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Topsoe, Inc. – EX1003
Page 931 of 1210

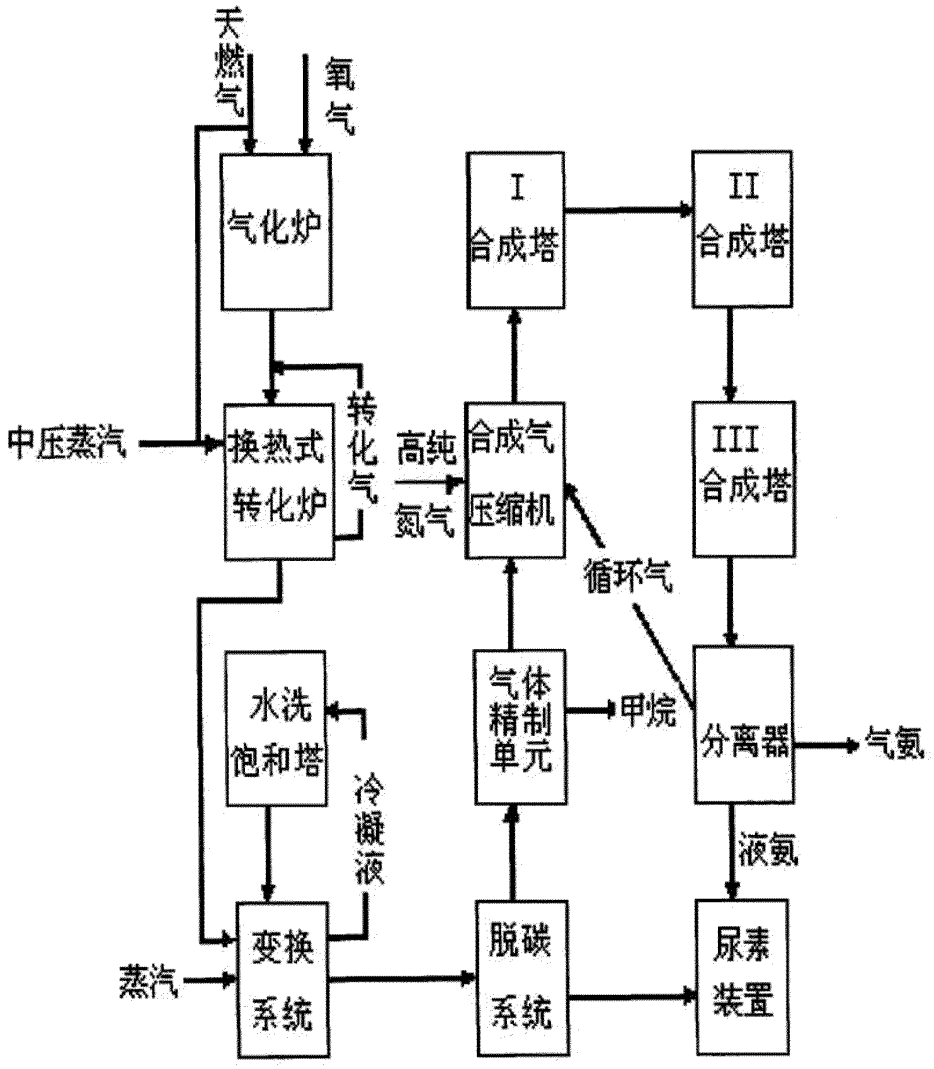


图 1

Topsoe, Inc. – EX1003
Page 932 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	)

NOTICE UNDER 37 C.F.R. § 1.565(a) OF LITIGATION INVOLVING U.S. PATENT NO. 11,286,168

VIA *e*FILE
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

As required under 37 C.F.R. § 1.565(a), Patent Owner apprises the PTO of litigation activity involving U.S. Patent No. 11,286,168. On January 31, 2024, Topsoe, Inc. ("Topsoe") filed a complaint ("Complaint," attached hereto as Exhibit A) in which U.S. Patent No. 11,286,168 is involved against Patent Owner in the United States District Court, Southern District of Texas, Galveston Division (Case No.: 3:24-cv-00033). The Complaint includes a first count requesting declaratory judgment of unenforceability of U.S. Patent No. 11,286,168, a second count alleging

unfair competition and false advertising under the Lanham Act, and a third count alleging common law unfair competition.

Notices of the court action were filed with the USPTO on January 31, 2024 (attached as Exhibit B) and February 1, 2024 (attached as Exhibit C). Topsoe filed a First Amended Complaint (attached as Exhibit D) on May 2, 2024. At this time, litigation remains ongoing, and no decision has been rendered or judgment issued.

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 28th day of May, 2024.

Respectfully submitted,

/Marcus S. Simon, Reg.# 50258/
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Topsoe, Inc. – EX1003
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NITROGEN +SYNGAS

Contents

Global Natural Gas Outlook
M. Al-Khalifa *(Bahrain Natural Gas Co., Bahrain)* 1

The Fertilizer Industry at the Crossroads
L. M. Maene *(International Fertilizer Industry Association, France)* 5

New Horizons for Jumbo Ammonia/Urea Complexes
V. F. Ciccotosto, S. Murello, F. Casagrande *(Saipem SpA, Italy)* 9

Life Cycle Benefits of Purifier™ Technology-Based Ammonia Plants
S. Singh, J. Gosnell *(KBR, USA)* 21

How the Operating Company Can Precisely Monitor the Low-Temperature Shift Catalyst
S. A. Abbas, T. R. Khan, S. Z. Ali, A. Naeem *(Fauji Fertilizer Co. Ltd, Pakistan)*

Revamping Out-of-Date "Hot Pot" Units: Better Efficiency, Less Energy
L. Tomasi *(Giammarco-Vetrocoke Srl, Italy)* 43

KM CDR® – MHI's CO_2 Recovery Process, Then and Now
N. Okuzumi, R. Mitchell *(Mitsubishi Heavy Industries Ltd, Japan)* 49

Commissioning and Start-up Experience in the Compressor House at AlexFert
Y. A. El-Ashry *(Alexandria Fertilizers Co., Egypt)* 59

Experience in Operation and Repair of Topsøe S-200 Ammonia Converters at Odessa Port Plant
N. E. Shnaydruk *(Odessa Port Plant, Ukraine)*, L. V. Izotov *(ZAO Haldor Topsøe, Russia)* 65

Redesigned Synthesis Loop Waste Heat Boiler Overcomes Corrosion Problem
P_3 Orphanides, P. Orphanides *(Consultants, Greece)* 73

From Science to Proven Technology: Development of New Topsøe Feed Purification Products
R. Kohler, M. Stenseng, F. A. Damand, H. J. Mortensen, M. Kustova, B. S. Hammershoi *(Haldor Topsøe A/S, Denmark)* 83

Recent Reforming Developments
J. R. Brightling *(Johnson Matthey Catalysts, UK)* 97

Autothermal Reforming: A Flexible Syngas Route with Future Potential
K. Noelker, J. Johanning *(Uhde GmbH, Germany)* 111

Syngas Production and CO_2 Emission Reduction Possibilities
Drs Mathiak, Ruthardt, von Trotha *(Uhde GmbH, Germany)* 125

KATALCO$_{JM}$ APICO – The First Step Change in Methanol Synthesis Catalyst for 50 Years
T. Fitzpatrick, T. Hicks *(Johnson Matthey Catalysts, UK)* 129

MEGAMAX® 800: Creating a Sustainable Methanol Industry
N. Ringer, K. Kesore *(Süd-Chemie AG, Germany)* 139

Toyo's Operation-Assisting Technologies Enhance Reliability, Safety and Productivity of Your Urea Plant
S. Nakamura *(Toyo Engineering Corporation, Japan)* 143

Efficient 3-D Modelling of Urea Plant. JSC NIIK Experience in Relocating a Urea Plant with a Simultaneous Capacity Expansion
M. Kartoveschenko *(JSC NIIK – Research & Design Institute of Urea, Russia)* 153

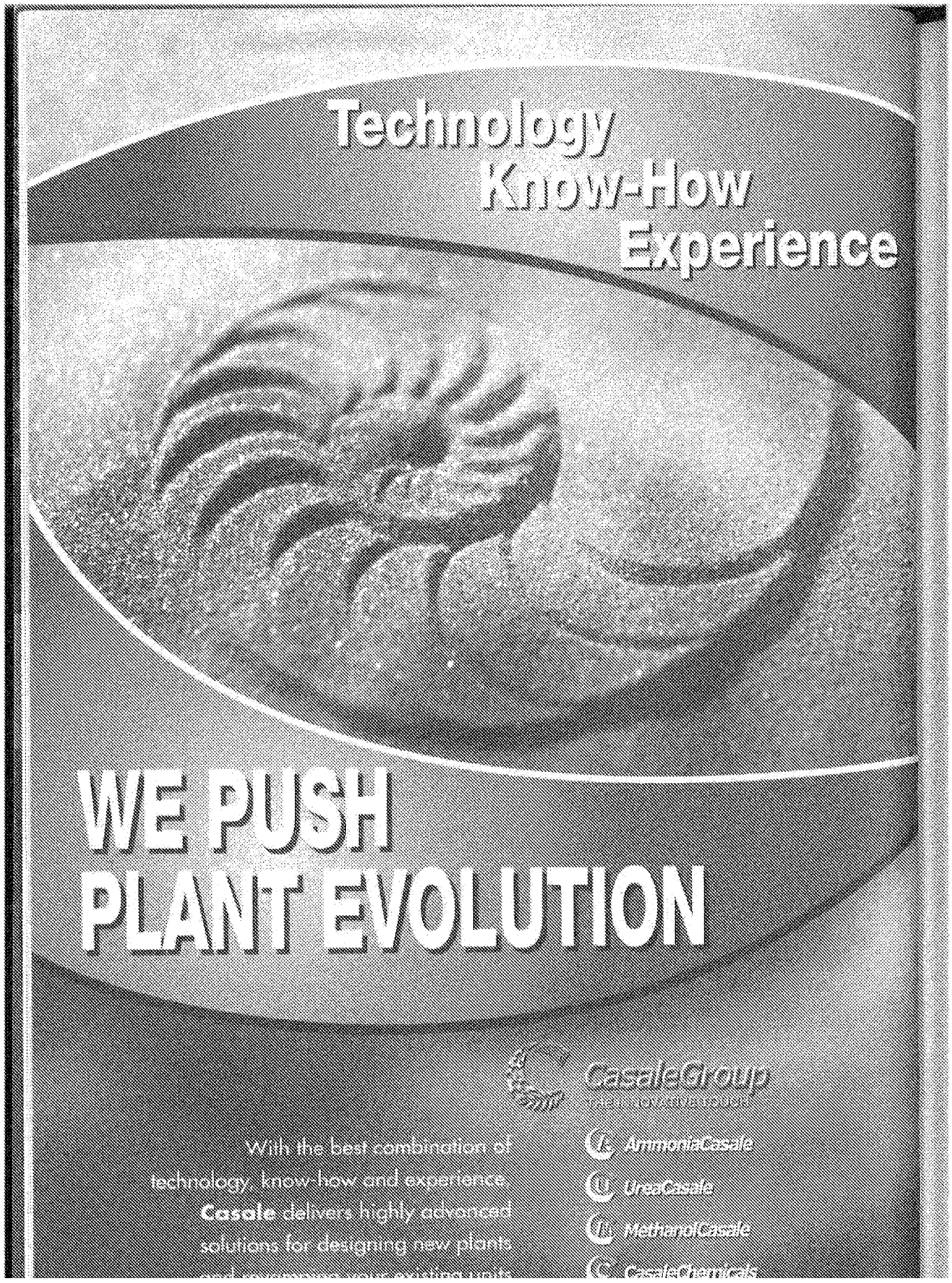
The Importance of Urea Screening Equipment for Urea Final Product Quality
N. Smith *(Rotex Europe, Belgium)* 159

Urea Reactor Pro-Active Modification and Repair: GPIC Experience
A. K. Kukkady, N. A. Rahim *(Gulf Petrochemical Industries Co., Bahrain)*, M. Orsini *(Axo Welding Srl, Italy)* 167

Stamicarbon's Approach in Mitigating the Environmental Impact of a Urea Plant
J. Dobrée *(Stamicarbon, The Netherlands)* 179

Ammonia and Urea Processing: AdBlue and Other Environmental Care-Related Applications
M. Skorupka, C. Kawalec, B. Koletka *(Prozap Engineering Ltd, Poland)* 187

Use of DP28W™ Reduces Passivation Air in Urea Plants
E. Nagashima, M. Takahashi, J. Higuchi, H. Kaminaka *(Toyo Engineering Corporation, Japan)* 193


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Autothermal Reforming: A Flexible Syngas Route with Future Potential

K. NOELKER, J. JOHANNING

Uhde GmbH
Dortmund, Germany

Autothermal reforming technology has been widely discussed in the past at conferences and in technical magazines. In comparison with the steam-methane reformer (SMR), with its multitude of tubes, the autothermal reformer (ATR) offers a much simpler mechanical set-up and superior operational robustness. The ATR can provide a wider syngas composition range than the SMR, especially significantly lower H_2:CO ratios.

Numerous ATRs are in operation worldwide. However, most of them operate as secondary reformers in ammonia and methanol plants in collaboration with steam reformers. Only a few true stand-alone ATRs have been realized up to now. For ammonia and methanol plants, the technology has so far been considered uneconomic. Natural gas-based GTL plants, for which the ATR is the best choice, have not been built in large numbers as yet.

A comprehensive evaluation of the economic viability of an ATR-based ammonia or methanol plant must take into consideration that the ATR requires oxygen. It also provides significantly less waste heat than the SMR for process media preheating and steam generation. So far, the additional operating costs for the utilities and the capital cost for the required equipment have eliminated the cost advantages of the stand-alone ATR for ammonia plants and, apparently, also for methanol plants.

However, with ever-growing plant capacities, the competitiveness of ATR-based plants is improving continually. Mainly responsible for this are the different building-cost-to-capacity relationships of SMRs and air separation plants.

Uhde established an ATR development programme some years ago. A pilot plant has been built and has been in operation since June 2009. There the applicability and robustness of the Uhde ATR concept is being validated.

The paper describes the pilot plant concept, its main design features, and experience gained during erection and commissioning, and it outlines the extensive test programme. Also, an ATR-based ammonia process flowsheet is presented. Finally, an economic comparison between a conventional SMR-based ammonia plant with an ATR-based plant for a large capacity is discussed.

INTRODUCTION

Gas mixtures composed mainly of hydrogen and carbon monoxide are commonly referred to as synthesis gases, often shortened to "syngas". They are the base for important processes such as the syntheses of ammonia and methanol.

As required by the reactions which take place in the syntheses, the syngases vary considerably in composition. Table 1 lists the most important processes and names the main requirements with respect to syngas composition.

Table 1
Synthesis Gas Composition Requirements of Downstream Processes

Process	Synthesis gas composition requirements
Ammonia	$(H_2 + CO) / N_2 \approx 3.0$
Methanol	$(H_2 - CO_2) / (CO + CO_2) \approx 2.0$
Hydrogen	max. H_2 content
Gas-to-liquids	$H_2 : CO \approx 2.0$

Given their main constituents hydrogen and carbon monoxide synthesis gases can be processed from practically any carbon containing feedstock such as natural gas, naphtha, coal or petrol coke plus water via cracking and (steam) reforming. Coking has also been an important source.

Due to the heats of formation of the species involved all these processes are highly endothermic. The transfer of heat to the process gases to force the desired reactions can be effected via heat transfer through surrounding walls or by internal (autothermal) heat generation through partial combustion of the process gas.

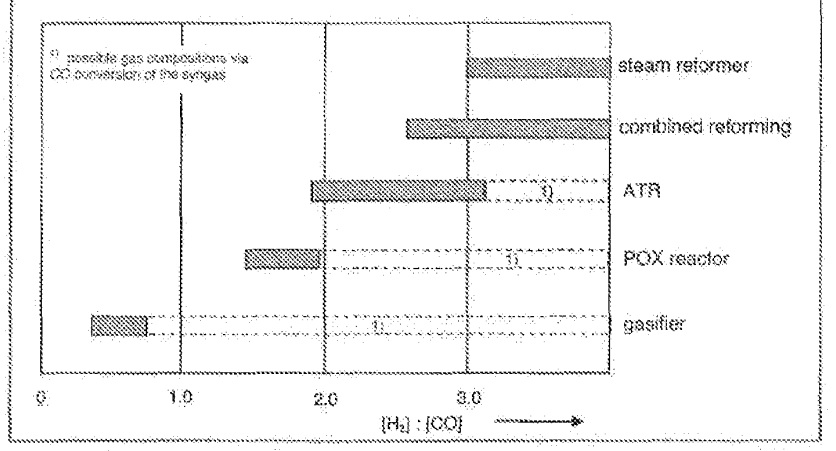
Table 2
Synthesis Gas Generator Types

Syngas generator	Feedstock
External heating	
Steam reformer	Natural gas, naphtha
Coke oven	Coal
Autothermal (internal) heating	
Autothermal reformer	Natural gas
Partial oxidation reactor	Natural gas
Gasifier	Coal, petroleum coke

A number of syngas generators are available competing with each other for the different downstream processes. Table 2 names the most important syngas generator concepts and differentiates between externally and autothermally heated devices. Most of the syngas generators operate on hydrocarbons as feedstocks. The coke oven basically extracts the volatile hydrocarbon components from coal (dry distillation). It delivers a syngas composition not too different from the steam reformer, albeit with a significantly higher hydrocarbon content.

By their very nature, syngas generators operating with autothermal heating have significantly higher CO and CO_2 contents in their syngases than the generators with external heating, i.e. much smaller $H_2 : CO$ ratios. In syngas generators with external heating, the carbon oxides are to be found in the flue gases of the external heating.

FIG. 1: COMPOSITION RANGES PROVIDED BY SYNGAS GENERATORS



This feature is most significant in the gasifier, where practically no hydrogen is provided by the feedstock. The hydrogen has to come entirely from cracked water molecules, which requires more energy compared to the cracking of hydrocarbons and hence is associated with higher CO and CO_2 production. This is illustrated by Fig. 1, which shows the individual ranges of H_2 : CO ratios in the syngases provided by the various syngas generators.

In general, matching the individual syngas-based processes with the syngas generators, which can provide the required gas compositions straight away, should give the most economical solutions. However, as discussed briefly below, the required gas compositions cannot always be delivered by one syngas generator type on its own.

Ammonia synthesis

The ammonia synthesis requires an H_2 : N_2 ratio in the order of 3.0. Obviously, this could not be realized by a steam reformer on its own. However, it can be met easily by combined reforming using an air blown secondary reformer. The version where the secondary reformer provides just the stoichiometric amount of nitrogen required in the synthesis has been the dominant syngas generation concept in ammonia plants for the last 50 years.

Other versions operating with an excess of nitrogen in the secondary reformer and a downstream process step to remove the surplus nitrogen have also been realized in considerable numbers. A stand-alone ATR is also capable of feeding an ammonia synthesis. It has to be operated with oxygen-enriched air or pure oxygen combined with a subsequent process step to introduce the required amount of nitrogen.

Methanol synthesis

Steam reforming alone cannot provide the syngas composition according to Table 1 best suited to the requirements of the methanol synthesis. A quite substantial purge from the synthesis or other means, e.g. a pressure swing absorption (PSA), are required to remove the surplus hydrogen. Pure autothermal reforming generates a syngas too low in hydrogen, requiring CO conversion and subsequent CO_2 removal.

Again, combined reforming can generate the optimum gas composition for the methanol synthesis straight away, leading to a significantly better consumption figure for the plant. Other advantages such as a smaller steam reformer size and a higher operating pressure in the syngas generation section are also associated with combined reforming. Hence, although requiring pure oxygen, combined re-forming appears to be the superior alternative for larger plant capacities.

