3/h）压缩至 2.5MPa 后升温至 100℃左右，再经原料气－蒸汽加热炉加热继续升温至 390℃，参照前述 CN85103555A 报道的方式经精脱硫处理后，使该富甲烷气硫含量小于 0.1ppm；

5'：将 2.6Mpa 转化／中变废热锅炉副产的中压蒸汽（约 27720 Nm^3/h）经原料气－蒸汽加热炉加热升温至 390℃后，加入精脱硫后的富甲烷气，使混合气的水／碳比 H_2O/C=2.7。该混合气（约 38300 Nm^3/h）进入转化气换热器，经与后序二段炉出口经换热式转化炉换热后的转化气预热，升温到 450℃后进入换热式转化炉，在换热式转化炉内进行部分烃类转化，约 28% 的甲烷和 C_2 以上的烃类被转化，剩余含甲烷（约 4060 Nm^3/h）的 680℃高温混合气（约 43920Nm^3/h）进入二段转化炉；

6'：将 2.6MPa 转化／中变废热锅炉副产的中压蒸汽（约 3240 Nm^3/h）混入来自空气压缩机压缩至 2.7Mpa 并加热至约 100℃的压缩空气（约 14080 Nm^3/h）后，混合气体经空气加热炉加热升温至 500℃后，再与上述 680℃的富甲烷高温气（约 43920Nm^3/h）通入二段转化炉，先进行部分氢燃烧放热，使混合气升温至 1100℃后进一步完成剩余甲烷的转化。经二段转化炉后的转化气（约 66180Nm^3/h）中残余甲烷约 0.3(v)%（约 140 Nm^3/h）。将该转化气（约 880℃高温）直接通入换热转化炉壳程，为换热转化炉中甲烷向一氧化碳和氢气转化提供反应所需的热；

7'：上步经换热转化炉换热降温后的转化气（约 66180Nm^3/h）降温至约 540℃后，通入转化气换热器，用于加热前述换热转化炉入口混合气，使温度进一步降至约 470℃后，将其通入转化／中变废热锅炉回收热量（可同时副产 2.6MPa 中压蒸汽）；

8'：降温至 330℃的转化气（约 66180Nm^3/h）送入中温变换炉约 80% 的 CO 与 H_2O 反应生成 H_2 和 CO_2，同时产生大量的反应热由中变气（中温变换炉变换后的出口气，含 H_2、CO_2 和水蒸汽及少量 CO）带出，该 470℃中变气经加热后序的甲烷化入口气后，降温至 400℃左右，送入转化／中变废热锅炉（可副产 2.6Mpa 的中压蒸汽）。降温至 200℃的中变气送入低温变换炉，使混合气中的 CO 进一步降低至 0.3(v)% 以下，产生的反应热由 220℃低变气带出（通过

Topsoe, Inc. – EX1003
Page 905 of 1210

低变废热锅炉可副产 0.3MPa 低压蒸汽)。140℃低变气再经过给水预热器和水冷器后,降温至 40℃左右,使其中的蒸汽冷凝成水分离除去 ;

9’:低变气(约 40000Nm^3/h),在 40℃左右和 1.9Mpa 下通过 PSA (变压吸附) 脱除混合气体中的 CO_2 至含量低于 0.3(v)% 后,加入之前被分离提出的 H_2 (约 12400Nm^3/h) 混合。混合气加热至 270℃后进入甲烷化炉,通过甲烷化除去混合气中的 CO 和 CO_2 后,使 $CO+CO_2 \leqslant 20ppm$,降温至 40℃左右, 通过甲烷化气水分离器除去其中的水 ;

10’:上述 H_2、N_2 混合气为含 H_2 (约 34200 Nm^3/h),N_2 (约 11400 Nm^3/h),$H_2/N_2=3.0$,残余 $CH_4 \leqslant 0.5$(v)%(约 232Nm^3/h),及 Ar 等剩余惰性气体的氨合成气。经合成压缩加压至 22MPa 左右送入氨合成塔生产合成氨。

[0026] 上述实施例生产合成氨,分离出氢后的剩余烃类解析气,部分用作原料气 - 蒸汽加热炉和空气加热炉燃料气,其余烃类解析气即用作合成转化变换的原料气(即本发明所说的焦炉气原料)。通过上述 24200Nm^3/h 焦炉气生产合成氨,每小时电耗 14700 度,每小时产氨 17 吨,主要消耗指标如下 :吨氨消耗焦炉气 1425 m^3,吨氨电耗 865kwh。二段转化燃烧所需的空气提供的氮即为氨合成气所需氮,转化 / 中变废热锅炉副产的中压蒸汽返回用于转化和变换所需工艺蒸汽,副产蒸汽和工艺消耗蒸汽基本平衡,生产过程还略有低压蒸汽输出。

Topsoe, Inc. – EX1003
Page 906 of 1210

VIA *e*FILE

PATENT APPLICATION
Docket No. 283386WOUS02_495230-102

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	)

AMENDMENT "B" AND RESPONSE UNDER 37 C.F.R. § 1.530

VIA *e*FILE AF
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

In response to the Final Office Action dated April 22, 2024, 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.

Remarks/Arguments begin on page 6 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.

Cancel claim 20.

Cancel claim 21.

Cancel claim 22.

Cancel claim 23.

Cancel claim 24.

Cancel claim 25.

Cancel claim 26.

REMARKS

A. BACKGROUND

The present Amendment is in response to the Office Action dated April 22, 2024 by the U.S. Patent and Trademark Office ("PTO"). Claims 1-26 were pending, of which claims 21-26 were rejected in view of prior art.[1]

By this Amendment, please cancel claims 21-26. Claims 1, 10, and 19 are indicated as amended as presented in the Amendment "A" dated November 2, 2024 and claim 20 was previously canceled. Patent Owner thanks the Examiner for his indication that claims 1-19 are patentable.

Reconsideration of the application is respectfully requested in view of the above amendments to the claims and the following remarks.