Hydrogen

Hydrogen plants aim for maximum hydrogen production from a given amount of feedstock. Hence, most of these plants are based on steam reforming, although several plants based on partial oxidation reactors are still in use. However, as ATR and POx reactors require pure oxygen, steam reforming is nowadays considered the more economic option. Whether that is valid for larger capacities in excess of 100,000 Nm^3/h, e.g. for heavy oil upgrader plants, remains to be seen.

Gas-to-liquids

As illustrated by Fig. 1, the ATR is the syngas generator best suited to Fischer-Tropsch (FT) syntheses, as it provides the required gas composition directly. Besides using pure oxygen, it is technically feasible to operate the ATR on plain air and feed the nitrogen containing syngas to the FT synthesis. However, this obviously increases the flow rates in the entire process considerably and does not seem to be the most economic solution.

This brief excursion into the basics of syngas production shows that autothermal reforming has already been an established element of synthesis gas production for quite some time. It should, however, be noted that – with the exception of the stand-alone ATR in GTL plants – all other

autothermal reformers so far operate as secondary reformers on pre-reformed gas or mixtures of pre-reformed gas with natural gas. In addition, the effective steam-to-carbon ratios for these secondary reformers are also quite high.

Both the presence of considerable amounts of hydrogen in the pre-reformed gases and the high steam-to-carbon ratios substantially reduce the risk of soot formation in the ATR's combustion zones. Hence, operating experience gained with secondary reformers cannot really be considered as a reliable basis for the design of "pure" ATR applications.

Recent years have brought a renewed interest in ATR based synthesis gas generation for ammonia plants. This is closely linked to further increases in plant capacity well beyond today's maximum of 3,300 metric tons per day (t/d) realized by Uhde in the SAFCO IV and Ma'aden ammonia plants. As mentioned above in connection with methanol plants, steam reformers are coming closer to their technical limits in this capacity range. ATR technology appears to be a promising alternative here.

This paper presents Uhde's assessment of the economic viability of this approach and outlines what Uhde has done in recent years to prepare itself for this scenario.

AMMONIA PLANTS BASED ON AUTOTHERMAL REFORMING

Flowsheet options

An autothermal reformer can be operated with the entire range of oxidizer compositions between plain air and pure oxygen. The amount of oxygen which has to be provided by the oxidizer is defined by the required reforming heat duty. It does not depend significantly on the overall oxidizer composition. The process steps required downstream of the ATR for syngas preparation are however closely linked to the oxidizer composition. Below, the consequences of the three most important oxidizer compositions plain air, oxygen-enriched air with stoichiometric nitrogen content and pure oxygen on the process configurations as well as on equipment sizes are discussed briefly.

Figure 2 (opposite) contains simplified block flow diagrams of the process variations. Obviously, the numbers of process units are not significantly different between the three concepts.

Option 1 – Plain air

Using plain air results in a large nitrogen surplus in the syngas. Hence, a cryogenic unit is required to extract the excessive nitrogen upstream of the syngas compressor or a very large purge stream from the ammonia synthesis. Obviously, this concept is associated with the largest flow rates and equipment sizes at least in the synthesis gas generation section.

Option 2 – Oxygen-enriched air

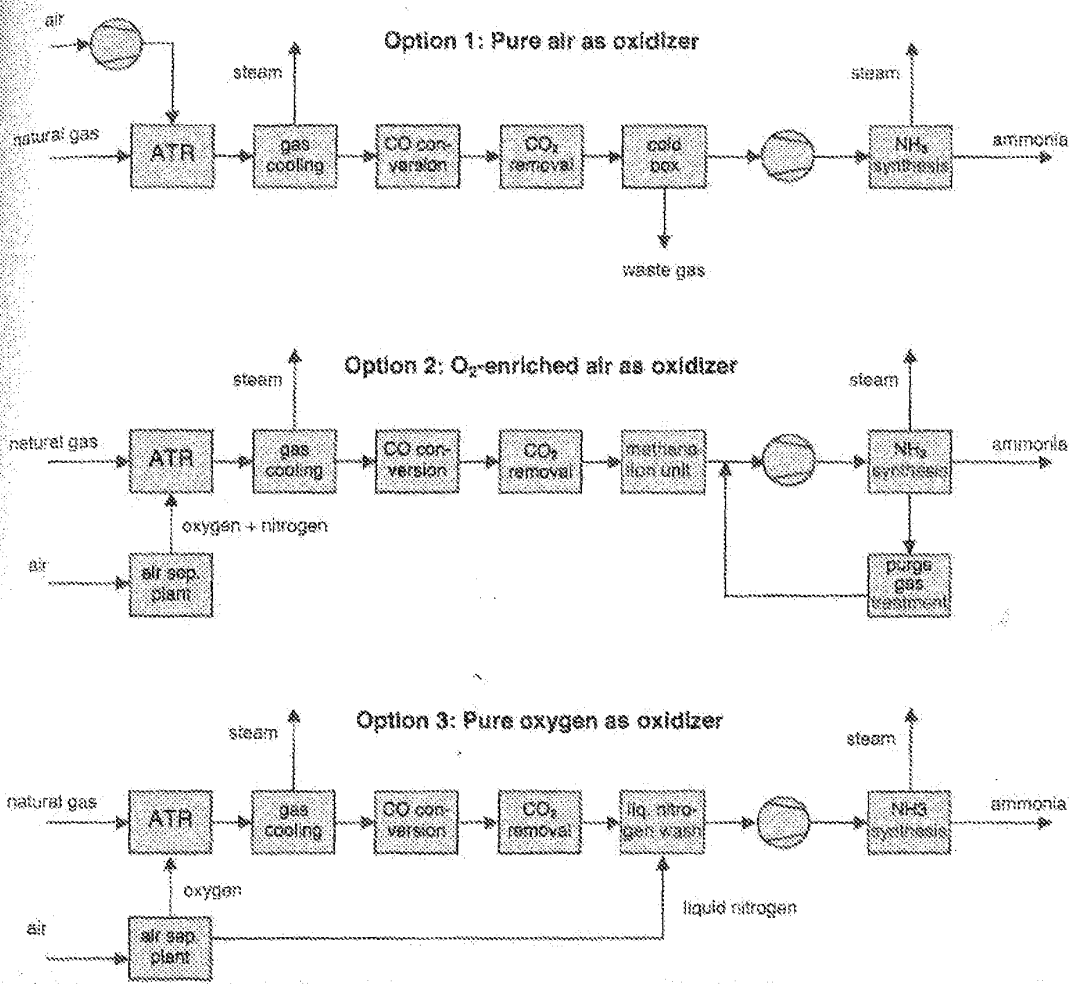
The option requires an air separation unit. The air flow rate is specifically selected to provide the correct amount of nitrogen for the ammonia synthesis. The oxygen coming in with the air and the added amount together meet the required reforming heat duty. Thus, the capacity of the air separation is minimized.

Option 3 – Pure oxygen

In this process concept only marginal amounts of nitrogen depending on the oxygen purity are introduced into the ATR. Hence, flow rates in the synthesis gas generation section take on their smallest values. The nitrogen required in the ammonia synthesis is introduced into the syngas just upstream of the syngas compressor, for example via a liquid nitrogen wash unit.

A natural advantage of the process concepts using final cryogenic units in the syngas preparation is the practically inert-free synthesis gas. Without accumulation of inerts, the size of the equipment in the ammonia synthesis can be reduced in the order of 10%.

FIG. 2: PROCESS OPTIONS FOR ATR-BASED AMMONIA PLANTS



Option 1 operates with significantly larger flow rates than option 2 in the syngas generation section. This may be compensated by a somewhat simpler cryogenic unit compared with the air separation, smaller flow rates in the synthesis and the missing purge gas treatment. Hence, the two options may have fairly similar investment costs.

Comparing option 3 with option 2, the following can be pointed out. The capacity of the air separation plant has to be about 40% larger. A nitrogen wash unit is considerably more complicated than a methanation section. Whether this is fully compensated by the somewhat larger equipment of the versions 1 and 2 remains doubtful at least. Hence, option 3 is likely to have the highest investment costs among the three pro-cess versions discussed.

Economic comparison with steam reforming based plants

The economics of ATR-based ammonia plants compared with plants using conventional tubular steam reformers has been addressed in a number of papers in recent years in more or less detail [1], [2]. The projections about possible investment cost reductions vary between 20% and none. With respect to operating costs, an even larger range between 30% reduction and none can be derived from the references. These assessments do not always reveal which cost components are taken into account and hence cannot really be compared.

Uhde's assessment outlined below leads to the conclusion that any definite figure is misleading, since plant capacity is the decisive parameter. The break-even point indeed appears to be in the

Topsoe, Inc. – EX1003
Page 945 of 1210

area of 4,000 t/d, as has been reported by other authors. However, with the limited accuracy possible at this moment, a range of uncertainty, at least in the order of ±500 t/d, should be expected.

An economic comparison between the two plant concepts must look at both operating and investment costs.

Operating cost

About 65% of the specific energy consumption of a modern ammonia plant is trans-ferred to the ammonia product as chemical energy. The remaining 35% are needed to enforce the required process steps, i.e. via preheating and compression of the pro-cess media. The energy balance of an entire ammonia plant is fairly complex. As both parts are affected by the quite significant changes in the process, the consumption side as well as the available waste heat have to be looked at.

Table 3 contains a comparison of the consumption side. It lists the most important energy consumers in ammonia plants for both plant concepts. The right hand side column of the table indicates the change in energy consumption which has to be expected for the respective process unit in the ATR-based plant. It has to be pointed out, however, that the individual energy consumptions of the consumers listed in the table differ significantly. By far the most important consumers are the reformer, the waste heat section/fired heater and the air separation.

Table 3
Comparison of Primary Ammonia Plant Energy Consumers

Energy consumers		Additional energy consumption ATR plant [%]
SMR-based plants	ATR-based plants	
Reformer (feed + related fuel)	Reformer feed	0
Waste heat section (related fuel)	Fired preheater	+ 15
Feed compression	Feed compression	+ 25
Feed preheating	Feed preheating	+ 25
Feed/steam preheating	Feed/steam preheating	+ 7
Process air compression	Air separation	+ 150 / + 188[1]
Process air preheating	Process air preheating	0[2]
Synthesis gas compression	Synthesis gas compression	0
Ammonia vapour compress.	Ammonia vapour compress.	0

1 enriched air / pure oxygen
2 reduced preheating temperature with regard to higher oxygen content

The feed flow rate in the ATR-based plant is about 25% larger compared to a steam reformer-based plant as it contains between 50 and 60% of the fuel flow for the reformer burners. Oxidation of this additional amount provides the heat for the reforming reactions. Owing to the resulting increase in natural gas flow rate, the related energy consumptions in the syngas generation section are likely to go up, though not always in the same order as indicated in Table 3.

On account of the larger process gas flow rate in the syngas generation section of the ATR-based plant more heat is available from this process stream. The surplus can be used to raise the additional steam required for the air separation.

The large amount of heat contained in the flue gas of the primary reformer is usually utilized for the process media preheating addressed in Table 3 as well as steam superheating. In the ATR-based plant this has to be supplied by a fired heater. Owing to the increased steam production, more heat for steam superheating has to be supplied by the fired heater in addition to the increased heat demand for feed and feed/steam preheating.

The heater operates with a smaller specific flue gas flow rate than the waste gas duct of the steam reformer. Hence, stack loss as well as heat duty for burner air preheating are reduced compared to the steam reformer.

In summary, our calculations carried out so far show an additional energy consumption for the ATR-based ammonia plant in the order of 6% for the process version operating on enriched air (option 2). For the version operating on pure oxygen (option 3) a somewhat higher additional consumption in the order of 10% has to be expected.

Investment cost

No ATR-based ammonia plant has been built as yet. Hence, a comprehensive cost database, comparable to that available for conventional plants, does not exist. Therefore, the qualitative analysis presented below is used to derive a cost relation between the two plant concepts.

Table 4 lists the main process steps in an ammonia plant and the respective units in the conventional plant based on steam reforming as well as in the ATR-based plant. The right hand side column of the table indicates whether the respective unit in an ATR based plant is expected to have lower (↓), equal (~) or higher (↑) investment costs. To keep the focus on the most relevant process units the ATR process concept based on enriched air is used for this comparison.

This qualitative approach illustrates that the two process steps "oxidizer preparation" and "reforming" are decisive for the investment cost relation between the two plant concepts. Minor cost differences can be expected for each other process step as equipment numbers, sizes and complexities vary moderately throughout the entire flowsheets. However, excluding the fundamentally different process steps "oxidizer preparation" and "reforming" it can be expected that these differences will not all be in favour of one plant concept and hence equal each other out.

Table 4
Investment Cost Comparison per Process Step

Process step	SMR plant	ATR plant	Unit cost ATR : SMR
Oxidizer preparation	Compressor	Air separation	↑
Desulphurization	Preheater / reactor		~
Process gas preheating	Flue gas duct	Fired heater	~
Reforming	Steam reformer	–	↓
	Secondary reformer	ATR	~
Process gas cooling	Steam generator / superheater		~
CO conversion	2 converter / 2 BFW preheater		~
CO_2 removal	aMDEA, alternatively physical solvent		~
Methanation	Preheater / reactor		~
Syngas compression	2-casing turbo compressor		~
Ammonia synthesis	3 converter dual-pressure synthesis		~
Refrigeration	Compression type		~
Purge gas treatment	Hydrogen recovery		~ / ↓ *

** Option 2 "enriched air" / option 3 "pure oxygen" with inert-free syngas*

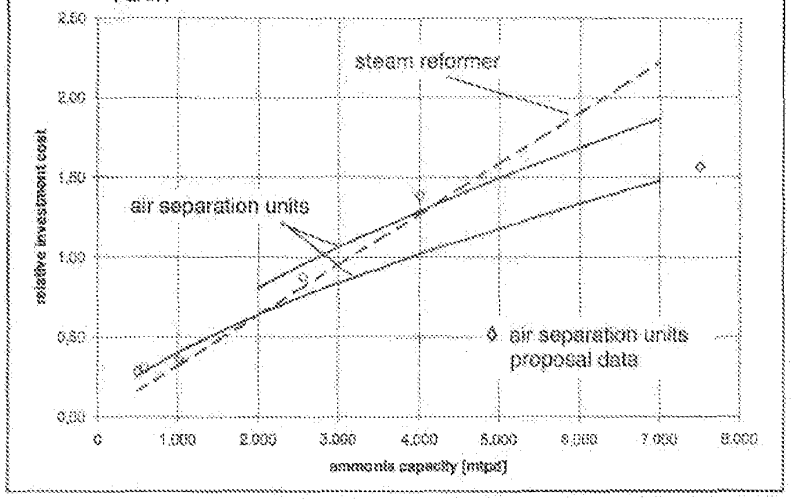
The cost structure for a steam reformer has a fairly linear relationship between capacity and unit cost. With few exceptions material and construction costs are directly proportional to the number of tubes, i.e. unit capacity.

The cryogenic air separation is by nature a single train unit. Hence, contrary to the steam reformer, a considerable reduction of the specific investment cost with growing capacity can be expected. This characteristic is illustrated in Fig. 3. The steam reformer cost curve is derived from Uhde's respective database. The figures for air separation plants are derived from proposals provided by plant vendors.

The cost data have been deliberately related to the SAFCO IV reformer costs, as it does not make sense to discuss absolute figures in this context. The actual costs depend very much on the region where the plant is to be built, specific requirements and the overall economic situation.

Topsoe, Inc. – EX1003
Page 947 of 1210

FIG 3: INVESTMENT COST RELATION, STEAM REFORMER VS. AIR SEPARATION PLANT



The figure illustrates that with the cost data available at present a single break-even capacity can hardly be determined. The cost figures of air separation units may be interpreted conservatively or optimistically by the continuous curves, as shown in the figure. Obviously, there is a considerable capacity range of uncertainty. However, the figure indicates that – even with a conservative approach – beyond plant capacities of 4,000 t/d an ATR-based plant is likely to have growing investment cost advantages compared to a steam reforming based plant.

UHDE'S ATR TECHNOLOGY

Description of Uhde's ATR test facility

The partial, i.e. substoichiometric combustion in autothermal reforming is in principal likely to generate soot. For any set of operating conditions defined by feed gas composition, pressure and steam-to-carbon ratio a minimum operating temperature exist below which soot is generated. Steam and hydrogen in principal reduce the soot forming potential, i.e. move the boundary move the boundary for soot-free operation to lower operating temperatures. The minimum temperature also depends on the burner design and the flow conditions in the combustion zone.

Uhde has extensive experience in the design of secondary reformers for ammonia plants. These vessels operate under similar pressure and temperature, but in the following two important aspects enjoy considerably milder conditions compared with pure autothermal reformers.

Secondary reformers process partly reformed gases which contain significant amounts of hydrogen and operate with quite high effective steam-to-carbon ratios. Hence, they do not provide a basis to determine the minimum possible operating temperatures with respect to soot formation. This temperature is directly related to the amount of oxygen supplied. Therefore, to minimize plant operating cost the ATR is to operate at the lowest possible operating temperature.

The heat generation rates of secondary reformers are relatively small. With the considerably higher heat generation in autothermal reformers, increased wear and tear on the burner and thermal insulation must be expected. They have to be taken care of by modified design features. Also catalyst bed design and size can be expected to vary.

To gain further insight into ATR operation and to produce the operational data required to adjust the design procedures, Uhde set up a development program several years ago. Subsequently to being successful in finding a cooperation partner in the russian company Kuibyshev Azot, a test facility was designed, built and commissioned at Kuibyshev Azot's production site.

Fig. 4: PROCESS FLOW DIAGRAM OF THE ATR TEST FACILITY

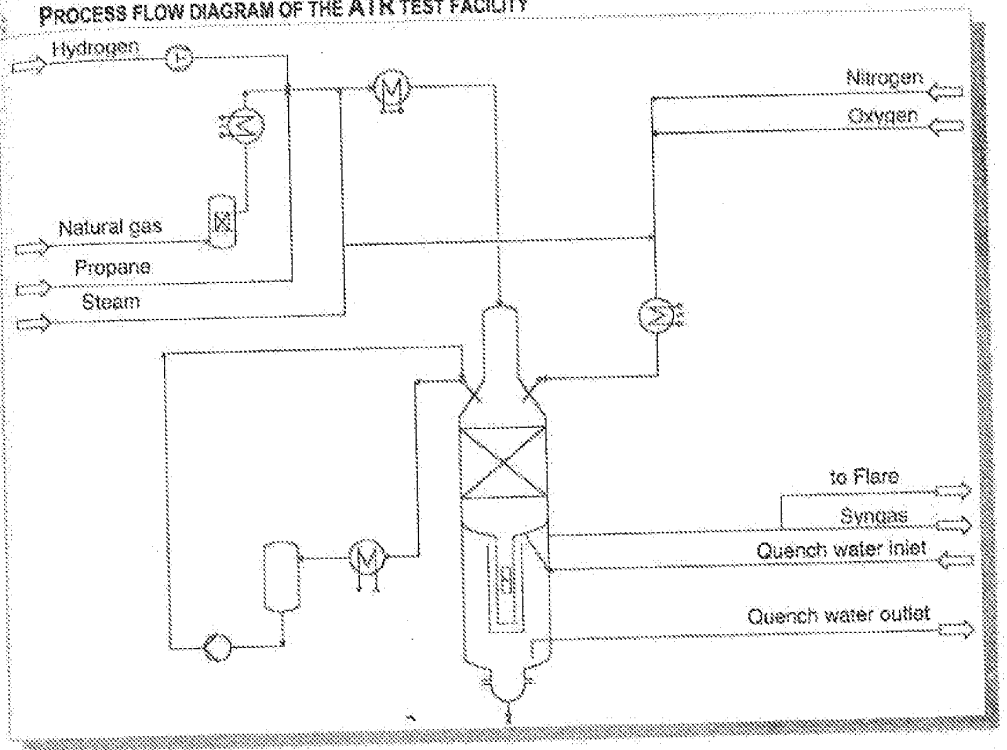


Figure 4 contains the process flowsheet of the test facility. The production site usually operates on fairly light natural gas with low contents of higher hydrocarbons and sulphur. Hence, to simulate heavier feedstocks, the test facility was equipped with a device to add propane to the incoming natural gas.

Provisions where also made for the addition of a hydrogen rich stream to the natural gas to simulate a pre-processed gas. With regard to the low sulphur content a further desulphurization of the incoming natural gas was considered unnecessary. It was also decided to take the required process steam from an external source. The heaters for natural, feed/steam mixture and oxidizer are powered electrically.

At the ATR gas outlet a water quench is installed. Hence, only moderate gas temperatures are present outside the ATR pressure vessel. The ATR design capacity can be best characterized by a syngas flow rate at reactor outlet in the order of 1,000 Nm^3/h at 30 bar operating pressure.

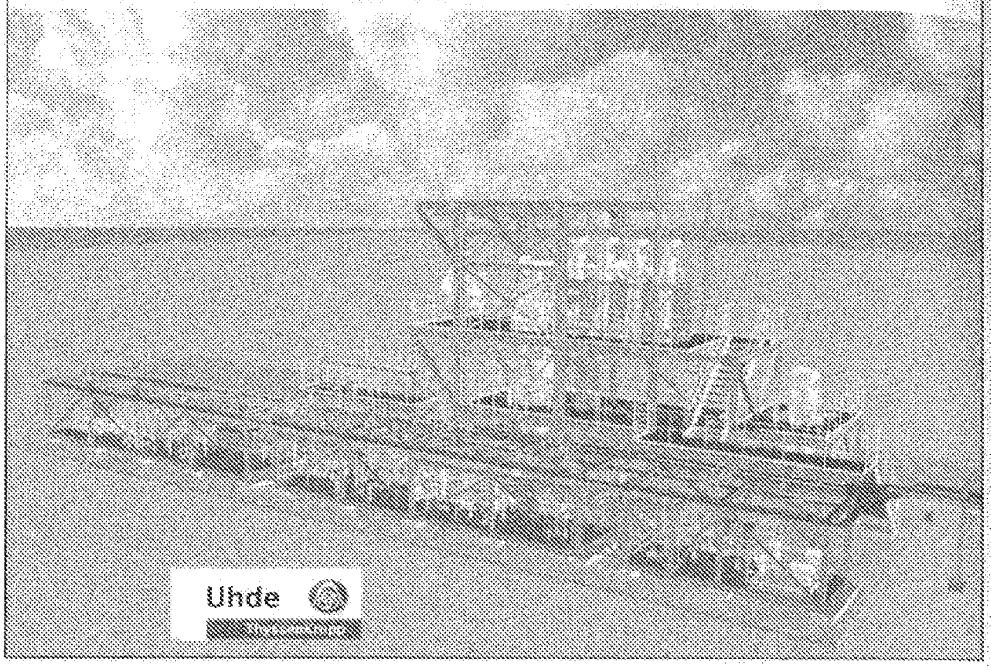
The test rig is equipped with optical light extinction measurement devices to detect soot in the gas phase as well as in the process condensate.

During the design phase of the ATR itself, considerable effort was spent to optimize the geometry of the combustion or partial oxidation (POx) zone, gas inlet velocity and swirl and to find the best position for the oxidizer nozzles. CFD analysis has been employed extensively for this step. As a result of these studies two ATR reactor tops with completely different shapes of the combustion zone have been manufactured.

With regard to the high design pressure and other restrictions it was decided early in the design phase to abandon the idea of installing an optical access to the combustion zone. Also, the number of nozzles which could be fitted to the reactor pressure vessel, is limited as each one is quite bulky due to the high design pressure.

Figure 5 shows a CAD drawing of the test rig. The lower steel structures in the front contain the modules for burner cooling, hydrogen compression and feed preheating. The high steel structure at the back contains the ATR itself and the feed/ steam pre-heaters.

FIG. 5: CAD DRAWING OF THE ATR TEST RIG



The process plant occupies an area of approximately 30 m by 11 m. The height of the central steel structure is about 10 m.

The main part of the test rig has been assembled on site from prefabricated parts. This was considered more cost-effective than complete preassembly and transport of the relatively huge structure to the production site. The three modules in front were preassembled and transported as complete units.

Experience during erection and commissioning

To obtain building and operating permission for the test rig turned out to be a time consuming and relatively costly procedure. A safety study had to be carried out to show conformity of the plant's design and instrumentation with russian regulations. Also, a special documentation conforming with russian standards had to be generated from the plants engineering documents.

Transportation of the material to the construction site did not present any problems.

Assembly of the test rig presented no major problem and could be continued even through the cold season. It should be mentioned, however, that the winter of 2008 to 2009 was unusually mild. Subsequently to the thorough execution of pre-commissioning and commissioning procedures the ATR was ignited for the first time in June 2009.

Operation of the optical soot detection devices has shown that the lowest soot content which can be detected in the samples taken from the quench water off-take is in the order of 1-3 ppm wt. Quench water and process gas mass flow rates are not really linked but usually of the same order. Hence, the soot concentration determined in the quench water should correspond roughly to the concentration in the process gas.

The minimum measurable soot concentration in the process gas named by the manufacturer of the measuring device should be in the order of 80 mg/Nm³ (0.1 ppm wt.). During the test runs the onset of soot always became apparent at first in the quench water. Hence, the actual sensitivity of the measurement device appears to be at least one order of magnitude lower than pronounced.

The target in the test runs so far has been the detection of the soot formation boundary. Therefore, as soon as the onset of soot was detected, the run conditions have been readjusted immediately to take the reactor away from the critical region. Any prolonged operation in the critical region always demanded a considerably longer period under soot free conditions to get the soot out again.

Operational results

Depending on the process an autothermal reformer is to serve as sole synthesis gas generator it has to meet certain

- outlet gas requirements
  - composition (e.g. $[CO + H_2]/N_2 \approx 3.0$ or $H_2 : CO \approx 2.0$)
  - pressure
  - methane content

To meet these requirements with the feedstock available at the respective production site and present the most economical solution with respect to investment and operating cost the following parameters have to be selected carefully:

- primary design parameters
  - combustion zone shape
  - combustion zone gas residence time
  - inlet velocity feed/steam mixture
  - inlet swirl feed/steam mixture
  - inlet velocity oxidizer
  - number of oxidizer nozzles
  - oxidizer nozzles direction
  - space velocity catalyst bed
- operating parameters
  - steam-to-carbon ratio
  - combustion zone temperature (→ oxygen-to-carbon ratio)
  - oxidizer composition

Obviously, it is not economically feasible, to investigate all of the above mentioned parameters in an experimental program. The number of test runs and individual pieces of equipment to be manufactured would be simply too large.

With the capabilities of modern CFD calculations this could be considerably reduced. As discussed in chapter 3.1 an optimization of the geometrical parameters around the combustion zone has been carried out to determine the most promising combinations for two different combustion zone shapes.

On this basis a still quite extensive test program has been devised to cover the relevant ranges of the parameters listed in Table 5.

As the first set of tests is specifically designed to determine the soot formation boundary, i.e. the minimum temperature for soot-free operation at given steam-to-carbon ratios, these tests were run without any catalyst in place to avoid damage to the catalyst.

Table 5
ATR Test Programme

Parameter	Unit	Lower limit	Upper limit
Feedstock higher hydrocarbon content	%	2	14
N_2 content oxidizer	%	0	55
Operating pressure	bar	20	30
Steam-to-carbon ratio	–	0.5	3.0
Combustion zone shape	–	A	B
Rel. gas residence time comb. zone	%	50	100
Combustion zone temperature	°C	1150	1250

These test runs carried out so far have delivered satisfying results. The performance of the ATR can be characterized by the three most important operating points depicted in Table 6. All points

showed reasonable margins against the soot formation boundary despite rather unfavourable feedstock compositions, i.e. relatively high contents of higher hydrocarbons.

Table 6
Operational Results of the Test ATR

Parameter	Unit	Operating point		
		A	B	C
		NH_3 syngas, Enriched air	NH_3 syngas, Pure oxygen	FT syngas
Feed composition				
CH_4	mol%, dry	89.2	82.9	88.7
C_{2+}	mol%, dry	7.1	14.5	7.4
Oxidizer N_2 content	mol%, dry	42.1	5.0	5.0
Steam-to-carbon ratio	---	3.0	2.0	0.7
Outlet temp. oxidat. zone	°C	1200	1250	1238
Oxygen-to-carbon ratio	---	0.85	0.74	0.60
Syngas pressure	bar abs	28.0	28.0	28.0
Outlet temp. catalyst zone	°C	1086		1100

Operating point A represents the situation where an ATR generates a stoichiometric syngas composition for an ammonia synthesis operating on oxygen-enriched air and a steam-to-carbon ratio of 3.0.

In point B the ATR is operating on pure oxygen. With the steam-to-carbon ratio of 2.0 the conditions tend to ammonia or methanol plants.

Point C represents ATR operating conditions typical for a syngas unit in a gas-to-liquid plant based on Fischer-Tropsch synthesis with an H_2 : CO ratio in the syngas in the order of 2.0.

Since no catalyst had been in place during these test runs the syngas still contains noticeable methane contents. Also, the relatively large specific heat losses of the still rather small test facility lead to extra CO_2 generation compared to a large production plant. Hence, gas compositions at the reactor outlet are not really significant and have therefore not being included in the table.

CONCLUSION AND OUTLOOK

So far only a very limited number of true stand-alone autothermal reforming applications have been realized though the technology has been investigated extensively for more than a decade now. As discussed above, the well established combination of autothermal reformers with steam reformers does not count in this respect. The operating conditions of these secondary reformers are considerably less severe than those of a true stand alone ATR.

The analysis presented in this paper investigates the reasons for this and illustrates – with the main focus on ammonia plants – why the conventional syngas generation based on combined steam and autothermal reforming still dominates newly built plants. The analysis also shows that the cost advantage of the conventional concept against ATR-based syngas generation is shrinking with increasing plant capacity.

The capacity of world scale ammonia plants has grown substantially since the early beginnings and markedly in the past 50 years. Though it is technically and logistically more challenging to provide the equipment for large capacity plants there is no indication that the economy of scale does no longer work for today's world scale capacities.

As discussed before it is difficult to determine the actual break-even capacity, where investment costs of both plant versions become equal. However, there are substantial arguments that for capacities beyond 4,000 t/d the ATR-based plants will have increasing advantages.

Such capacities are also feasible with steam reformer based plants as Uhde has shown with a concept presented on the AIChE ammonia safety symposium 2004 [3]. However, the ATR allows

to increase the pressure level in the syngas generation section considerably beyond the current limit of approximately 45 bar for steam reforming based plants. Hence, with reduced volumetric flow rates in the syngas generation section it will be much easier to realize larger capacities.

Uhde intends to prepare itself for this scenario. The test program for the ATR will be completed during the next months. The operating data will provide the basis to identify the most promising design and to update the design tools.

The currently feasible maximum operating pressure for the tests covers ATR applications for hydrogen production as well as GTL plants. It also provides a reasonable basis to judge the ATR behaviour under ammonia plant conditions.

Once the test results have been fully evaluated and transferred to the design tools Uhde intends to start offering its ATR technology to customers. In the beginning the focus will be on plants with medium size syngas capacities, e.g. in a revamp project, to limit the up-scaling factor from the test facility. In the long run, however, the prime target are larger plant capacities.

Since the consumption figures of ATR based ammonia plants are in the same order as those of steam reforming based plants, there will be no significant differences in the overall CO_2 balances. However, a natural advantage of the ATR-based plant is that a much larger part of the generated CO_2 is always contained in the syngas under high pressure. It is separated in the CO_2 removal section without additional equipment and marginal extra energy expenditure. This allows full conversion of the entire ammonia production into urea. A steam reforming plant would require an expensive removal system to extract the CO_2 from the atmospheric reformer flue gases.

A complete separation of the entire CO_2 could also be realized in the ATR-based plant with little extra investment and an only moderate increase of the plants consumption figure provided the fired heater would be fed with syngas instead of natural gas.

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Topsoe, Inc. – EX1003
Page 953 of 1210

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DESCRIPTION SU594048A1

10 Method for producing ammonia

[0001]

14 1

[0002]

18 The invention relates to a method for producing ammonia from gaseous hydrocarbons and can be used in the chemical industry.

[0003]

23 There is a known method for producing ammonia by “inversion of hydrocarbons and carbon monoxide, gas purification with subsequent synthesis of ammonia, with heat removal from the reaction of ammonia formation by evaporation of ammonia under pressure with multi-stage expansion of reheated ammonia vapor 1.

[0004]

30 The closest to the described invention in terms of technical essence and achieved result is a method for producing ammonia from hydrocarbons, including purification of natural gas from sulfur compounds, steam catalytic and steam-air conversion of hydrocarbons, two-stage conversion of carbon monoxide, purification of synthesis gas from carbon dioxide and ammonia synthesis at 320 atm with heat recovery at the indicated stages to produce steam and heat feed water with combustion of process emissions during the start-up period at flare unit 2J.

[0005]

38 However, according to this method, additional natural gas is used as fuel to heat natural gas at the desulfurization stage and during steam reforming, while process gases are burned in a flare, polluting the atmosphere with unburned harmful impurities.

42 In this case, up to 52 t/hour of steam is emitted with the process gas, which leads to an increase in the consumption of demineralized water during unit startup.

[0006]

47 The purpose of the invention is to reduce the consumption of natural gas and demineralized water, as well as to reduce emissions of harmful impurities into the atmosphere during the startup mode of the unit.

[0007]

53 This is achieved by the described method of producing ammonia, including purification of natural gas from sulfur, steam catalytic and; airy; conversion of hydrocarbons, two-stage conversion of carbon monoxide, purification of synthesis gas from carbon dioxide, synthesis of ammonia at elevated pressure with heat recovery at these stages to produce steam and heat the feed water.

58 At the same time, part of the process gas, after each stage of synthesis gas preparation during the startup mode of the unit, is sent through Heat recuperators and condensate separators for combustion at the steam conversion stage at a fuel ratio of natural gas: process gas 1: (O.ZO-O.ZZ) .

62 It is preferable to carry out steam-air conversion of hydrocarbons at a gas:air ratio of s 1:(2.O-2.2). Distinctive features of this method are the use of technological emissions from the stages of synthesis gas preparation as fuel during the catalytic conversion of hydrocarbons, as well as the ratio of gas and spirit supplied to the stage of super-ear conversion vapors.

66 The drawing shows a diagram for producing ammonia using the described method.

67 Natural gas enters separator 1, into fuel gas separator 2 and after compressor 3 enters desulfurization stage 4, and then mixed with process waste into steam reformer 5 (tubular furnace). After steam reforming, process gas with the addition of a steam-air mixture enters the steam-air mixture. reforming 6 with poKynefjaTopaMH heat, to produce steam f Air is supplied mixed with protective steam in an amount of 28,000 through a heater.

72 Natural gas load 14000 im/hour gas:air ratio 1:2, the vapor-gas mixture is poured and then into the first-stage medium-temperature carbon oxide converter 7. From here, the converted gas enters the heat recuperators 8 (recovery boiler and heater), and then into the low-temperature carbon dioxide converter 9. Next, the gas enters the gas cooling and moisture separation unit 10, which includes a condensate injection unit, solution heaters, a stage of gas purification from carbon dioxide, a water heater and a moisture separator. The cooled converted gas, separated from the excess condensate, is sent to carbon dioxide purification absorbers 11 with a moisture separator at the outlet and then to a methanation purification unit with heat recuperators and

refrigerator 12. The prepared and purified nitrogen-oxide mixture enters the separator 13 to the suction of the compressor 14. The synthesis gas is then compressed into the ammonia synthesis stage with an ammonia refrigeration unit and heat recuperators 15. In addition to the main flow of process gas, with this method, additionally through shut-off and control valves, process gases after desulfurization are pumped into the fuel gas manifold of steam reforming burners 5, as well as bypass through the heat recuperator 8, bypass past the converter 9 and through the cooling unit 10 in Tof, the collector at the fuel gas inlet is empty. The steam-gas mixture after steam 5 and steam-air reforming is also fed past converters 7, 9 through a heat recuperator 8 and a cooling unit 10.

88 The condensate formed from the process steam of the vapor-gas mixture in the cooling unit is supplied for use as feed water. Process gases, after separating the condensate in block 10, supply a portion (10000-12000 nm) to the collector at the thermal gas inlet to the tubular furnace 5, and the rest to the flare unit 16. Converted gas after medium temperature. temperature converter 7 carbon monoxide heat recuperator 8 past the low-temperature converter 9 carbon monoxide through a cooling unit .10 is supplied to the manifold, fuel gas is supplied to the tubular and to the flare unit 16. The converted gas after the low-temperature carbon monoxide converter 9 is also fed through the cooling unit 10 and, after separating the condensate, a part (1000-12000 HMV4ac) is distributed into the collector at the fuel gas inlet into the tubular furnace 5, and the rest is distributed to the flare unit 16. Converted gas after the stage of purification from carbon dioxide in the adsorber 11. also supplied to the manifold at the fuel gas inlet to the tube furnace 5 and to the flare unit 16.

109 The nitrogen-hydrogen mixture, after cleaning from the separator 13 at the suction of the synthesis gas compressor, is supplied: part to the suction of the natural gas compressor 3 (10000-10000), part (10000-12000 HMV4ac), to the manifold at the fuel gas inlet to the tubular furnace 5, and the rest to flare unit 16. In the drawing, additional introduced connections are shown with a dotted line. CDDTHO-LueHHe in the fuel at the inlet to the manifold of the tubular furnace is natural gas; process gas 1: (O,3O-O,33). Combustion of hydrogen during steam-air reforming due to the gas:air ratio of 1:(2.62.2) increases the amount of steam-gas mixture at the outlet of steam-air reforming, and also changes the composition of the gas towards increasing heat capacity, which increases steam formation in heat recuperators and condensate return.

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1

Изобретение относится к способу производства аммиака из газообразных углеводородов и может быть использовано в химической промышленности.

Известен способ получения аммиака путем конверсии углеводородов и окиси углерода, очистки газа с последующим синтезом аммиака, с отводом тепла реакции образования аммиака путем испарения аммиака под давлением с многоступенчатым расширением перегретых паров аммиака [1].

Наиболее близким к описываемому изобретению по технической сущности и достигаемому результату является способ получения аммиака из углеводородов, включающий очистку природного газа от сернистых соединений, паровую каталитическую и паровоздушную конверсию углеводородов, двухступенчатую конверсию окиси углерода, очистку синтез-газа от двуокиси углерода и синтез аммиака при 320 ат с рекуперацией тепла на указанных стадиях для получения пара и подогрева питательной воды с сжиганием технологических выбросов в пусковой период на факельной установке [2].

2

Однако по указанному способу для подогрева природного газа в стадии сероочистки и при паровом риформинге в качестве топлива используют дополнительно природный газ, в то время как технологические газы сжигают на факельной установке, загрязняя атмосферу не сгоревшими вредными примесями. При этом с технологическим газом выбрасывается до 52 т/час пара, что приводит к увеличению расхода деминерализованной воды при пусках агрегата.

Целью изобретения является уменьшение расхода природного газа, деминерализованной воды, а также уменьшение выбросов вредных примесей в атмосферу при пусковом режиме агрегата.