B. NOTICE OF EXISTENCE OF CONCURRENT LITIGATION PROCEEDINGS

As required under 37 C.F.R. § 1.565, Patent Owner informs the PTO of concurrent litigation proceedings in which U.S. Patent No. 11,286,168 (the "'168 Patent") is involved. As provided in greater detail in the Notice filed concurrently with this response, Topsoe, Inc. ("Topsoe") filed a complaint "Complaint" in which the '168 Patent is involved against Patent Owner on January 31, 2024 in the United States District Court, Southern District of Texas, Galveston Division (Case No.: 3:24-cv-00033). A notice of the court action was filed with the USPTO on January 31, 2024 and February 1, 2024. At this time, litigation remains ongoing, and no decision has been rendered or judgment issued.

Patent Owner notes the Complaint includes a first count requesting declaratory judgment of unenforceability of the '168 Patent, a second count alleging unfair competition and false advertising under the Lanham Act, and a third count alleging common law unfair competition. Included in the first count seeking unenforceability of the '168 Patent is an allegation by Topsoe that the Patent Owner committed fraud on the PTO in procuring the '168 Patent. Patent Owner strongly denies the allegations of fraud on the PTO, and is defending itself to the full extent against the allegations by Topsoe.

Specifically, Topsoe alleges that, prior to the filing date, Patent Owner knew of Topsoe's alleged prior art, including but not limited to a 2009 Fertilizer Association of India ("FAI")

[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.

Annual Seminar presentation and paper; Topsoe's technology installed in Indian Farmers Fertilizer Cooperative Ltd.'s Aonla Fertilizer plant, which Patent Owner was hired to revamp between 2014 and 2018; and a 2012 MEGAMMONIA® - the Mega-Ammonia Process paper. Patent Owner respectfully submits that it did not deliberately and knowingly withhold and/or omit any material information from the PTO during prosecution and reexamination of the '168 Patent, including the alleged prior art references listed above.

Patent Owner notes that the allegations are without merit at least because these references are cumulative and/or not material. Furthermore, while Topsoe has identified the individuals it contends were associated with the filing or prosecution of the '168 Patent, Topsoe has not tied specific knowledge of the prior art references to those specific individuals. Instead, Topsoe refers to Patent Owner's general knowledge of the alleged prior art references. Even general knowledge of a reference, without knowledge of the specific information within the reference is not enough to prove fraud on the PTO. Furthermore, Topsoe has not alleged facts to support its base allegation that Patent Owner deliberately and knowingly withheld and/or omitted material information. Instead, Topsoe has only asserted bare allegations of intent, which do not even rise to the level of inference of intent, and thus has failed to state a claim for invalidity due to inequitable conduct.

With respect to the 2009 Fertilizer Association of India ("FAI") Annual Seminar presentation and paper, **Patent Owner respectfully submits that this reference was submitted in an Information Disclosure Statement (IDS) filed on November 2, 2023** during these reexamination proceedings, when Topsoe made Patent Owner aware of the reference.

C. UPDATED INFORMATION DISCLOSURE STATEMENT

Also submitted herewith is an updated IDS including the Complaint and an Amended Complaint filed May 2, 2024, as well as references Patent Owner has become aware of during the above-reference litigation proceedings.

With respect to the 2012 MEGAMMONIA® - the Mega-Ammonia Process paper, Patent Owner has searched for this referenced paper and found only a brief description of a MEGAMMONIA® process in the January | February 2012 issue of *Nitrogen + Syngas* (see p. 39). This document will be included in the updated IDS. Patent Owner also has requested, from Topsoe, a copy of the 2012 MEGAMMONIA® - the Mega-Ammonia Process document alleged

by Topsoe to be prior art. Patent Owner has not received a copy of the 2012 MEGAMMONIA® - the Mega-Ammonia Process document from Topsoe.

With respect to Topsoe's technology installed in Indian Farmers Fertilizer Cooperative Ltd.'s Aonla Fertilizer plant, Patent Owner is submitting in the updated IDS a paper entitled "Experience of Energy Saving and Naphtha to Gas Conversion Projects at IFFCO" from the Ammonia Technical Manual, 2007.

Also included in the updated IDS are other references Topsoe has included in the Complaint: U.S. Patent No. 7,465,324; U.S. Patent Application Publication No. 2002/0151749; U.S. Patent Application Publication No. 2019/0023565; U.S Patent Application Publication No. 2012/0279033; U.S. Patent No. 11, 155,468; U.S. Patent No. 10,464,818; and EP Publication No. 3067318 (EP App. No. 16168159).

The updated IDS also includes additional references Patent Owner is submitting consistent with its duty of disclosure.

D. REJECTIONS UNDER 35 U.S.C. §§ 102 AND 103

Claims 21-23 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") and Foreign Patent No. EP2817260 ("EP '260"). Claims 24 and 25 stand rejected under 35 U.S.C. § 103(a) as allegedly being unpatentable over EP '260 in view of Non-Patent Literature Document "Ammonia: Principles and Industrial Practice" ("Ammonia"). Claim 26 stands rejected under 35 U.S.C. § 102(a)as allegedly being anticipated by EP '260.

Claims 21-26 are canceled, thereby rendering these rejections moot.

E. PATENTABLE SUBJECT MATTER

The Examiner's indication that claims 1-19 are patentable is appreciated.

Patent Owner submits the following comments concerning the Examiner's statements of reasons for the indication of patentable subject matter in the Office Action. Patent Owner respectfully submits that the claimed invention(s) as set forth in the independent claim 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 Patentability 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 Patentability 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.

F. CONCLUSION

Reservation of Rights

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Dated this 28th day of May, 2024.