Это достигается описываемым способом получения аммиака, включающим очистку природного газа от серы, паровую каталитическую и паровоздушную конверсию углеводородов, двухступенчатую конверсию окиси углерода, очистку синтез-газа от двуокиси углерода, синтез аммиака при повышенном давлений с рекуперацией тепла на указанных стадиях для получения пара и подогрева пи-

Topsoe, Inc. – EX1003
Page 957 of 1210

тательной воды. При этом часть технологических выбросов после каждой стадии подготовки синтез-газа при пусковом режиме агрегата направляют через рекуператоры тепла и отделители конденсата на сжигание в стадию паровой конверсии при соотношении в топливе природный газ: технологический газ = 1: (0,30-0,33).

Предпочтительно паровоздушную конверсию углеводородов проводить при соотношении газ:воздух = 1:(2,0-2,2).

Отличительными признаками способа является использование технологических выбросов стадий подготовки синтез-газа в качестве топлива при каталитической конверсии углеводородов, а также соотношение газа и воздуха, подаваемых на стадию паровоздушной конверсии.

На чертеже изображена схема получения аммиака по описываемому способу.

Природный газ поступает в сепаратор 1, в сепаратор топливного газа 2 и после компрессора 3 поступает в стадию сероочистки 4, а затем в смеси с технологическим паром в паровой реформинг 5 (трубчатую печь). После парового реформинга технологический газ с добавлением паровоздушной смеси поступает в паровоздушный реформинг 6 с рекуператорами тепла для производства пара. Подачу воздуха осуществляют в смеси с защитным паром в количестве 28000 нм^3/час через подогреватель. Нагрузка по природному газу 14000 нм^3/час соотношение газ:воздух=1:2 парогазовую смесь направляют и далее в среднетемпературный конвертор 7 окиси углерода первой ступени. Отсюда конвертированный газ поступает в рекуператоры тепла 8 (котел-утилизатор и подогреватель), а затем в низкотемпературный конвертор 9 окиси углерода.

Далее газ поступает в блок 10 охлаждения газа и отделения влаги, включающий узел впрыска конденсата, подогреватели раствора в стадии очистки газа от двуокиси углерода, подогреватель воды и сепаратор влаги. Охлажденный конвертированный газ, отделившийся от избыточного конденсата, направляют в абсорберы 11 очистки от двуокиси углерода с сепаратором влаги на выходе и далее в блок очистки метанированием с рекуператорами тепла и холодильником 12. Подготовленная и очищенная азотоводородная смесь поступает в сепаратор 13 на всос компрессора 14 синтез-газ и далее компремируется в стадию синтеза аммиака с аммиачно-холодильной установкой и рекуператорами тепла 15.

Кроме основного хода технологического газа, при этом способе дополнительно через запорно-регулирующую арматуру связи технологические газы после сероочистки подают в коллектор топливного газа горелок парового реформинга 5, а также по байпасу через рекуператор тепла 8, по байпасу мимо конвертора 9 и через блок охлаждения 10 в тот же коллектор на входе топливного газа в печь. Парогазовая смесь после парового 5 и паровоздушного 6 реформингов подается также мимо конверторов 7, 9 через рекуператор тепла 8 и блок охлаждения 10. Конденсат, образовавшийся из технологического пара парогазовой смеси в блоке охлаждения, подают для использования его в качестве питательной воды. Технологические газы после отделения конденсата в блоке 10 подают часть (10000-12000 нм^3) в коллектор на входе теплового газа в трубчатую печь 5, а остальную часть - на факельную установку 16.

Конвертированный газ после среднетемпературного конвертора 7 окиси углерода через рекуператор тепла 8 мимо низкотемпературного конвертора 9 окиси углерода через блок охлаждения 10 подают в коллектор топливного газа в трубчатую печь 5 и на факельную установку 16. Конвертированный газ после низкотемпературного конвертора 9 окиси углерода подают также через блок охлаждения 10 и после отделения конденсата распределяют часть (1000-12000 нм^9/час) в коллектор на входе топливного газа в трубчатую печь 5, а остальное - на факельную установку 16.

Конвертированный газ после стадии очистки от двуокиси углерода в адсорбере 11 также подают в коллектор на входе топливного газа в трубчатую печь 5 и на факельную установку 16.

Азотоводородную смесь после очистки из сепаратора 13 на всосе компрессора синтез-газа подают: часть на всос компрессора 3 природного газа (10000-10000 нм^3/час), часть (10000-12000 нм^3/час), - в коллектор на входе топливного газа в трубчатую печь 5, а остальное - на факельную установку 16.

На чертеже дополнительные введенные связи показаны пунктирной линией. Соотношение в топливе на входе в коллектор трубчатой печи составляет природный газ:технологический газ 1: (0,30-0,33). Сжигание водорода при паровоздушном реформинге вследствие соотношения газ:воздух 1:(2,0-2,2) увеличивает количество парогазовой смеси на выходе из паровоздушного реформинга, а также изменяет состав газа в сторону увеличения теплоемкости смеси, что увеличивает парообразование в рекуператорах тепла и возврат конденсата.

Topsoe, Inc. – EX1003
Page 958 of 1210

Использование предложенного способа получения аммиака обеспечит на один полный пуск при восстановленных катализаторах следующие преимущества (длительность пуска 48–62 часа), уменьшение расхода природного газа на 644,5 тыс.мм^3; возврат конденсата дополнительно (уменьшение расхода деминерализованной воды) 1000 м^3, а также уменьшение выбросов вредных примесей в атмосферу, двуокиси серы на 54,5 кг, двуокиси углерода на 229,5 тыс.нм^3, что в итоге приведет к экономии тепловой энергии на 393,7 мк.кал.

Формула изобретения

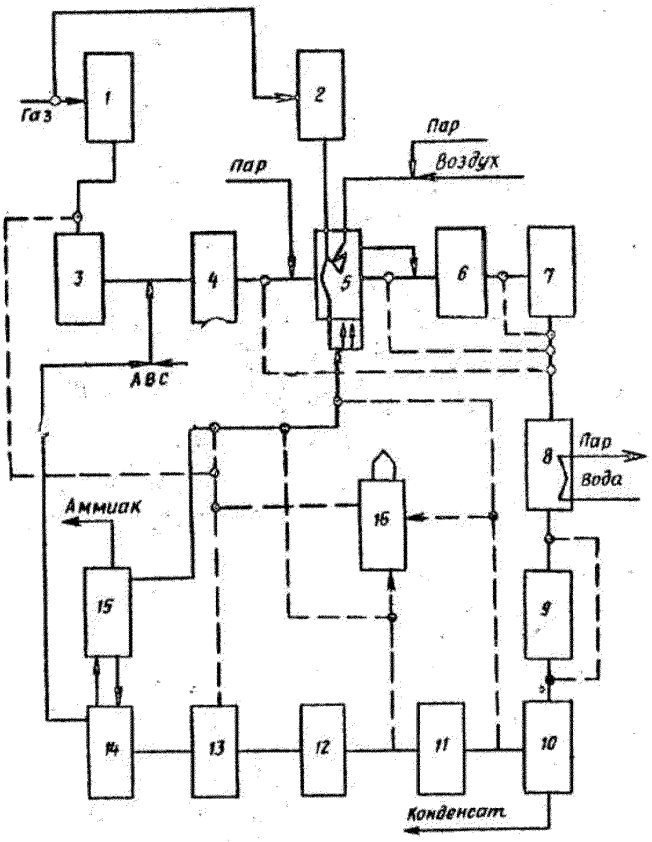
1. Способ получения аммиака из природного газа, включающий сероочистку, паровую каталитическую и паровоздушную конверсию природного газа, двухступенчатую конверсию окиси углерода, очистку синтез-газа от двуокиси углерода, синтез аммиака при высоком давлении с рекуперацией тепла на указанных стадиях для получения пара и подогрева питательной воды и сжигание технологических выбросов на факельной установке при пусковом режиме агрегата, отличающийся тем, что, с целью уменьшения расхода природного газа и воды, а также снижения вредных выбросов в атмосферу, технологические газы после каждой стадии подготовки синтез-газ направляют через рекуператоры тепла и отделители конденсата на стадию каталитической конверсии при соотношении в топливе природный газ :технологический газ=1:(0,30–0,33).

2. Способ по п. 1, отличающийся тем, что паровоздушную конверсию природного газа проводят при соотношении газ: воздух = 1:(2,0–2,2).

Источники информации, принятые во внимание при экспертизе:

1. Авторское свидетельство СССР № 280460, кл. С 01 С 1/04, 1969.

2. Тех. проект № 25226-О. "Агрегат синтеза аммиака для Березниковского АТЗ" ГИАП М., 1974.



ЦНИИПИ Заказ 755/24
Тираж 654 Подписное

Филиал ППП "Патент",
г. Ужгород, ул. Проектная, 4

Topsoe, Inc. – EX1003
Page 959 of 1210

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Espacenet

RU2561970C2 METHOD OF MODERNISATION OF PLANT FOR PRODUCTION OF AMMONIA WITH FLUSHING OF RINSE FLOW BASED ON NITROGEN

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Classifications:
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METHOD OF MODERNISATION OF PLANT FOR PRODUCTION OF AMMONIA WITH FLUSHING OF RINSE FLOW BASED ON NITROGEN

Abstract

FIELD: chemistry.SUBSTANCE: hydrocarbon raw material (5) and air (14) are fed to the conversion section (1) where the conditioned synthesis-gas (6) is received. The compressed conditioned synthesis-gas (6) is involved in reaction in the circuit (2) of high-pressure synthesis for obtaining ammonia. The flow (7) of rinse gas from the circuit (2) of the synthesis or the exhaust gas from the rinse gas recovery section, which comprises the inert impurities, is brought into contact with the nitrogen flow (10) produced in the process of air separation. The nitrogen flow (10) is in the liquid state or represents a mixture of liquid and gaseous nitrogen. The gas flow (8) is recycled to the synthesis circuit (2).EFFECT: invention enables to increase the productivity of the plant and to improve the efficiency of ammonia production process.12 cl, 4 dwg, 3 tbl, 3 ex

РОССИЙСКАЯ ФЕДЕРАЦИЯ

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(51) МПК
C01C 1/04 (2006.01)

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ПО ИНТЕЛЛЕКТУАЛЬНОЙ СОБСТВЕННОСТИ

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105082, Москва, Спартаковский пер., д. 2, стр. 1, секция 1, этаж 3, "ЕВРОМАРКПАТ"

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RU 2561970 C2

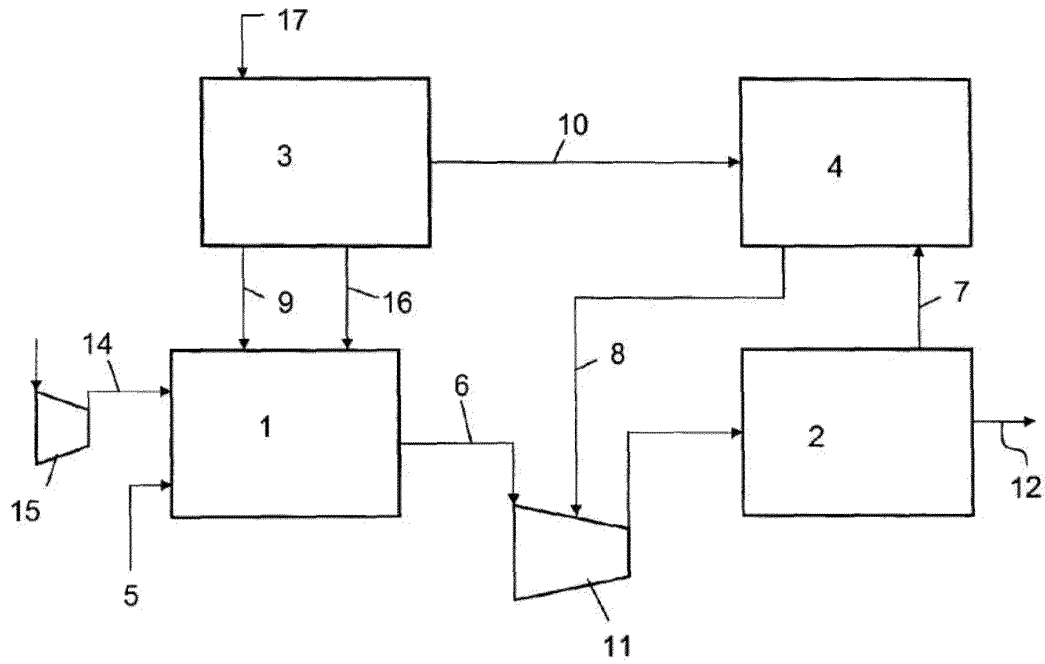
(54) СПОСОБ МОДЕРНИЗАЦИИ УСТАНОВКИ ДЛЯ ПРОИЗВОДСТВА АММИАКА С ПРОМЫВКОЙ ПРОДУВОЧНОГО ПОТОКА НА ОСНОВЕ АЗОТА

(57) Реферат:

Изобретение может быть использовано для производства аммиака паровой конверсией углеводорода, такого как природный газ. Углеводородное сырьё (5) и воздух (14) подают в секцию конверсии (1), где получают кондиционный синтез-газ (6). Сжатый кондиционный синтез-газ (6) вовлекают в реакцию в контуре (2) синтеза высокого давления для получения аммиака. Поток (7) продувочного газа из контура (2) синтеза или отходящий газ из секции извлечения продувочного газа, содержащий инертные примеси, вводят в контакт с потоком (10) азота, полученным в процессе разделения воздуха. Поток (10) азота находится в жидком состоянии или представляет собой смесь жидкого и газообразного азота. Газовый поток (8) рециркулируют в контур синтеза (2). Изобретение позволяет увеличить производительность установки и повысить эффективность процесса производства аммиака. 3 н. и 9 з.п. ф-лы, 4 ил., 3 табл., 3 пр.

RU 2561970 C2

Topsoe, Inc. – EX1003
Page 961 of 1210



ФИГ. 1

RU 2561970 C2

RU 2561970 C2

Topsoe, Inc. – EX1003
Page 962 of 1210

RUSSIAN FEDERATION

FEDERAL SERVICE
FOR INTELLECTUAL PROPERTY

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(73) Proprietor(s):
KASALE SA (CH)

RU 2561970 C2

(54) METHOD OF MODERNISATION OF PLANT FOR PRODUCTION OF AMMONIA WITH FLUSHING OF RINSE FLOW BASED ON NITROGEN

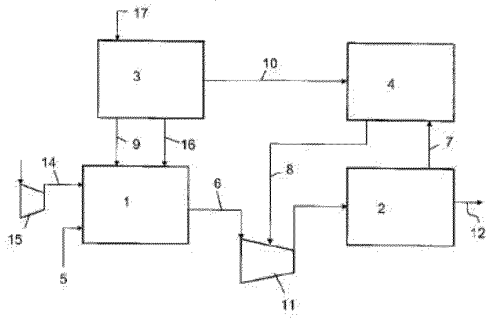
(57) Abstract:

FIELD: chemistry.

SUBSTANCE: hydrocarbon raw material (5) and air (14) are fed to the conversion section (1) where the conditioned synthesis-gas (6) is received. The compressed conditioned synthesis-gas (6) is involved in reaction in the circuit (2) of high-pressure synthesis for obtaining ammonia. The flow (7) of rinse gas from the circuit (2) of the synthesis or the exhaust gas from the rinse gas recovery section, which comprises the inert impurities, is brought into contact with the nitrogen flow (10) produced in the process of air separation. The nitrogen flow (10) is in the liquid state or represents a mixture of liquid and gaseous nitrogen. The gas flow (8) is recycled to the synthesis circuit (2).

EFFECT: invention enables to increase the productivity of the plant and to improve the efficiency of ammonia production process.

12 cl, 4 dwg, 3 tbl, 3 ex



Фиг. 1

RU 2561970 C2

Topsoe, Inc. – EX1003
Page 963 of 1210

Область техники

Настоящее изобретение относится к усовершенствованию способа и установки для производства аммиака паровой конверсией углеводорода, такого как природный газ.

Уровень техники

Аммиак производят путем каталитической реакции водорода и азота в контуре синтеза высокого давления. В уровне техники известна подача в этот контур высокого давления кондиционного (добавляемого/свежего) синтез-газа, состоящего, главным образом, из водорода (H_2) и азота (N_2) при соответствующем молярном соотношении, полученного паровой конверсией углеводородного сырья, обычно природного газа (метана) или нафты.

Синтез-газ получают в головной секции установки для производства аммиака, включающей, главным образом, установку первичной конверсии, установку вторичной конверсии, конвертер охлаждения/конверсии, секцию отделения CO_2, секцию метанирования и компрессор синтез-газа.

Установка первичной конверсии конвертирует пар и сырьевой обессеренный углеводород, например, природный газ или заменитель природного газа (ЗПГ), в смесь монооксида углерода, диоксида углерода и водорода путем пропуска над соответствующим катализатором при давлении, обычно в диапазоне от 15 до 35 бар, и высоких температурах около 800°C. Реакция протекает в ряде катализаторных труб, нагреваемых извне продуктами сгорания топлива.

Упомянутую смесь пропускают в установку вторичной конверсии, которая работает с избытком воздуха, для получения требуемого молярного соотношения $H_2|N_2$ (соотношения HN) и, следовательно, принимает дополнительный поток воздуха из соответствующего воздушного компрессора.

Конвертированный газ из установки вторичной конверсии далее обрабатывают в ряде единиц оборудования ниже по потоку для удаления оксидов углерода и получения состава газа, пригодного для синтеза аммиака, то есть имеющего соотношение HN близкое к 3. Обычная схема включает: CO-конвертер(ы), в которых большая часть монооксида углерода, содержащегося в конвертированном газе, каталитически превращается с непрореагировавшим паром в диоксид углерода и водород; колонну промывки CO_2, в которой диоксид углерода почти полностью удаляют промывкой газа соответствующим растворителем, таким как водный раствор амина или карбоната калия; реактор метанирования, в котором протекает каталитическая конверсия остаточных оксидов углерода в метан для исключения отравления катализатора синтеза аммиака ниже по потоку.

Затем давление синтез-газа в главном компрессоре синтез-газа увеличивают до рабочего давления в контуре синтеза аммиака, главным образом, в диапазоне от 80 до 300 бар и обычно около 150 бар.

Патент US 5736116 раскрывает способ модернизации путем монтажа установки разделения воздуха, обеспечивающей поток, обогащенный кислородом и азотом. Поток, обогащенный кислородом, используют для обогащения подачи воздуха в установку вторичной конверсии и увеличения содержания водорода в кондиционном газе до значений, по существу превышающих проектные показатели стехиометрии и производительности;

поток, обогащенный азотом, подают в контур синтеза для обеспечения требуемого соотношения водорода к азоту в подаче синтез-газа в конвертеры аммиака и компенсации избытка водорода в кондиционном газе.

Topsoe, Inc. – EX1003
Page 964 of 1210

Модернизация или увеличение производительности установки для производства аммиака ставит ряд проблем в связи с возросшей скоростью потока. Производительность установки первичной конверсии тесно связана с размером и числом труб в самой установке конверсии; вариант монтажа дополнительных труб, как правило, невозможен или очень ограничен; монтаж дополнительной установки предварительной конверсии возможен, однако это обходится дорого и дает преимущество лишь в 10-15%. Также необходимо обеспечить большую подачу кислорода в установку вторичной конверсии и увеличить производительность действующего воздушного компрессора. Оба варианта монтажа новых внутрикорпусных устройств в действующем воздушном компрессоре или обеспечения дополнительным компрессором, действующим параллельно с имеющимся, также дороги. Монтаж дожимного компрессора, то есть компрессора предварительного сжатия для увеличения давления на впуске главного воздушного компрессора, менее дорог, но так же менее эффективен. К возросшей скорости потока также приходится приспосабливаться путем размещения различного оборудования в головной секции, например, установки удаления CO_2, метанатора и т.п., что может потребовать значительных капитальных затрат, если какое-либо оборудование придется модифицировать.