Respectfully submitted,

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CN102381717A Method for converting natural gas to produce ammonia and device

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Method for converting natural gas to produce ammonia and device

Abstract

The invention relates to a method for converting natural gas to produce ammonia and a device. 70%-80% of natural gas is partially oxidized with oxygen to generate coarse synthesis gas, 20%-30% of natural gas is mixed with medium-pressure steam and enters a converting tube of a heat exchange type converter to realize reaction so as to generate oxide of hydrogen and carbon, high-temperature dry gasis fed into a changing system to be added with steam prior to being fed to a washing saturator, saturation of gas is carried out by the aid of condensate from the changing system, steam required to be fed enters the changing system to realize reaction prior to entering a decarburization system, purified gas of the decarburization system is fed to a gas refining unit, removed CO2 is fed to a urea device, liquid-phase methane of the gas refining unit is recycled, carbon monoxide, methane and argon are used as fuel, purified technical gas is added with high-purity nitrogen, then fed into a synthesis gas compressor, synthesized by a synthesis tower and separated by a separator, and liquid ammonia is fed to the urea device. The method and the device have the advantages that the device is low in investment, and energy consumption is low.

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CLAIMS CN102381717A

1.

13 A method for producing ammonia by converting natural gas, characterized in that:

14 After two stages of compression, the natural gas with a pressure of 6.52MPa (G), a temperature of 135.7℃ and a total sulfur content of 10mg/l, of which 70-80% by mass and oxygen from air separation enter two gasifiers through nozzles respectively, and undergo partial oxidation reaction in the reaction chamber of the gasifier. The temperature in the gasifier is controlled at 1100-1200℃ by the oxygen/natural gas ratio to generate crude synthesis gas with H₂, CO, CO₂ as raw materials and a small amount of methane;

19 After desulfurization, natural gas with a mass of 20-30% is mixed with medium-pressure steam, and the water-carbon mass ratio is controlled to be 3:1. After the mixed gas is preheated to 540-560° C by the mixed gas at the outlet of the gasifier and the heat exchange reformer, it enters the heat exchange reformer, and the natural gas and the medium-pressure steam undergo a conversion reaction in the reforming tube equipped with a nickel catalyst to generate hydrogen and carbon oxides; the gas pressure out of the heat exchange reformer is 6.3MP(G), the temperature is about 860° C, and the methane content is 7.75% (mol%); the process gas from the outlet of the gasifier and the heat exchange reformer is still a high-temperature dry gas of 547.8° C after heat exchange, and is sent to the conversion system, added with steam, and sent to the water washing saturation tower, and the gas is saturated with the condensate from the conversion system;

28 The mixed gas at the outlet of the heat exchange reformer at 6.4MPa and 220.5℃, which has been humidified by the water washing saturation tower, is supplemented with the required amount of steam and heated to 320℃ by the outlet gas of the conversion system. It enters the conversion system. Under the action of the catalyst, part of CO is converted into CO₂, releasing reaction heat. The process gas at the outlet contains 0.412% CO and has a temperature of 249℃, and enters the decarbonization system.

33 The decarbonization system adopts a process flow of two-stage absorption, two-stage regeneration and one-stage high-pressure flash evaporation; the process gas after decarbonization by MDEA solution is sent to the gas refining unit after defoaming and separation of liquid droplets; the CO₂ gas removed in the decarbonization system is sent to the urea unit after cooling and separation;

37 The gas refining unit uses liquid nitrogen washing technology under cryogenic conditions. The process gas is

gradually cooled to -188° C. During the cooling process, methane condenses at -175-185° C, and most of the methane is separated from the process gas in liquid phase. The liquid methane is decompressed to 1.5MPa and then recycled after reheating. The carbon monoxide, methane and argon in the gas phase are reheated and sent to the outside of the boundary area for use as fuel. The purified process gas is then mixed with high-purity nitrogen, and the hydrogen-nitrogen mass ratio is adjusted to 3:1 before being sent to the synthesis gas compressor.

39 The synthesis gas compressor is divided into three stages for compression. In the third stage, the synthesis gas is mixed with the circulating gas and the pressure is raised to 151 bar (G). After being heated to 380° C by the outlet gas of the third synthesis tower and the outlet synthesis gas of the first synthesis tower, it enters the first synthesis tower. The outlet gas temperature of the first synthesis tower is 497.2° C. After preheating the feed gas of the first synthesis tower, the temperature is reduced to 380° C before entering the second synthesis tower; the outlet gas temperature of the second synthesis tower is 472.8° C, and the temperature is reduced to 380° C before entering the third synthesis tower; the outlet gas temperature of the third synthesis tower is 442.2° C, which is used to heat the synthesis gas at the outlet of the synthesis gas compressor, and is cooled to 4.4° C before entering the separator; the circulating gas separated by the separator recovers the cold and goes to the inlet of the synthesis gas compressor; in the separator, the liquid ammonia is separated and becomes a liquid ammonia product after flash evaporation, condensation and pressure reduction to go to the urea device.

2.

59 The method for producing ammonia by natural gas reforming according to claim 1 is characterized in that: a non-quenching process gasifier is used, the gasification pressure is 6-7Mpa; and the operating temperature should be in the range of 1102-1150° C.

3.

65 The method for producing ammonia by converting natural gas according to claim 1 is characterized in that: a normal temperature desulfurization tank is provided at the natural gas compression inlet to remove inorganic sulfur in the natural gas, and the H2S content in the natural gas after desulfurization is less than 2ppm.

4.

71 The method for producing ammonia by converting natural gas according to claim 1, characterized in that:

72 Liquid ammonia separation is post-tower separation, with two-stage ammonia cooling, and the ammonia condenser temperatures are 17-19° C and 1-3° C respectively.

5.

77 1. A device for producing ammonia by natural gas reforming as claimed in claim 1, comprising a gasifier, a heat exchange reformer, a water washing saturation tower, a conversion system, a decarbonization system, a gas refining unit, a synthesis gas compressor, a first synthesis tower, a second synthesis tower, a third synthesis tower, a separator, and a urea device; characterized in that: the gasifier inlet is connected to the natural gas and

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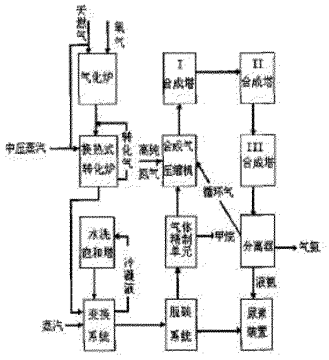
权利要求书 2 页 说明书 9 页 附图 1 页

(54)发明名称

一种天然气转化生产氨的方法及装置

(57)摘要

本发明涉及一种天然气转化生产氨的方法及装置，70～80%天然气与氧气进行部分氧化，生成粗合成气；20～30%的天然气与中压蒸汽混合，进入换热式转化炉转化管内反应，生成氢和碳的氧化物；高温干气送入变换系统配入蒸汽送入水洗饱和塔，用来自变换系统的冷凝液对气体进行饱和；补入需要的蒸汽量进入到变换系统反应后进入脱碳系统；脱碳系统的净化气送往气体精制单元；脱除的CO_2送往尿素装置；气体精制单元液相甲烷回用；一氧化碳、甲烷和氩作燃料使用；净化后的工艺气再配入高纯氮气，送入合成气压缩机；经合成塔合成，分离器分离，液氨去尿素装置；本发明具有装置投资低，能耗小的优点。



CN 102381717 A

1. 一种天然气转化生产氨的方法，其特征在于：

经两段压缩后压力为 6.52MPa(G)，温度为 135.7℃、总硫 10mg/l 的天然气，其中质量 70 ～ 80％与来自空分的氧气分别通过喷嘴进入两台气化炉，在气化炉的反应室进行部分氧化反应，以氧 / 天然气比来控制气化炉内的温度 1100 ～ 1200℃，生成以 H_2、CO、CO_2 为原料的粗合成气和少量的甲烷；

质量为 20 ～ 30％的天然气经脱硫后与中压蒸汽混合，控制水碳质量比为 3 ： 1，混合气被气化炉和换热式转化炉出口的混合气预热到 540 ～ 560℃后，进入换热式转化炉内，天然气与中压水蒸汽在装有镍催化剂的转化管内发生转化反应，生成氢和碳的氧化物；出换热式转化炉的气体压力为 6.3MP(G)，温度约 860℃，含甲烷 7.75％ (mol％)；来自气化炉和换热式转化炉出口的工艺气经过换热后仍然为 547.8℃的高温干气，送入变换系统，配入蒸汽，送入水洗饱和塔中，用来自变换系统的冷凝液对该气体进行饱和；

经过水洗饱和塔增湿的 6.4MPa，220.5℃的换热式转化炉出口的混合气体，补入需要的蒸汽量，用变换系统出口气加热到 320℃，进入到变换系统，在催化剂作用下，CO 部分转化为 CO_2，放出反应热，出口的工艺气中含有 0.412％的 CO，温度为 249℃，进入脱碳系统；

脱碳系统采用两段吸收、两段再生加一级高压闪蒸的工艺流程；经 MDEA 溶液脱碳后的工艺气，经除沫和离液滴后的净化气送往气体精制单元；脱碳系统中脱除的 CO_2 气体经降温、分离后送往尿素装置；

气体精制单元采用深冷条件下液氮洗技术，工艺气逐渐冷却至 -188℃，在冷却过程中，甲烷在 -175 ～ 185℃冷凝，大部分的甲烷以液相被从工艺气中分离出来，液相甲烷减压至 1.5MPa 后经回收冷量复热后回用；气相中的一氧化碳、甲烷和氩复热回温后送往界区外作燃料使用；净化后的工艺气再配入高纯氮气，调整氢氮质量比为 3 ： 1 送入合成气压缩机；

合成气压缩机分三段进行压缩，在第三段中与循环气混合提压到 151bar(G)，被第三合成塔出口气和第一合成塔出口合成气加热到 380℃后进入第一合成塔，第一合成塔的出口气温度 497.2℃，预热第一合成塔的进料气后温度降到 380℃进入第二合成塔；第二合成塔出口气中温度 472.8℃，温度降低至 380℃进入第三合成塔；第三合成塔出口气温度 442.2℃，去加热合成气压缩机出口的合成气，被冷却到 4.4℃进入分离器；分离器分离出来的循环气回收冷量后去合成气压缩机入口；在分离器中液氨被分离出来经闪蒸、冷凝、降压后成为液氨产品去尿素装置。

2. 根据权利要求 1 所述的天然气转化生产氨的方法，其特征在于：采用非激冷流程气化炉，气化压力 6 ～ 7Mpa；操作温度应该在 1102 ～ 1150℃范围内。

3. 根据权利要求 1 所述的天然气转化生产氨的方法，其特征在于：天然气压缩入口设置常温脱硫槽，脱除天然气中的无机硫，脱硫后天然气中的 H2S 含量＜ 2ppm。

4. 根据权利要求 1 所述的天然气转化生产氨的方法，其特征在于：

液氨分离为塔后分离，两级氨冷，氨冷凝器温度分别为 17 ～ 19℃和 1 ～ 3℃。

5. 一种权利要求 1 所述的天然气转化生产氨的装置，包括气化炉、换热式转化炉、水洗饱和塔、变换系统、脱碳系统、气体精致单元、合成气压缩机、第一合成塔、第二合成塔、第三合成塔、分离器、尿素装置；其特征在于：气化炉进口与天然气和氧气进气喷嘴连接，出口与换热式转化炉转化管壳程入口连接，换热式转化炉设有天然气和中压蒸汽入口与转化管连接，转化管出口与转化管壳程入口连接；转化管壳程出口与变换系统壳程连接；变换系

Topsoe, Inc. – EX1003
Page 921 of 1210

统壳程与蒸汽管线连接，变换系统壳程出口与水洗饱和塔连接，水洗饱和塔与变换系统冷凝液出口连接，水洗饱和塔出口与变换系统反应管连接；变换系统反应管与脱碳系统连接；脱碳系统与气体精制单元、尿素装置连接；气体精制单元合成气压缩机连接；合成气压缩机通过第一合成塔、第二合成塔、第三合成塔与分离器连接；分离器的循环气出口与合成气压缩机连接；分离器液氨出口与尿素装置连接。