Также критическим параметром и потенциальным узким местом является производительность компрессора синтез-газа. Монтаж любого дожимного компрессора или дополнительного компрессора обычно неприемлем, так как выход из строя любого дополнительного оборудования может подвергнуть риску надежность всей установки и причинить серьезный вред главному компрессору. Обычно предпочитают замену внутрикорпусного устройства компрессора и турбины, однако это вмешательство обходится дорого.

Другой проблемой является возможное накопление инертных газов в контуре синтеза. Этот контур синтеза часто работает в присутствии газообразных соединений или веществ, являющихся инертными, по меньшей мере в реакции синтеза аммиака. Примерами таких соединений являются метан и аргон. Накопление инертных газов означает увеличение скорости потока и снижение выхода конверсии. При увеличении производительности эта проблема, соответственно, становится более существенной. Инертные газы имеют низкую растворимость в аммиаке, который выводят из контура синтеза, и единственным способом исключения их накопления является продувка части синтез-газа. В уровне техники упомянутый продувочный газ обычно обрабатывают в специальных модулях, таких как мембраны или криогенный модуль, для извлечения содержащегося в нем водорода, или указанный продувочный газ используют в качестве топлива.

Все вышеупомянутые проблемы имеют место при модернизации действующей установки, но также при проектировании новой установки с попыткой увеличения общей производительности, что касается размера главных единиц оборудования, таких как установки конверсии и компрессоры.

Уровень техники дает лишь частичное решение вышеуказанных проблем. Предложенное изобретение направлено на обеспечение лучшей и/или более подходящей интеграции установки разделения воздуха с процессом/установкой для производства аммиака.

Сущность изобретения

Первым объектом изобретения является способ производства аммиака, в котором: кондиционный синтез-газ получают паровой конверсией углеводородного сырья, паровая конверсия включает стадии первичной и вторичной конверсии, стадии

Topsoe, Inc. – EX1003
Page 965 of 1210

последующей обработки или конверсии, удаления CO_2 и метанирования; кондиционный синтез-газ сжимают с последующей реакцией в контуре синтеза высокого давления с получением аммиака; подачу воздуха подвергают процессу разделения на поток кислорода и по меньшей мере один поток азота, поток кислорода направляют в установку вторичной конверсии для обеспечения дополнительного окислителя, поток азота, полученный в упомянутом процессе разделения воздуха, используют для обработки потока продувочного газа, содержащего инертные примеси, получая таким образом водородсодержащий и по существу свободный от инертных примесей рециркулирующий поток газа, который рециркулируют в контур синтеза.

Указанный продувочный поток в предпочтительных вариантах осуществления изобретения представляет собой продувочный газ, продутый из контура синтеза, или отходящий газ из секции извлечения продувочного газа.

Поток продувочного газа, содержащий инертные примеси, в соответствии с предлагаемым изобретением, контактирует с потоком азота, полученным с помощью процесса разделения воздуха.

Термины "поток кислорода" и "поток азота" в данном описании используются со ссылкой на потоки, имеющие требуемую степень чистоты. Потоки кислорода и азота представляют собой поток, обогащенный кислородом и азотом, соответственно. Предпочтительно, поток кислорода имеет степень чистоты по меньшей мере 95%, однако в любом случае может использоваться менее чистый поток кислорода; поток азота предпочтительно имеет чистоту 99% или более для того, чтобы избежать отравления O_2 катализатора, используемого в контуре синтеза аммиака. Процесс разделения воздуха выполняют по меньшей мере в одной установке разделения воздуха, в соответствии по сути с известной техникой.

Поток азота может находиться в жидком или газообразном состоянии или представлять собой смесь жидкого и газообразного азота. Раздельные жидкие и газообразные потоки азота можно также получить из установки разделения воздуха. В соответствии с предлагаемым изобретением, возможны разные варианты осуществления изобретения при использовании жидкого или газообразного потока (ов) азота.

В соответствии с другими вариантами осуществления изобретения, процесс разделения воздуха обеспечивает подачу первого потока азота, используемого для регулирования соотношения водорода и азота в синтез-газе, и второго потока азота, используемого для обработки продувочного потока, то есть продувки или отходящего газа.

Другой вариант осуществления изобретения основан на том, что подача кислорода, обеспечиваемая упомянутым потоком кислорода в установку вторичной конверсии, обеспечивает избыток водорода в выпуске синтез-газа из головной секции, то есть соотношение HN более 3, что будет компенсировать более низкое соотношение HN (менее 3) в рециркулирующем потоке. В соответствии с этим вариантом осуществления изобретения, при модернизации, направленной на увеличение производительности действующей установки, количество кислорода, подаваемого в установку вторичной конверсии, больше теоретического количества, соответствующего требуемому увеличению производительности. Другое преимущество состоит в снижении нагрузки действующего воздушного компрессора.

В соответствии с другим вариантом осуществления изобретения, поток продувочного газа обрабатывают в криогенном процессе, при котором по меньшей мере часть продувочного газа сжижается с получением жидкого потока, обогащенного метаном, и отделением потока рециркулирующего газа, содержащего, главным образом, водород

Topsoe, Inc. – EX1003
Page 966 of 1210

и азот. В соответствии с конкретными вариантами осуществления изобретения, поток рециркулирующего газа подают на всасывание циркуляционного насоса контура синтеза или в главный компрессор синтез-газа.

В некоторых вариантах осуществления изобретения продувочный поток промывают чистым жидким или смешанным потоком жидкого/газообразного азота. Промывка смешанным потоком жидкого/газообразного азота является более эффективным процессом в сравнении со смешением лишь с газообразным азотом, в частности, благодаря меньшей поверхности теплообмена, более низкой температуре синтез-газа на всасывании циркуляционного насоса и/или ступенях сжатия и, следовательно, увеличивает производительность циркуляционного насоса/компрессора. Упомянутый процесс промывки жидким или смешанным жидким/газообразным азотом выполняют при криогенной температуре, то есть в низкотемпературном узле. В других вариантах осуществления изобретения продувочный поток смешивают с потоком газообразного азота перед впуском упомянутого потока в низкотемпературный узел.

В предпочтительном варианте осуществления изобретения используют поток жидкого азота из процесса разделения воздуха для противоточной промывки продувочного потока в криогенной аппаратуре, предпочтительно в криогенной колонне. Предпочтительно, промывку продувочного газа проводят в соответствии со следующим процессом. Продувочный или отходящий газ охлаждают до криогенной температуры и затем охлажденный продувочный газ промывают в криогенной колонне потоком, содержащим жидкий азот; промытый продувочный поток отбирают из указанной колонны, газообразную фракцию промытого продувочного потока отделяют с получением промытого продувочного газа, который используют для охлаждения продувочного газа, подаваемого в теплообменник, затем промытый продувочный газ рециркулируют в контур синтеза или компрессор синтез-газа. Жидкую фракцию, отделенную из промытого продувочного потока, рециркулируют в криогенную колонну.

В другом предпочтительном варианте осуществления изобретения устройство разделения воздуха (УРВ) обеспечивает подачу потока азота в форме газообразного потока под давлением. Этот поток азота подают в устройство извлечения продувочного газа, где по меньшей мере часть продувочного газа сжижают с помощью криогенного процесса, получая жидкий поток. Этот жидкий поток обогащен метаном, и поэтому газообразный поток, выходящий из устройства извлечения продувки, содержит, главным образом, водород и азот и может быть возвращен в контур синтеза или соответствующий компрессор. Предпочтительно, добавленное количество азота является избыточным в сравнении со стехиометрическим значением.

Вышеуказанные варианты осуществления изобретения, использующие жидкий и газообразный азот, соответственно, можно комбинировать друг с другом. Следовательно, можно также использовать комбинированный раствор жидкого плюс газообразного азота.

Другим альтернативным вариантом осуществления изобретения, известным в уровне техники, является обработка продувочного газа в секции извлечения продувки с получением отходящего газа, называемого также сбросный газ, содержащего некоторое количество остаточного водорода. В соответствии с предлагаемым изобретением, этот отходящий газ обрабатывают азотом для извлечения остаточного водорода.

Продувочный газ перед промывкой/обработкой азотом предпочтительно не содержит аммиак. Аммиак можно удалить, например, противоточной промывкой водой продувочного газа. Затем воду удаляют, используя, например, сушильные аппараты.

Кислородный поток предпочтительно сжимают в соответствующем компрессоре и

Topsoe, Inc. – EX1003
Page 967 of 1210

смешивают с подачей воздуха в установку вторичной конверсии, обеспечивая таким образом подачу обогащенного кислородом воздуха в эту установку.

Другим объектом предлагаемого изобретения является установка, приспособленная к проведению вышеописанного процесса и разных его вариантов. В соответствии с предлагаемым изобретением, установка для производства аммиака включает: контур синтеза и головную секцию для снабжения кондиционным синтез-газом указанного контура синтеза, упомянутая головная секция включает установку первичной конверсии, установку вторичной конверсии и дополнительное оборудование для конверсии, удаления CO_2 и метанирования; главный компрессор синтез-газа для подачи кондиционного синтез-газа в контур синтеза; по меньшей мере одно устройство разделения воздуха, обеспечивающее поток кислорода и по меньшей мере один поток азота;

поточную линию, подающую поток кислорода в установку вторичной конверсии или воздушный компрессор, питающий установку вторичной конверсии;

установка отличается включением средств, приспособленных для промывки продувочного газа, содержащего инертные примеси, продутые из контура синтеза, или отходящего газа из секции извлечения продувочного газа, по меньшей мере одним потоком азота для получения водородсодержащего, по существу не содержащего инертные примеси рециркулирующего потока, и поточной линии, предназначенной для рециркуляции этого потока в контур синтеза.

В соответствии с раскрытыми выше вариантами осуществления изобретения, устройство разделения воздуха (УРВ) обеспечивает снабжение азотом в жидкой или газообразной форме или в обеих формах. Установка может включать криогенный аппарат, предпочтительно криогенную колонну, в которой продувочный газ промывают противоточным потоком жидкого азота, полученным в УРВ, для извлечения водородсодержащего газа, не содержащего инертные примеси. В дополнительных вариантах осуществления изобретения установка может включать устройство для извлечения продувочного газа, где его ожижают и куда подают газообразный азот, полученный в УРВ, для извлечения газообразного потока, содержащего водород и азот.

Предлагаемое изобретение также пригодно для модернизации действующей установки для производства аммиака. Дополнительным вариантом осуществления изобретения затем является способ увеличения производительности установки для производства аммиака, включающей контур синтеза аммиака и головную секцию, обеспечивающую подачу потока синтез-газа, содержащего водород и азот, в контур синтеза, причем головная секция включает установки первичной и вторичной конверсии и дополнительное оборудование для конверсии, удаления CO_2 и метанирования, а также компрессор синтез-газа для подачи потока синтез-газа в контур синтеза. Способ модернизации включает стадии: обеспечения устройством разделения воздуха, приспособленным для снабжения потоком кислорода и по меньшей мере одним потоком жидкого или газообразного азота; обеспечения средствами подачи потока кислорода в установку вторичной конверсии или воздушный компрессор, питающий установку вторичной конверсии; обеспечения средствами, приспособленными для использования потока азота для промывки продувочного газа, отбираемого из контура синтеза, или отходящего газа, выделяющегося при обработке продувочного газа, с получением водородсодержащего, по существу свободного от инертных примесей рециркулирующего потока для рециркуляции этого потока в контур синтеза.

При модернизации действующей установки можно реализовать раскрытые выше

Topsoe, Inc. – EX1003
Page 968 of 1210

варианты осуществления изобретения в соответствии с потребностями и/или характерными особенностями старой установки для производства аммиака. Например, если установка уже обеспечена секцией извлечения продувки (например, мембранами или другой системой), можно продуть из контура больше газа путем обработки дополнительной продувки азотом из УРВ.

В предпочтительном варианте осуществления изобретения количество азота из УРВ, подаваемого в установку вторичной конверсии, больше, чем теоретическое количество, соответствующее увеличению производительности всей установки, для снижения нагрузки действующего воздушного компрессора.

Основное преимущество предлагаемого изобретения заключается в использовании потока азота из УРВ для увеличения эффективности процесса путем извлечения водорода продувочного газа не только для регулирования соотношения HN сырьевого синтез-газа.

Предлагаемое изобретение позволяет увеличить производительность установки, уменьшает возрастание скорости потока во всей головной секции и связанные с этим проблемы, включая падение давления и нагрузку секции удаления CO_2 и метанирования. Головная секция получает лишь чистый поток кислорода, необходимый для увеличения производительности конверсии, тогда как поток азота, который должен проходить через головную секцию по существу как инертный газ, соответственно подают лишь в секцию извлечения продувочного газа, где он требуется как один из реагентов для производства аммиака и для установления требуемого соотношения HN кондиционного синтез-газа.

Использование жидкого азота для извлечения водорода, содержащегося в продувочном газе, вместо ввода или непосредственного использования в головной секции, имеет преимущество, которое заключается в значительном снижении капитальных затрат; фактически эту промывку/обработку выполняют в отношении продувочного газа, скорость потока которого, как правило, в десять раз меньше, чем скорость потока кондиционного синтез-газа, подаваемого в контур синтеза. Другое преимущество заключается в том, что для промывки потока, а именно продувочного или отходящего газа, используют азот, содержащий более высокое количество инертных примесей, чем кондиционный синтез-газ, и поэтому промывка продувки азотом является высокоэффективной.

Подача кислорода в установку вторичной конверсии имеет дополнительные преимущества. Нагрузка воздушного компрессора, питающего установку вторичной конверсии, снижается, так как часть кислорода, необходимого для установки вторичной конверсии, теперь обеспечивается УРВ. Это означает, что производительность установки можно увеличить при данных размере и пропускной способности воздушного компрессора без необходимости в более крупном и дорогом компрессоре. При модернизации действующей установки предлагаемое изобретение обеспечивает дополнительную пропускную способность/удобство и простоту использования действующего воздушного компрессора в случае ухудшения внешних условий, увеличение производительности, возможность использования резервного сжатого воздуха в другом месте установки для производства аммиака. Питание действующего воздушного компрессора потоком, обогащенным кислородом, позволяет добиться большей производительности конверсии при той же скорости потока на впуске компрессора, то есть без необходимости модификации самого компрессора.

Подача дополнительного кислорода в установку вторичной конверсии также имеет преимущество, заключающееся в значительном увеличении производительности

Topsoe, Inc. – EX1003
Page 969 of 1210

конверсии без модификации установки первичной конверсии, находящейся выше по потоку. Это является важным преимуществом потому что, как утверждалось выше, увеличение производительности установки первичной конверсии, как правило, невозможно или обходится слишком дорого.

Путем разделения основных компонентов воздуха (кислород и азот) предлагаемое изобретение позволяет добавлять кислород и азот в оптимальных точках схемы установки. При необходимости можно увеличить количество кислорода, а именно на впуске установки вторичной конверсии, а азот подают лишь в случае необходимости, то есть в контур синтеза аммиака.

Следует отметить, что скорость потока и давление на впуске главного компрессора синтез-газа по существу остаются неизменными, даже при увеличении производительности установки. Предлагаемое изобретение позволяет также снизить нагрузку действующего оборудования, главным образом, упомянутого главного компрессора синтез-газа и воздушного компрессора простым увеличением нагрузки УРВ, обеспечивая дополнительное "пространство" для упомянутых устройств; кроме того, уменьшение нагрузки воздушного компрессора позволяет снизить падение давления в головной секции из-за азота, ранее подаваемого компрессором.

Парциальное давление CO_2 в синтез-газе возрастает вследствие меньшей концентрации азота. Это означает, что секция удаления CO_2 может работать более эффективно, и что предлагаемое изобретение способствует также решению проблемы увеличения производительности секции удаления CO_2.

Суммируя вышеизложенное, можно констатировать, что предлагаемое изобретение обеспечивает эффективное и рентабельное увеличение производительности действующей установки для производств аммиака или увеличение пропускной способности и эффективности новой установки при данных капитальных затратах, то есть размере главных единиц оборудования, таких как установки конверсии, воздушный компрессор и компрессор синтез-газа, установки удаления CO_2 и т.п. В частности, предлагаемое изобретение обеспечивает стратегическое использование кислорода и азота из устройства разделения воздуха.

Преимущества будут более очевидны при следующем детальном описании предпочтительного варианта осуществления изобретения.

Краткое описание чертежей

На прилагаемых к описанию чертежах показано:

на фиг.1 - блок-диаграмма установки для производства аммиака в соответствии с предлагаемым изобретением или модернизированной в соответствии с предлагаемым изобретением,

на фиг.2 - упрощенная схема варианта осуществления изобретения с использованием азота для промывки продувочного газа в колонне,

на фиг.3 - упрощенная схема другого варианта осуществления изобретения с использованием азота для промывки отходящего газа,

на фиг.4 - схема дополнительного варианта осуществления изобретения с использованием газообразного азота для обработки продувочного газа.

Подробное описание вариантов осуществления изобретения

Как видно из фиг.1, традиционная установка для производства аммиака включает, в основном, головную секцию 1 конверсии, работающую под давлением около 25-35 бар, контур синтеза 2, работающий под более высоким давлением, например, 150 бар; устройство 3 разделения воздуха (УРВ) и устройство 4 извлечения продувки.

Topsoe, Inc. – EX1003
Page 970 of 1210

В секцию конверсии 1 подают соответствующее углеводородное сырье, такое как природный газ 5 и воздух 14 из воздушного компрессора 15. Кондиционный синтез-газ 6 из секции 1 конверсии поступает в контур 2 через главный компрессор 11 синтез-газа. Головная секция 1 и контур 2 известны как таковые и далее не будут описаны.

В контуре синтез-газа 2 получают аммиак 12 и продувочный газ 7 из этого контура подают в устройство 4 извлечения продувки. Продувочный газ 7 содержит водород, азот и некоторое количество инертных примесей, главным образом метан и аргон. В устройстве 4 извлечения продувки извлекают водород, содержащийся в продувочном газе 7, обеспечивая контур 2 рециркулирующим потоком 8, содержащим водород, и по существу не содержащим инертные примеси. Указанный рециркулирующий поток 8 возвращают обратно в контур 2, подавая его, например, на промежуточную ступень главного компрессора 11.

УРВ 3 принимает подачу воздуха 11 и снабжает кислородом 9 установку вторичной конверсии, расположенную в головной секции 1, и жидким и/или газообразным азотом 10 устройство 4 извлечения продувочного газа. Устройство 4 извлечения продувки включает, например, промывную колонну, в которой промывают продувочный газ 7 жидким азотом 10 для получения рециркулирующего потока 8. УРВ 3 необязательно поставляет дополнительный поток 16 азота, который используют для регулирования соотношения водорода и азота в синтез-газе 6.

На фиг.2 показан предпочтительный вариант осуществления изобретения для криогенной обработки продувочного газа. Продувочный газ 100, содержащий 60-70% водорода, около 20% азота и 5-6% метана и аргона, отбирают из контура синтеза. Указанный газ 100 охлаждают в соответствующем теплообменнике 150 до криогенной температуры, такой как - 150°C. Охлажденный продувочный газ 101 подают в криогенную колонну 120, где его промывают жидким азотом 105 из УРВ. В примере продувочный газ промывают потоком 112, содержащим жидкий азот 105, и дополнительным жидким потоком 104, содержащим, главным образом, азот и водород, который рециркулируют из сепаратора 104.

Метан и частично аргон, содержащиеся в газе 101, удаляют в колонне 120. Сверху колонны 120 отводят продувочный газ 102, по существу не содержащий метан, тогда как жидкий поток 110, содержащий, главным образом, азот, конденсат метана и аргон, отбирают снизу той же колонны 120. Жидкость 110 подвергают мгновенному испарению в клапане 121, получая поток 106 со сброшенным давлением.