Topsoe, Inc. – EX1003
Page 922 of 1210

一种天然气转化生产氨的方法及装置

技术领域

[0001] 本发明涉及一种天然气转化生产氨的方法及装置。

背景技术

[0002] 合成氨工艺主要包括气化（转化）、变换、净化、氨合成四个过程，目前世界各大合成氨装置的生产工艺均是组合工艺，即各单元采用不同工艺，经过优化、合理的组合构成合成氨的生产工艺。

[0003] 传统的合成氨工艺中一般都是采用两段加压蒸汽转化流程，目前的低能耗大型合成氨蒸汽工艺主要有 Kellogg 的 MEAP 工艺、Topsoe 工艺、Braun 的深冷净化工艺和 Uhde-ICI-AMV 工艺。

[0004] 蒸汽转化法与部分氧化法相比，具有从水中获得氢气的优势，生成的有效气体要比传统的部分氧化法多 1.45%，最新的天然气蒸汽转化法工艺制合成氨，在能量消耗角度上仍有明显优势。但天然气蒸汽转化需要燃气在换热管外加热提供需要的反应热，这就存在燃烧尾气排放带来的环境污染和热量损失；由于高的加热温度对炉管的材质要求较高，在设备上的一次性投资较大；且烧嘴燃烧系统的调节操作较为复杂。

[0005] 天然气的非催化部分氧化工艺的设备相对简单，没有催化剂，投资低；而且操作方便，易于控制；热量交换直接在反应物料间完成，不需要外界供热，因此没有废气和废热的排放；而且反应后干气中二氧化碳的生成量比蒸汽转化法少 40%。由于气化炉出口温度高，目前采用的激冷工艺造成的热量损失较大，能耗高；但如果不采用激冷工艺，直接回收高品位热量，对设备材质的要求高；同时部分氧化工艺需要装置配套空分单元。

[0006] 目前先进的二段蒸汽转化工艺是与深冷净化配套使用的，在二段炉里加入过量 50%的空气。空气中多余 50%的氮跟随工艺气通过变换和脱碳，造成了气相负荷的浪费。另外空气中的氩进入工艺气后只有 50%在深冷净化中脱除，剩余的部分进入合成回路，造成合成回路有弛放气排放，从而形成了氢的损失。

[0007] 通过目前开发出的各种换热式蒸汽转化工艺的对比，可以看出以上工艺都是基于两段蒸汽转化基础上，利用的都是自热式二段蒸汽转化的反应热。虽然减少了一段蒸汽转化炉的加热燃料气，但由于热负荷不足，装置仍然需要增加一个前置直热式加热炉提供原料气、空气预热的热量，或者仍存在外热式常规一段蒸汽转化炉，装置仍然存在烟气的排放和热量损失。

[0008] 一段蒸汽转化炉设备庞大，转化炉管为高温合金材料，一次投资昂贵。一段转化炉为间接加热炉，加热燃烧产生的废气有热量损失，并且对环境造成污染。

[0009] 蒸汽转化法能够从水中获得工艺需要的氢，但是需要外界提供转化反应所需要的热量；部分氧化工艺的设备简单、投资低，而且气化炉出口工艺气具有较高的温度。将这两种工艺的优点结合起来，形成的工艺应具有流程简单、流程短、催化剂使用量少、能量利用合理、热效率高、操作简单、消耗低、国产化力度大、设备台数少、一次性投资低等优点。

Topsoe, Inc. – EX1003
Page 923 of 1210

发明内容

[0010] 本发明的目的是提供一种天然气转化生产氨的方法及装置，将蒸汽转化法与部分氧化法结合起来，实现能量的合理配置和低的原料消耗，即在部分氧化炉后配置蒸汽转化工艺，使部分氧化后的高温工艺气替代燃料气为蒸汽转化反应提供需要的热量。这样既充分利用了高温位的热量，又避免了常规蒸汽转换工艺的烟气排放带走的热量损失和环境污染。在原料分配上，70 ～ 80％的天然气进入两台气化炉，其余 20 ～ 30％送入换热式蒸汽转化炉。

[0011] 本发明所述的一种天然气转化生产氨的方法是经两段压缩后压力为 6.52MPa(G)，温度为 135.7℃、总硫 10mg/l 的天然气，其中质量 70 ～ 80％与来自空分的氧气分别通过喷嘴进入两台气化炉，在气化炉的反应室进行部分氧化反应，以氧 / 天然气比来控制气化炉内的温度 1100 ～ 1200℃，生成以 H_2、CO、CO_2 为原料的粗合成气和少量的甲烷；其余质量 20 ～ 30％天然气进入换热式蒸汽转化炉；

[0012] 从气化炉反应室出来的 1050 ～ 1150℃的粗合成气和少量的甲烷直接进入后续的换热式转化炉，与换热式转化炉出口的 800 ～ 900℃的 20 ～ 30％的转化工艺气混合，混合后 1000 ～ 1050℃的高温气体作为换热式转化炉蒸汽转化反应的加热热源；利用该温度把蒸汽转化的原料气加热至 540 ～ 560℃，送入到换热式转化炉的转化管中进行反应，转化管出口的工艺气温度为 850 ～ 880℃；

[0013] 换热式转化炉中，转化管外部加热介质为换热式转化炉和气化炉中出来的混合气，加热温度稳定，且炉管内外的压差小，炉管可以采用不太昂贵的合金作为管材，转化压力的提高，使得庞大的方箱炉可以被较小的圆筒形换热转化炉所代替，这样材料的用量将会减少，同时占地小、投资省，节约了高温合金管道，热损失减小，没有烧嘴燃烧加热的烟气排放和引风机动力设备。

[0014] 经两段压缩后压力为 6.52MPa(G)，温度为 135.7℃、总硫 10mg/l 的质量为 20 ～ 30％的天然气经脱硫后与中压蒸汽混合，控制水碳质比为 3 ： 1，混合气被气化炉和换热式转化炉出口的混合气预热到 540 ～ 560℃后，进入换热式转化炉内，天然气与中压水蒸汽在装有镍催化剂的转化管内发生转化反应，生成氢和碳的氧化物；出换热式转化炉的气体压力为 6.3MP(G)，温度约 860℃，含甲烷约 7.75％ (mol％)；来自气化炉和换热式转化炉出口的工艺气经过换热后仍然为 547.8℃的高温干气，送入变换系统，配入蒸汽，以满足变换反应需要的汽气比，将该气体送入水洗饱和塔中，用来自变换系统的冷凝液对该气体进行饱和，以增加气体中的水含量从而降低工艺蒸汽的加入量，通过饱和塔饱和的水蒸汽量可以满足变换所需工艺蒸汽量的 75％，这样既利用了工艺气的热量，又免去了处理变换冷凝液耗用的蒸汽量。把常规的工艺冷凝液排放、处理分部进行，改进为循环回收利用。从而节约了大量的能耗。这样在饱和塔出口的气体中就仅需要加入工艺蒸汽 9.73 吨就可以满足变换的需要。

[0015] 经过水洗饱和塔增湿的 6.4MPa，220.5℃的换热式转化炉出口的混合气体，补入需要的蒸汽量，用变换系统出口气加热到 320℃，进入到变换系统，在催化剂作用下，CO 部分转化为 CO_2，放出反应热，出口的工艺气中含有 0.412％的 CO，温度为 249℃，进入脱碳系统；脱碳系统采用两段吸收、两段再生加一级高压闪蒸的工艺流程；经 MDEA 溶液脱碳后的工艺气，经除沫和离液滴后的净化气送往气体精制单元；脱碳系统中脱除的 CO_2 气体经降温、分

Topsoe, Inc. – EX1003
Page 924 of 1210

离后送往尿素装置；

[0016] 气体精制单元采用深冷条件下液氮洗技术，工艺气逐渐冷却至 -188℃，在冷却过程中，甲烷在 -175 ～ 185℃冷凝，大部分的甲烷以液相被从工艺气中分离出来，液相甲烷减压至 1.5MPa 后经回收冷量复热后回用；气相中的一氧化碳、甲烷和氩复热回温后送往界区外作燃料使用；净化后的工艺气再配入高纯氮气，调整氢氮比为 3 ： 1 送入合成气压缩机；

[0017] 合成气压缩机分三段进行压缩，在第三段中与循环气混合提压到 151bar(G)，被第三合成塔出口气和第一合成塔出口合成气加热到 380℃后进入第一合成塔，第一合成塔的入口气中含有氨 3 ～ 4%，出口气含 11 ～ 12%的氨，温度约 497 ～ 499℃，预热第一合成塔的进料气后温度降到 380℃进入第二合成塔；第二合成塔出口气中氨含量 17 ～ 18%，温度 472 ～ 474℃，温度降低至 380℃进入第三合成塔；第三合成塔出口气中氨含量 22 ～ 23%，温度 442 ～ 444℃，去加热合成气压缩机出口的合成气，被冷却到 4 ～ 5℃进入分离器；分离器分离出来的循环气回收冷量后去合成气压缩机入口；在分离器中液氨被分离出来经闪蒸、冷凝、降压后成为液氨产品去尿素装置。

[0018] 本发明中的换热式转化工艺是利用部分氧化炉出口的工艺气作为换热式转化的加热热源，不需要额外的加热炉供热，系统没有燃烧烟气和由此产生的热量损失。减少了常规部分氧化气化炉冷激工艺造成的热量损失，同时又通过蒸汽转化法获得较多的氢，降低了原料天然气的消耗。70 ～ 80%的天然气与来自空分的氧气分别通过工艺喷嘴进入气化炉，在气化炉的反应室进行部分氧化反应，以氧 / 天然气比来控制气化炉内的温度 1100 ～ 1200℃。从气化炉反应室出来的 1050 ～ 1150℃的粗合成气直接送往后续的换热式转化炉，与换热式转化炉出口的 800 ～ 900℃的 20 ～ 30%的转化工艺气混合，混合后 1000 ～ 1050℃的高温气体作为换热式转化炉蒸汽转化反应的加热热源。

[0019] 本发明中的要求的换热式转化炉制造难度和制造成本低，因为部分氧化炉的制造已经有成熟技术，换热式转化炉在甲醇工业中有应用，国内小型合成氨装置中也有应用业绩，同时由于工艺条件相对也不是很苛刻，因此在材料选用和设备的制造上都不会有大的障碍存在。

[0020] 本发明采用非激冷流程气化炉，气化压力选则为 6 ～ 7MPa。在此压力下，两台非激冷流程气化炉的生产能力能够达到 33 万吨合成氨（单台炉能力达到 700 吨氨 / 天）。

[0021] 本发明中气化的最佳操作温度应该在 1102 ～ 1150℃范围内。

[0022] 本发明中天然气不预热。

[0023] 本发明中，在天然气压缩入口设置常温脱硫槽，脱除天然气中的无机硫，脱硫后天然气中的 H_2S 含量＜ 2ppm。

[0024] 本发明是用换热式转化炉出口的工艺气将混合原料气加热到 540 ～ 560℃，转化管出口的工艺气温度为 850 ～ 880℃。

[0025] 本发明中蒸汽转化水碳比远大于 6.0MPa 下甲烷蒸汽转化的理论最小水碳比，从而保证不发生析炭反应。

[0026] 本发明中采用 MDEA 脱碳工艺。

[0027] 本发明采用液氮洗进行气体精制。

[0028] 本发明采用三塔三废锅的流程合成反应热用于加热锅炉给水副产 6 ～ 7MPa 的过热蒸汽。液氨分离为塔后分离，两级氨冷，氨冷凝器温度分别为 17 ～ 19℃和 1 ～ 3℃。冰