Упомянутый газ 102, не содержащий метан, по меньшей мере частично конденсируют в соответствующем теплообменнике 130 путем теплообмена с потоком 106 со сброшенным давлением. Выпуск конденсата 113 из конденсатора 130 обрабатывают в сепараторе 140 жидкость/газ с получением газообразного потока 103 и жидкого потока 104. Газообразный поток 103 охлаждает теплообменник 110 и выходит как повторно нагретый поток 108 до температуры, например, около - 40°C. Этот поток 108 по существу свободен от метана и содержит меньшее количество аргона (1-2%), чем впускной продувочный газ 100, после чего его можно рециркулировать как реагент (кондиционный синтез-газ) для контура синтеза аммиака.

Жидкий поток 104 предпочтительно рециркулируют в промывную колонну 120, смешивая, например, с жидким азотом 105, как показано на фиг.2.

Остаточный поток 106, обогащенный метаном, по меньшей мере частично испаряют в теплообменнике 130, получая таким образом газообразный поток 109, который повторно нагревают в теплообменнике 150, обеспечивая таким путем дополнительный источник охлаждения для поступающего продувочного газа 100. Повторным нагревом

Topsoe, Inc. – EX1003
Page 971 of 1210

потока 106, обогащенного метаном, получают топливный газ 107 на выходе из теплообменника 150, который рециркулируют в систему топливного газа.

Главными единицами оборудования, образующими низкотемпературный узел для обработки продувочного газа 100, являются колонна 120, теплообменник 130, сепаратор 140 и теплообменник 150. Вспомогательное оборудование, такое как клапаны, насосы, экспандеры и т.п. не показано.

Альтернативный вариант осуществления изобретения показан на фиг.3. Продувочный газ 100 предварительно обрабатывают в устройстве 160 извлечения продувочного газа с извлечением части содержащегося в нем водорода. Из упомянутого устройства извлечения продувочного газа отводят отходящий газ 100a, содержащий азот, метан, аргон и остаточный водород, в количестве, например, около 15%. Остаточный водород далее извлекают обработкой отходящего газа 100a вышеописанным способом со ссылкой на фиг.2.

В другом варианте осуществления изобретения, показанном на фиг.4, используют поток газообразного азота. Газообразный азот 205 смешивают с продувочным газом 100 перед подачей в «низкотемпературный узел», то есть перед подачей газа 100 в часть установки при криогенной температуре. Полученный таким образом поток ЮОЬ продувочного газа, обогащенного азотом, охлаждают затем в теплообменнике 150 и подают в промывную колонну 120, где его промывают потоком 105 жидкого азота. Другие подробности вариантов осуществления изобретения, представленных на фиг.3 и 4, аналогичны таковым, раскрытым со ссылкой на фиг.2.

Пример 1

Цифры, приведенные в нижеследующем примере, относятся к фиг.1. Традиционную установку для производства аммиака модернизируют путем монтажа УРВ 3, обеспечивая поток 9 кислорода и поток 10, азота, используемый для промывки продувочного газа. Следует отметить следующее: выход аммиака (поток 12) увеличился на 14%, тогда как подача воздуха 14 в воздушный компрессор снизилась на 11%; однако, общая подача кислорода в установку вторичной конверсии возросла примерно на 37%, так как воздух 14 содержит 21% кислорода, тогда как поток 9 содержит 95% кислорода. Таблица 1 раскрывает подробный состав потоков, показанных на фиг.1 (модернизированный вариант).

Таблица 1a

(базовый вариант)

Поток		5	9	14	12
Паровая фракция (моль)		1,00	-	1,00	0,08
Температура	°F	76,5	-	333,5	3,0
Давление	Psig	630,80	-	493,10	17,26
Молярный поток	фунтмоль/ч	4185,0	-	5840,0	8791,3
Массовый поток	фунт/ч	69206,8	-	169153,9	149716,3

Таблица 1b

(модернизированный вариант)

Поток		5	9	14	12
Паровая фракция (моль)		1,00	1,00	1,00	0
Температура	°F	72,8	104,0	330,4	3,0
Давление	Psig	645,00	522,14	508,15	17,26
Молярный поток	фунтмоль/ч	4953,0	618,0	5200,0	10085,1
Массовый поток	фунт/ч	81907,2	19947,8	150616,5	171750,8

Таблица 1c

Поток		5	6	7	8	9

Topsoe, Inc. – EX1003
Page 972 of 1210

Паровая фракция(моль)		1,00	1,00	1,00	1,00	1,00
Температура	°F	72,8	45,0	-15,4	-73,9	104,0
Давление	Psig	645,00	355,60	1986,67	899,00	522,14
Молярный поток	фунтмоль/ч	4953,0	22376,8	1440,0	1316,4	618,0

Поток		5	6	7	8	9
Массовый поток	фунт/ч	81907,2	192860,8	14854,0	12692,2	19947,8
Состав	%моль					
H_2		-	74,495%	66,144%	71,248%	-
N_2		3,403%	24,557%	19,474%	27,489%	1,000%
NH_3		-	-	1,869%	-	-
CH_4		95,991%	0,499%	6,000%	-	-
Ar		-	0,373%	5,522%	1,263%	4,000%
He		0,121%	0,035%	0,991%	-	-
H_2O		-	0,042%	-	-	-
O2		-	-	-	-	95,000%
CO2		0,118%	-	-	-	-

Таблица 1c (продолжение)

Поток		10	12	14	16
Паровая фракция (моль)		0,00	0,06	1,00	1,00
Температура	°F	-240,0	3,0	330,4	122,0
Давление	Psig	900,00	17,26	508,15	900,00
Молярный поток	фунтмоль/ч	198,4	10085,1	5200,0	837,7
Массовый поток	фунт/ч	5558,2	171750,8	150616,5	23472,8
Состав	%моль				
H_2		-	-	-	-
N_2		99,950%	-	78,086%	99,950%
MH_3		-	99,968%	-	-
CH_4		-	0,007%	-	-
Ar		0,050%	-	0,934%	0,050%
He		-	-	-	-
H_2O		-	0,025%	-	-
O2		-	-	20,948%	-

Пример 2

Следующая таблица 2 относится к установке, показанной на фиг.2, где продувочный газ 100, содержащий около 66% водорода и 21,5% азота плюс 6,4% метана и 5,8% аргона, обрабатывают в криогенной секции с получением рециркулирующего потока 108 без метана, содержащего около 70% водорода и 28% азота.

Таблица 2

Пар		100	101	102	103	104
Паровая фракция (моль)		1,00	0,95	1,00	1,00	0,00
Температура	°F	14,0	-239,7	-266,7	-277,0	-277,0
Давление	psig	1976,67	1975,67	900,00	900,00	900,00

Пар		100	101	102	103	104
Молярный расход	фунтмоль/ч	1384,1	1384,1	1542,8	1278,1	264,7
Массовый расход	фунт/ч	14884,8	14884,8	19336,3	12648,4	6687,9
Состав	%мол					
H_2		66,092%	66,092%	60,446%	70,245%	13,139%
N_2		21,586%	21,586%	37,589%	28,541%	81,272%
CH_4		6,473%	6,473%	0,001%	-	0,004%

Topsoe, Inc. – EX1003
Page 973 of 1210

Ar		5,848%	5,848%	1,964%	1,214%	5,585%
Пар		105	106	107	108	
Паровая фракция (мол))		0,00	0,26	1,00	1,00	
Температура	°F	-240,0	-294,4	-22,0	-44,0	
Давление	psig	900,00	29,01	28,01	899,00	
Молярный расход	фунтмоль/ч	198,4	304,5	304,5	1278,1	
Массовый расход	фунт/ч	5558,2	7794,9	7794,9	12648,4	
Состав	%мол					
H_2		-	5,584%	5,584%	70,245%	
N_2		100,000%	43,504%	43,504%	28,541%	
CH_4		-	29,427%	29,427%	-	
Ar		-	21,485%	21,485%	1,214%	

Пример 3

Нижеследующая таблица 3 относится к установке, показанной на фиг.3, где отходящий газ 100a, содержащий около 15% водорода и 48% азота, обрабатывают в криогенной секции. Полученный рециркулирующий поток 108 содержит около 42% водорода и 56% азота.

Таблица 3						
Пар		100a	101	102	103	104
Паровая фракция (моль)		1,00	0,97	1,00	1,00	0,00
Температура	°F	122,0	-194,6	-248,7	-264,3	-264,3
Давление	psig	901,45	900,00	435,11	435,11	435,11
Молярный расход	фунтмоль/ч	557,0	557,0	553.9	170,0	383,9
Массовый расход	фунт/ч	12585,5	12585,5	12962,9	2915,1	10047,8
Состав	%mol					
H_2		14,542%	14,542%	18,758%	42,334%	8,319%
N_2		48,474%	48,474%	79,002%	56,492%	88,970%
CH_4		25,314%	25,314%	0,009%	0,002%	0,012%
Ar		11,670%	11,670%	2,231%	1,172%	2,699%

Пар		105	106	107	108
Паровая фракция(моль)		0,00	0,43	1,00	1,00
Температура	°F	-234,4	-288,5	96,7	50,0
Давление	psig	454,33	26,11	23,21	433,66
Молярный поток	фунтмоль/ч	44,1	431,1	431,1	170,0
Массовый поток	фунт/ч	1235,1	10906,9	10906,9	2915,1
Состав	%mol				
H_2		-	2,096%	2,096%	42,334%
N_2		100,000%	50,582%	50,582%	56,492%
CH_4		0,000%	32,704%	32,704%	0,002%
Ar		0,000%	14,618%	14,618%	1,172%

В вышеприведенных таблицах давление дается в фунт-силе на квадратный дюйм относительно атмосферы (psig). Перевод в единицы СИ можно сделать с помощью уравнения 1 psi=6894,76 Па. Массовый расход дан в фунт/ч (фунты в час), где 1 lb=0,4536 кг.

Формула изобретения

1. Способ производства аммиака, в котором получают кондиционный синтез-газ (6) паровой конверсией углеводородного сырья (5), включающей стадии первичной конверсии и вторичной конверсии и дополнительные стадии обработки продуктов

Topsoe, Inc. – EX1003
Page 974 of 1210

конверсии, удаления CO_2 и метанирования; сжимают кондиционный синтез-газ и вовлекают в реакцию в контуре (2) синтеза высокого давления для получения аммиака; подвергают подаваемый воздух (17) процессу разделения на поток кислорода (9) и по меньшей мере один поток азота (10, 16); обеспечивают за счет этого потока кислорода дополнительный окислитель для установки вторичной конверсии;

отличающийся тем, что поток (7) продувочного газа из контура (2) синтеза или отходящий газ из секции (160) извлечения продувочного газа, содержащий инертные примеси, вводят в контакт с потоком (10) азота, полученным в процессе разделения воздуха и находящимся в жидком состоянии или представляющим собой смесь жидкого и газообразного азота, с получением водородсодержащего и по существу не содержащего инертные примеси рециркулирующего газового потока (8), который рециркулируют в контур синтеза.

2. Способ по п. 1, отличающийся тем, что поток (7) продувочного газа контактирует с потоком азота при криогенной температуре, в результате чего по меньшей мере часть продувочного газа (7) ожижается с получением потока (107), обогащенного метаном, и отделением рециркулирующего газового потока (108), содержащего, главным образом, водород и азот.

3. Способ по п. 2, отличающийся тем, что упомянутый поток (100) продувочного газа промывают потоком жидкого азота или смешанным потоком газообразного/жидкого азота посредством процесса противоточной промывки в криогенном устройстве (120).

4. Способ по п. 3, отличающийся тем, что продувочный газ (100) или отходящий газ (100a) охлаждают до криогенной температуры в теплообменнике (150), получая охлажденный продувочный газ (101), который затем промывают в криогенной колонне (120) потоком (112), содержащим жидкий азот (105); отбирают из этой колонны промытый продувочный поток (102); газообразную фракцию (103) промытого продувочного потока отделяют для получения промытого продувочного газа, который используют для охлаждения теплообменника (150) путем теплообмена с поступающим продувочным газом (100); промытый продувочный газ (108) затем рециркулируют в контур синтеза.

5. Способ по п. 4, в котором продувочный газ (100) или отходящий газ (100a) смешивают с газообразным азотом (205) перед его охлаждением до криогенной температуры в теплообменнике (150).

6. Способ по п. 1, отличающийся тем, что поток азота в виде газообразного потока под давлением подают в устройство извлечения продувочного газа, где в криогенном процессе по меньшей мере часть продувочного газа ожижается с получением жидкого потока, обогащенного метаном; а газообразный поток, выходящий из устройства извлечения продувки, содержащий главным образом водород и азот, рециркулируют обратно в контур синтеза или соответствующий компрессор.

7. Установка для производства аммиака, включающая контур (2) синтеза аммиака и головную секцию (1) для обеспечения подачи кондиционного синтез-газа в упомянутый контур синтеза, включающую установку первичной конверсии, установку вторичной конверсии и дополнительное оборудование для конверсии, удаления CO_2 и метанирования, а также главный компрессор синтез-газа для подачи кондиционного синтез-газа в контур синтеза; и установка дополнительно включает по меньшей мере одно устройство (3) разделения воздуха, обеспечивающее поток (9) кислорода и по меньшей мере один поток азота, и поточную линию для подачи потока кислорода в установку вторичной конверсии или воздушный компрессор, питающий установку

Topsoe, Inc. – EX1003
Page 975 of 1210

вторичной конверсии,

отличающаяся тем, что она включает:

устройство (4) извлечения продувки, содержащее по меньшей мере криогенное промывное устройство для промывки продувочного газа (7), содержащего инертные примеси, продутые из контура синтеза, или отходящего газа из секции извлечения продувочного газа потоком (10) азота из устройства (3) разделения воздуха с получением по существу свободного от инертных примесей рециркулирующего потока (8), причем этот поток азота находится в жидком состоянии или представляет собой смесь жидкого и газообразного азота, и

поточную линию для подачи рециркулирующего потока (8) в контур синтеза.

8. Установка по п. 7, в которой устройство (4) извлечения продувки включает по меньшей мере криогенную промывную колонну (120), в которой поток продувочного газа или отходящего газа промывают противотоком жидким азотом (105) или смесью газообразного/жидкого азота из устройства разделения воздуха.

9. Установка по п. 7 или 8, включающая низкотемпературный узел, в котором промывают поток (100) продувочного газа или поток (100a) отходящего газа азотсодержащим потоком, и дополнительно включающая линию (205) для добавки газообразного азота к продувочному или отходящему газу выше по потоку от низкотемпературного узла.

10. Способ модернизации установки для производства аммиака, включающей контур (2) синтеза аммиака и головную секцию (1) для обеспечения подачи потока синтез-газа, содержащего водород и азот, в контур синтеза, содержащую установку первичной конверсии, установку вторичной конверсии и дополнительное оборудование для конверсии, удаления CO_2 и метанирования и компрессор (11) синтез-газа для подачи потока синтез-газа в контур синтеза,

включающий стадии:

монтажа устройства (3) разделения воздуха, приспособленного для обеспечения потока (9) кислорода и по меньшей мере одного потока (10, 16) жидкого или газообразного азота;

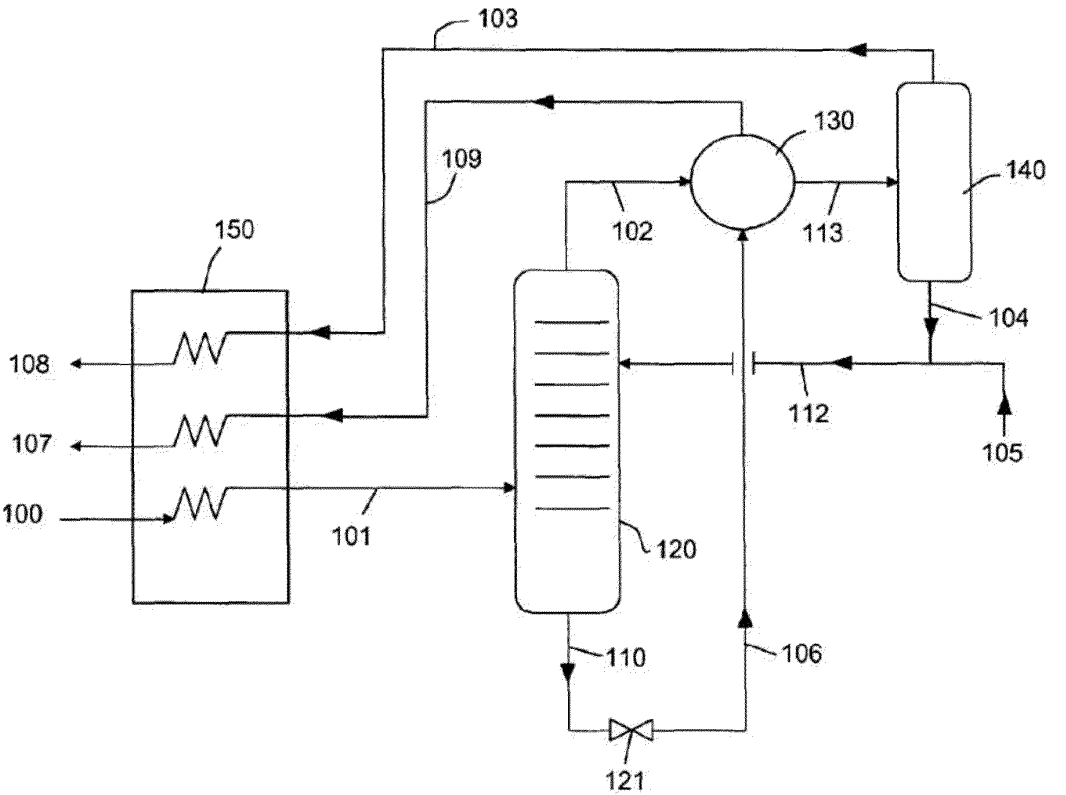
подачи потока кислорода (9) в установку вторичной конверсии или в воздушный компрессор, питающий установку вторичной конверсии;

обеспечения устройства (4) извлечения продувки, в котором поток (10) азота из устройства (3) разделения воздуха используют для промывки продувочного газа (7), отбираемого из контура синтеза, или отходящего газа, выделяющегося при обработке продувочного газа, причем поток азота находится в жидком состоянии или представляет собой смесь жидкого и газообразного азота, с получением таким образом по существу не содержащего инертные примеси рециркулирующего потока (8) и подачей его в контур синтеза.

11. Способ по п. 10, включающий обеспечение по меньшей мере одной криогенной промывной колонны (120), где поток продувочного газа или отходящего газа промывают противотоком жидким азотом (105) или смесью газообразного/жидкого азота из устройства разделения воздуха.