Topsoe, Inc. – EX1003
Page 925 of 1210

机为两段压缩，压缩后的气氨经水冷却后，送入热氨储罐，最终送往用户。

[0029] 和现有技术相比，本发明的方法具有如下主要的优点：

[0030] 1、本发明改变了目前大型合成氨装置造气工艺单一选择蒸汽转化法或部分氧化法的理念，创造性的充分利用两种工艺的优点，将它们合理的组合在一起，实现能量的合理利用和装置能耗的降低。由于造气过程中降低了部分氧化的温度，而且通过蒸汽转化从水中获得了一部分氢，所以在同样天然气耗量的情况下，产生的有效气体要比蒸汽转化法多 2 ～ 3%；同时由于后续气体净化工艺的合理配置，系统中没有弛放气造成的氢损失，使得天然气耗量也大幅下降，吨合成氨消耗天然气 690 ～ 700Nm^3，吨合成氨综合能耗为 30 ～ 31GJ；

[0031] 2、本发明提出通过降低天然气部分氧化过程甲烷的单程转化率，减少气化炉中燃烧消耗的氢气和气化炉的耗氧量，从而实现原料消耗的下降和装置综合能耗降低的理念；本发明中未转化的甲烷通过后续配置的液氮洗流程完全回收，返回到天然气压缩机入口回用。气化炉中没有反应的的甲烷的循环回收，只是增加了天然气压缩机的动力能耗。传统部分氧化工艺出口甲烷含量为 0.46%左右。本发明中气化炉出口的甲烷含量为 4%左右，天然气压缩机因此而增加了压缩功耗，但与减少气化炉燃烧的氢气量和减少的耗氧量相比，能量是节约的。本发明的这种思路打破了传统工艺造气部分高甲烷转化率，并通过工艺的模拟计算证明了这种思路的合理性；

[0032] 3、本发明中气化炉出口部分氧化的工艺气与蒸汽转化出口的转化气在换热式蒸汽转化炉前混合，使转化管外的加热气体的温度降低了 100℃左右，达到 1000℃左右，降低了对换热式转化炉设备材质及机械强度的苛刻要求。这种流程配置巧妙、合理，给设备的设计和制造提供了有利的空间；

[0033] 4、目前世界上的低能耗工艺都是采用的蒸汽转化法工艺，蒸汽转化法虽然能耗低，但是一段转化炉设备的投资较大，而且存在大量的催化剂消耗。本发明通过合理的工艺组合和工艺创新，使部分氧化工艺实现了与蒸汽转化相同的低能耗；而且该工艺与蒸汽转化工艺相比催化剂的使用量大幅下降；

[0034] 5、在常规的蒸汽转化工艺中，按照一段炉中燃烧用氧气过量 3%计算，1500 吨氨 / d 的装置中一段炉的排放废气为 300 吨 / 小时，其中含有 1.5ppm 的硫氧化物和 110mg/m^3 的氮氧化物。本发明中由于合理的进行了热量配置，蒸汽转化部分没有常规的一段炉烟气排放，同时减少了烟气排放造成的热量损失，属于环境友好的合成氨生产工艺，同时装置也没有污水排放；

[0035] 6、本发明中气化部分采用 6 ～ 7MPa 的高压反应，有利于降低后续合成气压缩机的功耗；在高压下气化和净化设备的的生产强度大、容积小、布置紧凑、占地小，设备材料的投资都可以降低；

[0036] 7、本发明利用变换反应热加热工艺冷凝液和用工艺冷凝液饱和气化后的干气，减少了造气过程的水蒸气气消耗。通过饱和塔饱和的水蒸汽量可以满足变换所需工艺蒸汽量的 85%左右，这样既利用了工艺气的热量，又免去了处理变换冷凝液耗用的蒸汽量。把常规的工艺冷凝液排放、处理分步进行，改进为循环回收利用，从而节约了大量的能耗。

[0037] 8、本发明中合成回路通过增加一台蒸汽过热器，可以副产 6.4MPa 的过热高压蒸汽供本装置自用。装置整个工艺需要蒸汽的 75%左右蒸汽可以自给，仅需要外界供给小部分的工艺蒸汽；

Topsoe, Inc. – EX1003
Page 926 of 1210

[0038] 9、本发明中配套的空分装置，通过降低分子筛的吸附温度对设计进行优化，可以减少再生氮气的用量，氮气量有一定的富裕，这样就可以适当增加氮压机的循环量，从而增加空分系统的制冷量，增加的制冷量在必要时可以为国产化设计的液氮洗系统补充冷量，保证装置国产化设计的可靠性；

[0039] 10、本发明的设置上，系统的能量主要都用于制氢，不足的能量部分考虑用煤来代替，这样可以有效降低生产成本费用，提高产品的竞争力。

附图说明

[0040] 图 1 是该发明的工艺流程图。

具体实施方式

[0041] 参考图 1，天然气转化生产氨的装置，包括气化炉、换热式转化炉、水洗饱和塔、变换系统、脱碳系统、气体精致单元、合成气压缩机、第一合成塔、第二合成塔、第三合成塔、分离器、尿素装置；气化炉进口与天然气和氧气进气喷嘴连接，出口与换热式转化炉转化管壳程入口连接，换热式转化炉设有天然气和中压蒸汽入口与转化管连接，转化管出口与转化管壳程入口连接；转化管壳程出口与变换系统壳程连接；变换系统壳程与蒸汽管线连接，变换系统壳程出口与水洗饱和塔连接，水洗饱和塔与变换系统冷凝液出口连接，水洗饱和塔出口与变换系统反应管连接；变换系统反应管与脱碳系统连接；脱碳系统与气体精制单元、尿素装置连接；气体精制单元合成气压缩机连接；合成气压缩机通过第一合成塔、第二合成塔、第三合成塔与分离器连接；分离器的循环气出口与合成气压缩机连接；分离器液氨出口与尿素装置连接。