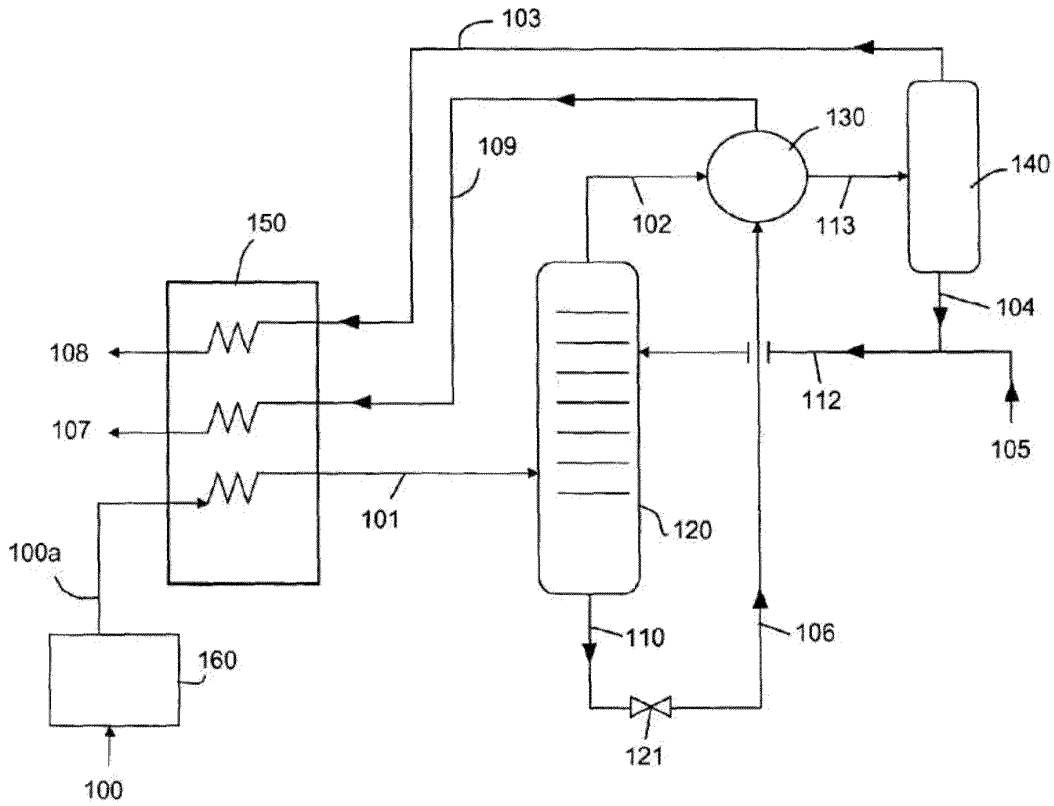
12. Способ по п. 11, отличающийся тем, что количество кислорода, полученного в устройстве разделения воздуха и подаваемого в установку вторичной конверсии, больше, чем теоретическое количество, соответствующее увеличению производительности всей установки, для снижения нагрузки на действующий воздушный компрессор.

Topsoe, Inc. – EX1003
Page 976 of 1210



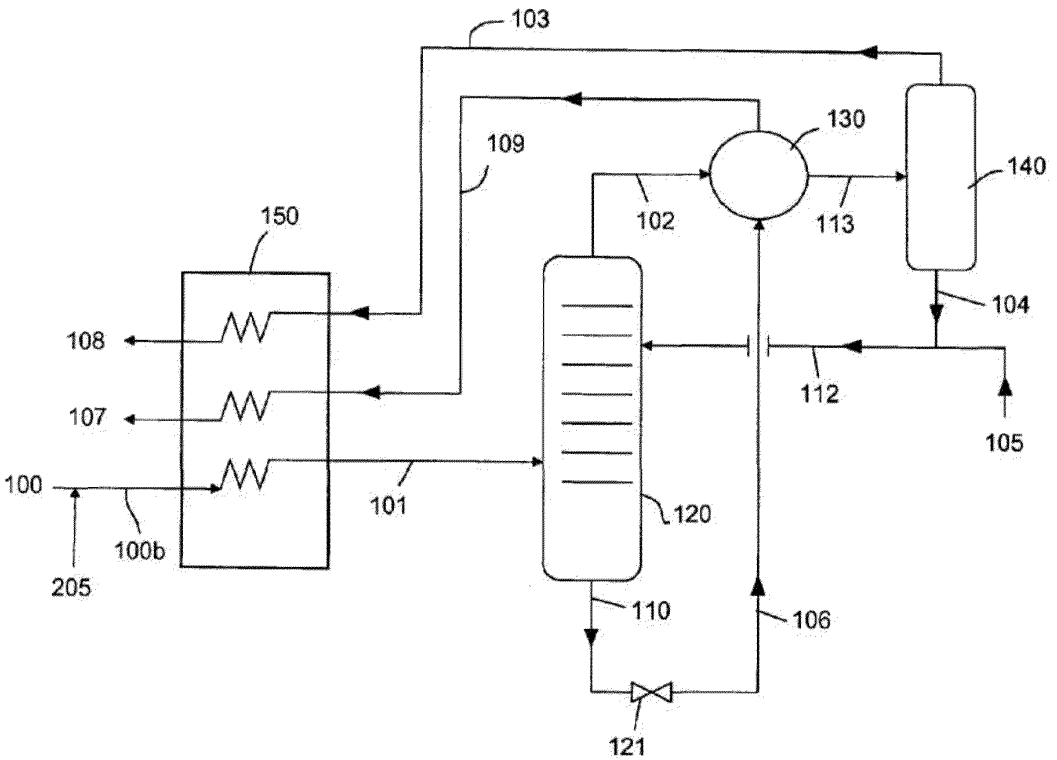
ФИГ. 2

Topsoe, Inc. – EX1003
Page 977 of 1210



ФИГ. 3

Topsoe, Inc. – EX1003
Page 978 of 1210



ФИГ. 4

Topsoe, Inc. – EX1003
Page 979 of 1210

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

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 for the Southern District of Texas on the following Trademarks or Patents.

Docket No. 3:24−cv−00033	Date Filed: 1/31/2024	U.S District Court SOUTHERN DISTRICT OF TEXAS
Plaintiff(s) Topsoe, Inc.		Defendant(s) Casale US, Inc., et al.
PATENT OR TRADEMARK NO.	DATE OF PATENT OR TRADEMARK	HOLDER OF PATENT OR TRADEMARK
A copy of the complaint is attached.		
1.		
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 judgment issued:		
DECISION/JUDGMENT		

Clerk: Nathan Ochsner, Clerk	By Deputy Clerk: Vanesa Aranda	Date: 2/1/2024

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CN102502702A Method for preparing ammonia with natural gas as raw material

Applicants: PETROCHINA CO LTD,CHINA HUANQIU CONTRACTING & ENG CORP

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Classifications:
IPC ***C01C1/04;***

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Method for preparing ammonia with natural gas as raw material

Abstract

The invention provides a method for preparing ammonia with natural gas as a raw material. The process comprises the steps of: first-stage conversion, second-stage conversion, carbon monoxide conversion, carbon dioxide removal, methanation, ammonia synthesis, membrane separation of purge gas and the like, wherein during the first-stage conversion, mild reaction conditions are adopted and the conversion outlet temperature is 740-780 DEG C; the molar content of residual methane in the product obtained in the two-stage conversion step is 1.6-3.0%; the molar ratio of H2 to N2 in the product obtained in the methanation step is 2.6-2.8; and the molar ratio of H2 to N2 in the charge of the ammonia synthesis step is controlled to be 2.9-3.0 by increasing or decreasing the purge gas amount in the synthesis system to adjust the hydrogen return amount of a membrane separation unit. According to the invention, the load of a first-stage conversion unit of natural gas is reduced to a greater extent, thus the equipment investment of the ammonia synthesis device is significantly reduced.

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CLAIMS CN102502702A

1.

A method for preparing ammonia using natural gas as raw material, the process includes primary conversion, secondary conversion, carbon monoxide shift, carbon dioxide removal, methanation, ammonia synthesis and membrane separation of purge gas, characterized in that the temperature of the primary conversion outlet is 740-780° C.

2.

The method for preparing ammonia using natural gas as raw material according to claim 1 is characterized in that the conversion rate of natural gas in the first-stage conversion step is 48-55%.

3.

The method for preparing ammonia using natural gas as raw material according to claim 1 is characterized in that the temperature of the second-stage conversion is 880-920° C.

4.

The method for preparing ammonia using natural gas as raw material according to claim 1 is characterized in that the molar content of residual methane in the product obtained in the second-stage conversion step is 1.6-3.0%.

5.

The method for preparing ammonia using natural gas as raw material according to claim 1 is characterized in that the molar ratio of H₂:N₂ in the product obtained through the methanation

step is 2.6-2.8.

6.

44 The method for preparing ammonia using natural gas as raw material according to claim 1 is characterized in that: after the product after the synthesis tower in the ammonia synthesis step is cooled and condensed to separate the liquid ammonia, part of it is used as the purge gas to carry out the membrane separation step to obtain the permeate gas and the non-permeate gas, wherein the hydrogen-rich permeate gas and the product obtained in the methanation step are mixed and used as the feed of the ammonia synthesis step; the non-permeate gas contains nitrogen, CH₄ and Ar and is sent as fuel.

7.

53 The method for preparing ammonia using natural gas as raw material according to claim 5 is characterized in that the molar ratio of H₂:N₂ in the feed of the ammonia synthesis step is controlled to be 2.9-3.0 by adjusting the amount of purge gas.

8.

59 The method for preparing ammonia using natural gas as raw material according to any one of claims 1 to 7 is characterized in that the molar content of inert gas (CH₄+Ar) in the feed to the synthesis tower in the ammonia synthesis step is 18-25%.

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C01C 1/04(2006.01)

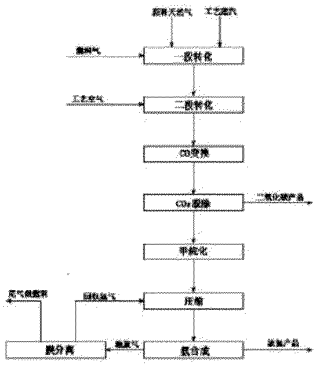
权利要求书 1 页 说明书 6 页 附图 1 页

(54)发明名称

以天然气为原料制备氨的方法

(57)摘要

本发明提出一种以天然气为原料制备氨的方法，其工艺过程包括一段转化、二段转化、一氧化碳变换、二氧化碳脱除、甲烷化、氨合成和驰放气的膜分离等步骤。上述过程中，一段转化采用温和的反应条件，转化出口的温度为740-780℃；二段转化步骤得到的产物中残余甲烷的摩尔含量为1.6-3.0%；经过甲烷化步骤得到的产物中H_2:N_2摩尔比为2.6-2.8，通过增减合成系统驰放气量来调节膜分离单元的返氢量，从而控制氨合成步骤进料中H_2:N_2摩尔比为2.9-3.0。本发明较大程度地降低天然气一段转化单元的负荷，从而显著降低了合成氨装置的设备投资。



CN 102502702 A

1. 一种以天然气为原料制备氨的方法，其过程包括一段转化、二段转化、一氧化碳变换、二氧化碳脱除、甲烷化、氨合成和驰放气的膜分离，其特征在于：所述的一段转化出口的温度为 740-780℃。

2. 根据权利要求 1 所述的以天然气为原料制备氨的方法，其特征在于：所述的一段转化步骤中天然气的转化率为 48-55%。

3. 根据权利要求 1 所述的以天然气为原料制备氨的方法，其特征在于：二段转化的温度为 880-920℃。

4. 根据权利要求 1 所述的以天然气为原料制备氨的方法，其特征在于：所述的二段转化步骤得到的产物中残余甲烷的摩尔含量为 1.6-3.0%。

5. 根据权利要求 1 所述的以天然气为原料制备氨的方法，其特征在于：经过甲烷化步骤得到的产物中 H_2：N_2 摩尔比为 2.6-2.8。

6. 根据权利要求 1 所述的以天然气为原料制备氨的方法，其特征在于：氨合成步骤中合成塔后产物进行冷却、冷凝分离出液氨后，部分作为驰放气进行膜分离步骤得到渗透气和非渗透气，其中，富含氢的渗透气和甲烷化步骤得到的产物混合后作为氨合成步骤的进料；非渗透气含有氮气、CH_4 和 Ar 送出作为燃料。

7. 根据权利要求 5 所述的以天然气为原料制备氨的方法，其特征在于：通过调节驰放气的量控制氨合成步骤进料中 H_2：N_2 摩尔比为 2.9-3.0。

8. 根据权利要求 1-7 任一项所述的以天然气为原料制备氨的方法，其特征在于：氨合成步骤合成塔的进料中惰性气体（CH_4+Ar）摩尔含量为 18-25%。

Topsoe, Inc. – EX1003
Page 985 of 1210

以天然气为原料制备氨的方法

技术领域

[0001] 本发明涉及一种氮肥技术领域的合成氨技术，特别是涉及一种降低一段蒸汽转化负荷的以天然气为原料制备氨的方法。

背景技术

[0002] 现有的以天然气为原料的合成氨技术主要包括天然气转化制备富氢合成气的过程、合成气进行一氧化碳变换过程、二氧化碳脱除过程、甲烷化过程以及氨合成过程。合成氨工艺主要有 KELLOGG 合成氨工艺、BRAUN 合成氨工艺和 UHDE AMV 合成氨工艺。

[0003] 以KELLOGG工艺为代表的传统合成氨工艺，其特征为转化气成分满足 (H_2+CO) ： N_2 接近氨合成的化学计量比 3 ： 1，同时为减少合成圈驰放气量，控制转化气中惰性气体 CH_4 的含量小于0.6%（干）。为实现上述目标，转化系统必须满足水碳比＞3.0、一段转化出口温度＞800℃、二段转化出口温度约1000℃。随后针对上述工艺进行的技改方案中，增加了膜分离装置回收合成驰放气中氢气的节能措施。上述工艺有如下不足：

[0004] a) 一段转化出口温度高（＞800℃），对转化炉管等材料应力要求高，限制了较高转化压力、较大转化炉管的应用。

[0005] b) 一段转化负荷高。由于一段转化能效低于二段绝热转化，因而转化综合能效较低。

[0006] c) 一段蒸汽转化投资远高于绝热的二段转化，且与其负荷成正比。上述工艺由于一段转化负荷重，因而转化总投资高，从而将整体的合成氨系统投资提高。

[0007] 因此本领域的技术人员为降低合成氨系统的总体投资，希望能够有一种工艺在保证整体蒸汽转化效率的前提下，将一段炉的负荷部分 转移到二段炉，从而降低一段炉设备的投资。

[0008] 为此，产生了 BRAUN 合成氨工艺，其特征是打破了转化气中 (H_2+CO) ： N_2 接近氨合成的化学计量比 3 ： 1 的法则，最大限度将转化负荷从一段炉转移到二段炉。降低转化投资，提高转化能效。其一段炉转化出口温度为 680-720℃，二段加入过量 50% 以上空气以满足后续深冷净化的冷量需要，合成气进入合成圈前设置冷箱除去过量氮及部分惰性气体。但是该 BRAUN 工艺有如下不足：

[0009] a) 工艺空气加入量过大，空压功耗大。综合高能效需要配置高能效燃气轮机驱动空压机才能体现。

[0010] b) 增设冷箱投资较大。

[0011] c) 上述工艺在操作中必须严格控制操作条件以便使一段炉的负荷控制在合适的范围内，在实际生产中工艺条件的波动很敏感，造成稳定运行的难度增大，且运行成本提高。

[0012] 另外，还提出了 UHDE AMV 合成氨工艺，其特征是提高转化压力＞40bar，稍稍转移一段转化负荷到二段。一段出口温度约为800℃，二段出口甲烷残留＜0.9%（干），转化气中 (H_2+CO) ： N_2 约 2.6。设置冷箱回收合成驰放气中氢气返回系统。

Topsoe, Inc. – EX1003
Page 986 of 1210

[0013] 上述工艺有如下不足：

[0014] a) 一段转化出口温度稍高（约为 800℃）。由于一段转化负荷重，因而转化总投资高。

[0015] b) 工艺空气加入量稍大，空压功耗大，从而也导致了整体运行成本的增加。

[0016] 由此可见，现有的二段法合成氨工艺，在一段炉负荷的处理上，或者是一段炉负荷大导致整体投资大，或者将一段炉负荷转移到二段炉，但需要增加其他的设备，也依然存在设备投资大的缺陷。

发明内容

[0017] 本发明的主要目的在于，克服现有的合成氨方法存在的缺陷，而提供一种新的合成氨方法，所要解决的技术问题是选择一段转化出口 温度在合适的范围内，降低天然气一段转化的负荷，从而降低了整体合成氨系统的设备投资。

[0018] 本发明的目的及解决其技术问题是采用以下技术方案来实现的。依据本发明提出的一种以天然气为原料制备氨的方法，其过程包括一段转化、二段转化、一氧化碳变换、二氧化碳脱除、甲烷化、氨合成和驰放气的膜分离等步骤。其中所述的一段转化的温度为 740-780℃，一段转化步骤中天然气的转化率为 48-55％，所述二段转化的温度为 880-920℃，二段转化步骤得到的产物中甲烷的摩尔含量为 1.6-3.0％；经过甲烷化步骤得到的产物中 H_2 ： N_2 摩尔比为 2.6-2.8；氨合成步骤中合成塔后产物进行冷却、冷凝分离出液氨后，部分作为驰放气进入膜分离步骤得到渗透气和非渗透气。其中，富含氢的渗透气返回系统，和甲烷化步骤得到的产物混合后作为氨合成步骤的进料；氮气、CH_4 和 Ar 等进入非渗透气送出作为燃料，从而从系统脱除。通过调节所述驰放气的量来控制氨合成步骤进料中 H_2 ： N_2 摩尔比为 2.9-3.0。氨合成步骤合成塔的进料中惰性气体（CH_4+Ar）的总摩尔含量为 18-25％。

[0019] 借由上述技术方案，本发明的方法相对于 KELLOGG 工艺为代表的传统合成氨工艺，具有如下优点：

[0020] a) 降低了一段转化出口温度，相应降低对转化炉管等材料应力要求，因而允许采用较高转化压力、较大转化炉管。

[0021] b) 降低了一段转化负荷，由于一段转化能效低于二段绝热转化，因而转化综合能效较高。

[0022] c) 一段蒸汽转化投资远高于绝热的二段转化，且与其负荷成正比。由于一段转化负荷低，因而转化总投资低。

[0023] 本发明的方法相对于以 BRAUN 工艺为代表的合成氨工艺具有如下优点：

[0024] a) 工艺空气加入量小，空压功耗小。

[0025] b) 无需增设冷箱，仅设置膜分离，投资较小。

[0026] 本发明的方法相对于以 UHDE AMV 工艺为代表的合成氨工艺具 有如下优点：

[0027] a) 一段转化出口温度稍低，一段转化负荷低，因而转化总投资低。

[0028] b) 无需增设冷箱，仅设置膜分离，投资较小。

附图说明

Topsoe, Inc. – EX1003
Page 987 of 1210

[0029] 图 1 是本发明的合成氨方法的基本流程图。

具体实施方式

[0030] 为更进一步阐述本发明为达成预定发明目的所采取的技术手段及功效，以下结合附图及较佳实施例，对依据本发明提出的合成氨方法其具体实施方式、结构、特征及其功效，详细说明如后。

[0031] 请参阅图 1 所示，是本发明的合成氨方法的基本流程图。本发明所述的以天然气为原料的合成氨方法主要包括以下步骤：天然气蒸汽转化、CO 变换、CO_2 脱除、甲烷化、氨合成以及驰放气的膜分离步骤，其中的天然气蒸汽转化步骤包括一段转化和二段转化两个过程。以下详细描述上述各个步骤的具体内容。

[0032] 一段转化

[0033] 所述的一段转化是将脱硫后的天然气与水蒸气组成的原料输入蒸汽转化一段炉，在催化剂存在的条件下进行反应，使原料中的部分天然气转化为氢气，出口气体温度为 740-780℃，甲烷含量（摩尔百分数）约 22%（干）。在本过程中，天然气的转化率控制在 48-55%范围内。该过程的主要反应式如下：

[0034] $CH_4+H_2O \rightarrow CO+3H_2$

[0035] $CO+H_2O \rightarrow CO_2+H_2O$

[0036] 二段转化

[0037] 二段转化使将一段转化的出口气体进一步转化为氢气的步骤，将一段转化的出口其与压缩空气混合后进入二段炉进行绝热反应，反应温度范围为 880-920℃，从二段炉出口气体中甲烷残留摩尔百分比为 1.6-3.0%（干）。该过程的主要反应式如下：