[0042] 按日产合成氨 1500 吨（以 100％ NH3 计），所操作日按 333(8000 小时）计，进行了模拟计算，主要控制参数如下：

[0043] 部分氧化气化炉天然气与换热转化天然气气量比为 3 ： 1；

[0044] 换热转化水碳比为 3.10；

[0045] 气化炉炉温 1100℃；

[0046] 变换反应水气比为 0.85；

[0047] 低变出口甲烷干基含量 0.68

[0048] 合成塔入口温度 380℃等。

[0049] 其中气化炉炉温和气化炉天然气与换热转化天然气气量比的确定依据主要是在满足换热转化所需温差的前提下尽可能降低氧气的消耗，减小空分的规模。

[0050] 各反应器的反应平衡温距如下：

[0051] 气化反应：0℃；

[0052] 换热转化反应：-20℃；

[0053] 高温变换反应：10℃；

[0054] 低温变换反应：20℃；

[0055] 第一合成塔：15℃；

[0056] 第二合成塔：15℃；

[0057] 第三合成塔：15℃。

Topsoe, Inc. – EX1003
Page 927 of 1210

[0058] 装置的能耗计算中空分装置的能力按照22000Nm^3/h O_2进行计算，空压机选用高效等温压缩机，合成气压缩机、天然气压缩机、氮压机为多轴压缩机；空气压缩机、氮气压缩机为电驱动，天然气压缩机、合成气压缩机、冰机为蒸汽透平驱动。根据目前国际上的压缩机制造技术，机械效率均能达到80%。表1为主要设备及其他动设备的水、电、汽消耗表；表2为装置的吨氨综合能耗表。其中电的折能指标中已考虑了电厂发电的能量消耗；变换系统的反应热用于加热锅炉给水向外输出热量。

[0059] 表1主要设备和其他动设备的水、电、汽消耗量

[0060]

项 目	蒸汽用量 (t/h)	耗电量 (kW.h)	功率 (kW)	消耗水 (t/h)	压缩机效率	透平效率
原料气压缩机	24				80	80
合成气压缩机	40.1				84	80
冰机	9.6				75	80
转化用汽	33.9					
变换用汽	9.7					
冷凝液汽提塔	0.6					
贫液泵		909				
半贫液泵		2210.4				
水利透平		-1000.8				
空压机		9620	9620	470		
氮压机		8360	8360	788		
其他		2150	287	325		
合计	117.9	22248.6	18537	1583		

[0061] 表2新型合成氨工艺系统的吨氨综合能耗表

[0062]

	折能指标 (MJ)	单位	小时消耗量	吨氨消耗量	能耗 (GJ)
天然气	34.76	标方	43483.00	695.73	24.18
脱盐水	96.3	吨	78.20	1.25	0.12
工艺冷凝液	320.3	吨	-4.82	-0.08	-0.02
电	11.84	千瓦时	22248.60	355.98	4.21
循环水	4.19	立方米	10208.92	163.34	0.68
透平冷凝液	152.8	吨	-73.70	-1.18	-0.18
6.4MPa 蒸汽	3680	吨	40.90	0.65	2.41
预热锅炉水的余热（MDEA 提供）	4186	Mkcal	-18.90	-0.30	-1.27
合计					30.14

[0063]

Topsoe, Inc. – EX1003
Page 928 of 1210

[0064] 本发明的合成氨装置的吨氨综合能耗为 30.14GJ，目前代表国际先进技术的海南二期化肥的吨氨能耗为 28.7GJ。但海南二期化肥天然气入界区的压力为 3.0MPa，本发明的压力指标为 0.8MPa，两项目相比压差的折能为 1.03GJ，如果将本项目的天然气压力提高至与海南二期项目相同水平，那么本项目的能耗应为 29.11GJ，比海南二期项目低 0.4GJ。通过以上与国际先进工艺装置的能耗对比，说明本发明的工艺技术路线已达到世界先进水平。

[0065] 本发明中主要投资费用参照 2005-2006 年乌石化一化肥扩能改造期间设备采购价格估算。

[0066] (1) 空气分离装置是按照乌石化一化肥扩能 50％实际投资 110％计。

[0067] (2) 天然气压缩机是按照乌石化日产千吨规模价格为 4200 万元，日产 1500 吨规模价格按照 140％考虑。乌石化第三系列气化系统投资 5000 万，本项目此考虑。

[0068] (3) CO 变换、MDEA 脱碳按照乌石化一化肥扩能改造 110％考虑。

[0069] (4) 液氮洗按照乌石化更换冷箱 4000 万的 200％考虑。

[0070] (5) 氨合成和冷冻中三个合成塔按每台 1500 万考虑，三台废热锅炉按每台 1000 万考虑，合成压缩机按 700 万美元考虑。

[0071] (6) 配套公用工程按乌石化一化肥扩能改造 150％考虑。

[0072] (7) 其他二次费用是根据工程费用适当估算。

[0073]

Topsoe, Inc. – EX1003
Page 929 of 1210

序号	工程项目（费用）名称	费用合计（万元）	其中：（万元）	
	工程项目总投资	**108576**		
（一）	工程费用	94554		
1	新建空分	13557	氮气压缩机	3530
			空气压缩机	2968
			空分装置成套	4525
			其他	2534
2	天燃气脱硫、气化、换热转化	21641	天然气压缩	5817
			气化炉	9938
			换热式转化炉	1812
			其他	4074
3	CO 变换	8736	变换炉	4162
			变换催化剂	1215
			其他	3359
4	MDEA 脱除 CO	7497	溶液	1200
			静设备	3356
			水利透平及贫液泵	794
			其他	2147
5	液氮洗	7899	液氮洗冷箱	5761
			其他	2138
6	氨合成及冷冻、氢回收	21233	氨合成塔	5453
			合成废锅及过热器	3526
			合成气压缩机	5857
			冷冻系统设备	2930
			其他	3467
7	配套公用设施	13991	变配电室	4956
			锅炉及供热系统	2346
			纯水制备	995
			循环水、消防水	3758
			DCS 系统	1543
			装置内电讯系统	225
			分析化验	168
（二）	建设工程其他费用			11022
1.	固定资产及其他费用			7621
1.1	建设单位管理费			1563
1.2	工程勘察设计费			5106
1.2.1	地质详勘费			25
1.2.2	可研报告收费			150

[0074]

Topsoe, Inc. – EX1003
Page 930 of 1210