[0038] $H_2+O_2 \rightarrow H_2O$

[0039] $CH_4+H_2O \rightarrow CO+H_2$

[0040] $CO+H_2O \rightarrow CO_2+H_2$

[0041] CO 变换

[0042] CO 变换步骤是将二段炉出口气体换热后进入 CO 变换装置以便将其中的 CO 转变为 CO_2。CO 变换反应式如下：

[0043] $CO+H_2O \rightarrow CO_2+H_2$。

[0044] CO_2 脱除

[0045] 来自 CO 变换步骤的变换气进入 CO_2 脱除装置，采用 MDEA（甲基二乙醇胺）溶液吸收变换气中的 CO_2。

[0046] 甲烷化

[0047] 经过 CO_2 脱除步骤的工艺气体进入到甲烷化装置中，在高镍催化剂催化下，工艺气体中的碳氧化物发生反应生成甲烷，经过甲烷化的物料中的 H_2 ： N_2（摩尔比）为 2.6-2.8。甲烷化反应式为：

[0048] $CO+3H_2 \rightarrow CH_4+H_2O$

[0049] $CO_2+4H_2 \rightarrow CH_4+2H_2O$

[0050] 氨合成

[0051] 经过甲烷化的工艺气体经压缩机压缩并被加热后进入合成塔，在其中进行氨合成

Topsoe, Inc. – EX1003
Page 988 of 1210

反应。反应式为：

[0052] $N_2+3H_2 \rightarrow 2NH_3$

[0053] 合成塔出料经过换热和冷凝，其中的氨从气态转变为液态，经氨分离器分离液氨后，气态组分中的一部分直接送到上述的压缩机中，另一部分送入到膜分离器。经过膜分离的渗透气主要为氢气，被送入上述的压缩机，非渗透气（包括氢气、氮气、甲烷和氩气）经燃料气管网送入一段炉。由于膜分离得到的渗透气的主要成分为氢气，所以，通过控制膜分离的处理量则可以控制进入合成塔的工艺气中的 H_2 ： N_2 摩尔比为 2.9-3.0。

[0054] 按照上述的合成氨方法提供实例 1-5，具体数据如下表 1

[0055] 表 1 实例 1-5 工艺数据表

[0056]

Topsoe, Inc. – EX1003
Page 989 of 1210

		实例 1	实例 2	实例 3	实例 4	实例 5
原料天然气流量 Kmol/hr		2105	2105	2105	2105	2105
一段炉出口气	一段炉出口温度 ℃	740	750	760	770	780
	总流量 Kmol/hr（干）	5161	5296	5434	5534	5717
	H_2 流量 Kmol/hr	3014	3150	3288	3428	3571
	CH_4 流量 Kmol/hr	1241	1198	1154	1109	1063
	CH_4 一段转化率 %	48	49	50	51.5	55
二段炉出口气	总流量 Kmol/hr（干）	9105	9247	9376	9479	10391
	温度 ℃	870	879	892	904	918
	H_2 流量 Kmol/hr	4821	4916	5022	5114	5202
	CH_4 流量 Kmol/hr	321	287	243	207	171
	N_2 流量 Kmol/hr	2159	2159	2185	2196	2207
甲烷化装置出口气	总流量 Kmol/hr（干）	8244	8341	8475	8583	8686
	H_2 流量 Kmol/hr	5706	5836	5983	6114	6238
	CH_4 流量 Kmol/hr	351	318	279	245	212
	N_2 流量 Kmol/hr	2159	2159	2185	2196	2207
膜分离装置进气	总流量 Kmol/hr	1839	1612	1474	1281	1038
	H_2 流量 Kmol/hr	959	839	784	684	539
	CH_4 流量 Kmol/hr	377	341	296	258	221
	N_2 流量 Kmol/hr	394	333	300	253	202
	Ar 流量 Kmol/hr	32	32	32	32	32
膜分离装置渗透气（富氢）	总流量 Kmol/hr	752	659	612	534	424
	H_2 流量 Kmol/hr	667	583	545	476	375
	CH_4 流量 Kmol/hr	38	34	30	26	22
	N_2 流量 Kmol/hr	42	36	32	27	21
	Ar 流量 Kmol/hr	5.2	5.2	5.2	5.2	5.2
膜分离装置非渗透气（燃料）	总流量 Kmol/hr	1013	889	803	696	572
	H_2 流量 Kmol/hr	292	256	239	209	164
	CH_4 流量 Kmol/hr	338	306	266	232	199
	N_2 流量 Kmol/hr	352	297	268	226	180
	Ar 流量 Kmol/hr	27	27	27	27	27
合成塔进气	总流量 Kmol/hr	28988	30022	31359	32904	34227
	H_2 流量 Kmol/hr	16786	17344	18360	19285	19643
	CH_4 流量 Kmol/hr	4496	4806	4796	5077	5606
	N_2 流量 Kmol/hr	6479	6532	6748	6913	7103
	Ar 流量 Kmol/hr	382	451	520	634	813
液氨产品	NH_3 流量 Kmol/hr	3558	3665	3777	3884	3996
合成塔出口气	总流量 Kmol/hr	25417	26340	27568	29007	30217
	H_2 流量 Kmol/hr	11429	11821	12674	13439	13628
	CH_4 流量 Kmol/hr	4496	4806	4796	5077	5606
	N_2 流量 Kmol/hr	4694	4690	4853	4964	5099

[0057]

Topsoe, Inc. – EX1003
Page 990 of 1210

	Ar 流量 Kmol/hr	382	451	521	634	814
	NH_3 流量 Kmol/hr	4416	4571	4725	4893	5070
合成系统进气	总流量 Kmol/hr	8932	8936	9021	9052	9044
	H_2 流量 Kmol/hr	6327	6373	6481	6543	6565
	CH_4 流量 Kmol/hr	387	351	307	267	233
	N_2 流量 Kmol/hr	2185	2179	2201	2207	2212
	Ar 流量 Kmol/hr	33	33	33	33	33

[0058] 上述的合成氨方法中，由于在一段转化的过程中采用了相对温和的反应温度，如740-780℃，从而可以控制在一段转化过程中甲烷的转化率为48-55%，可以在一段炉的设计上相应降低对转化炉管等材料应力要求，因而允许采用较高转化压力、较大转化炉管。由于一段转化能效低于二段绝热转化，因而转化综合能效较高。由于一段蒸汽转化投资远高于绝热的二段转化，所以降低一段炉的负荷可以减少整套合成氨反应系统的设备投资。

[0059] 本方法在上述的二段转化过程中，对出口气体中甲烷残留摩尔百分比控制为1.6-3.0%（干），比现有技术具有更大的运行值，从而可以减少加入的空气量，降低了氮气的过量程度，降低了空压功耗。另外，惰性气体（甲烷）含量的气体不经脱除直接进入合成塔系统省去了惰性气体脱除装置，从而减少了设备投资。

[0060] 本方法中采用膜分离的手段来调节氢氮比，多余的氮气及惰性气体通过膜分离装置被排除，并进入燃料管网。

[0061] 本申请中所述的负荷是指原料天然气的转化率。

[0062] 以上所述，仅是本发明的较佳实施例而已，并非对本发明作任何形式上的限制，虽然本发明已以较佳实施例揭露如上，然而并非用以限定本发明，任何熟悉本专业的技术人员，在不脱离本发明技术方案范围内，当可利用上述揭示的技术内容作出些许更动或修饰为等同变化的等效实施例，但凡是未脱离本发明技术方案的内容，依据本发明的技术实质对以上实施例所作的任何简单修改、等同变化与修饰，均仍属于本发明技术方案的范围内。

Topsoe, Inc. – EX1003
Page 991 of 1210

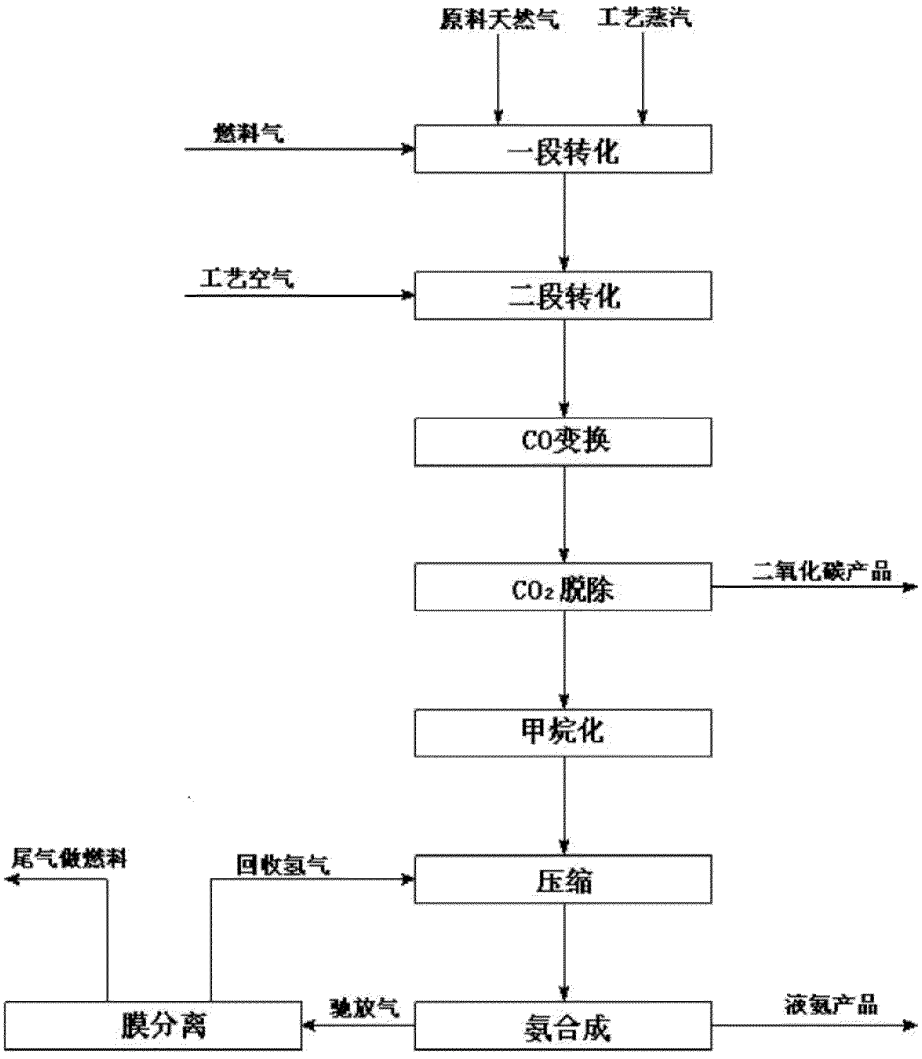


图 1

Topsoe, Inc. – EX1003
Page 992 of 1210

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

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.

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 to Topsoe 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.

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 at Zardi & Co. SA in an attempt to enforce its improperly obtained and unenforceable 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 located in the state of Texas to dissuade that customer from installing Topsoe's ammonia technology at its

facilities in Texas. 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 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). 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.

19. 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.

20. Venue is proper in the Southern District of Texas pursuant to 28 U.S.C. §§ 1391(b) and (c), and 1400(b), at least because Casale is incorporated in the State of Texas, has its principal place of business in the Southern District of Texas and Defendants have committed acts of false advertising in the Southern District of Texas and attempted to enforce their unenforceable patent in the Southern District of Texas.

FACTUAL ALLEGATIONS

Topsoe's Contributions to the Field of Low Carbon Ammonia Technology

21. 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.

22. 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.

23. 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.

24. 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.

25. 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.

26. 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.

27. 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."

28. 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

29. Casale has long been aware of Topsoe's low carbon ammonia technology.

30. 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.

31. Casale also gained access to the IFFCO plant in India described above 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.

32. 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.

33. 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").

34. 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

35. 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.

36. The '168 Patent issued on March 29, 2022.

37. 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.

38. Attorneys of Dorsey & Whitney LLP, including Marcus S. Simon (Reg. No. 50,258) represented Casale in the prosecution of the '168 patent.

39. 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.

40. 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.[1] 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.

41. 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

[1] 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.

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.

42. 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.

43. 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

44. As noted above, the European counterpart to the '168 Patent, is the '067 Patent.

45. 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.

46. 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.

47. Both the '067 Patent and the related '770 patent were prosecuted on behalf of Casale by European law firm M. Zardi & Co. SA ("Zardi").

48. Zardi was founded in 1999 by Marco Zardi and is a Swiss law firm specializing in intellectual property.

49. Both the US and European patents are based on the same PCT application filed by Zardi, and specifically, Marco Zardi.

50. Zardi also is representing Casale in the European Opposition.

51. Zardi, including Marco Zardi and Riccardo Biazzi, also were substantively involved in the prosecution of the '168 Patent.

52. The current Chief Executive Officer of Casale is Frederico Zardi.

53. On information and belief, Marco Zardi and Federico Zardi are blood relatives.

54. 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

55. 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.

56. 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.

Topsoe, Inc. – EX1003
Page 1003 of 1210

57. 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.

58. 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."

59. 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.

60. 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.

61. 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.

62. 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.

63. 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.

64. 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.

65. Casale knew that its patent was invalid and unenforceable but engaged in these communications regardless.

66. Casale's statements were also false and misleading 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

67. 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.

68. 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]."

69. 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."

70. 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:

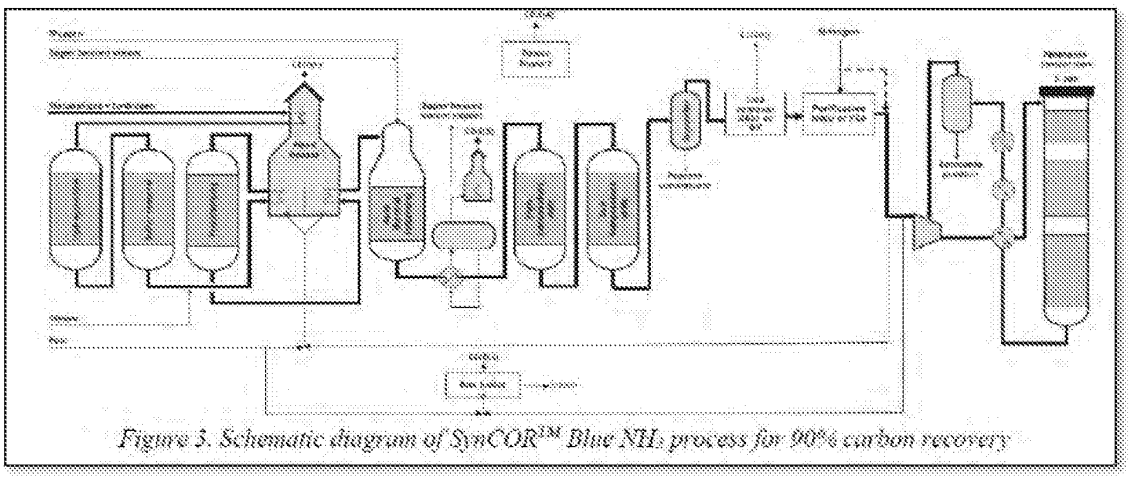


Figure 3. Schematic diagram of SynCOR™ Blue NH3 process for 90% carbon recovery

71. 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."

72. 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.

73. 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 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.

74. 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

75. 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.

76. 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. 3583067B1) to U.S. Patent No. 11,286,168 was challenged via two Notices of Opposition both filed before the European Patent Office on June 8, 2022. These opposition proceedings remain pending before the European Patent Office, with the Patent Owner having filed a reply to the Notice of Opposition on November 3, 2022. Out of an abundance of caution, the Patent Owner is submitting this Request, which includes as the items of information to be considered the references cited in the Notice of Opposition.

Corrected Request for Supplemental Examination dated April 16, 2023.

77. 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.

78. 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.

79. 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.

80. 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.

81. 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.

82. 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."

83. Casale has never retracted any of its statements to Topsoe's customers regarding the Disputed Patents and their enforceability, despite knowing that the US PTO has now 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)

84. Topsoe incorporates by reference the allegations set forth in this Complaint as though fully set forth herein.

85. An actual and justiciable controversy exists between Topsoe and Casale concerning the '168 patent.

86. 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.

87. 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.

88. 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"). These individuals deliberately and knowingly withheld and/or omitted material information from Topsoe prior art in connection with the prosecution 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 and was withheld and omitted with an intent to deceive the PTO and/or '168 patent examiner, as described below.

89. The '168 Patent lists two inventors, Francesco Baratto and Raffaele Ostuni.

90. 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.

91. As a registered patent attorney for Casale, Simon was aware, or should have been aware, of his duty of candor to the US PTO.

92. 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.

93. 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.

94. Both Ostuni and Simon have been actively involved in communications regarding Casale's assertion of claims of infringement against Topsoe. Ostuni and Simon were both present during the September 15, 2023, call between Casale and Topsoe.

95. The '168 Patent has an effective filing date of January 31, 2018.

96. Prior to the effective filing date of the '168 Patent, Casale had access to and knowledge of 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.

97. 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 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.

98. On information and belief, Ostuni also had direct, firsthand knowledge of at least one 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.

99. In addition, Topsoe has published and presented frequently on its low carbon ammonia process and it is used commercial in many facilities worldwide. Casale and Topsoe are direct competitors and aware of one another generally in the industry.

100. The '168 Patent is directed towards a process for synthesis of ammonia from natural gas. The '168 Patent includes two independent claims.

101. 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.

Ex. 1 at col. 18, ll. 38-57.

102. 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.

Ex. 1 at col. 20, ll. 22-38.

103. 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.

104. 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.

105. 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, <u>said first and second streams having the same composition</u>." 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.[2]

106. 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 information from the Examiner in order to secure allowance of the patent.

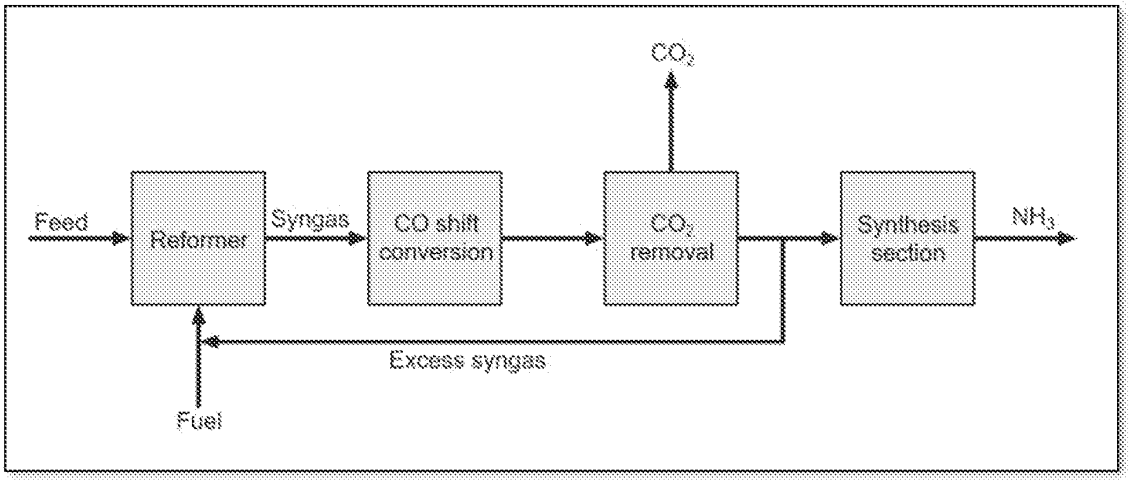
107. Casale's concealment strategy worked, and the Examiner withdrew the rejection. The reason the Examiner gave for allowing the claims was the "distinguishing feature of the first and second streams having the same composition." Notice of Allowance dated Nov. 18, 2021. As a result, the claims were 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.

108. 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

[2] 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 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.

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, this reference is highly material to the patentability of the '168 Patent and should have been disclosed during prosecution.

109. 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.



110. 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.

111. 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.

112. 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.

113. 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.

114. 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 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.

115. Casale knew of the materiality of the Topsoe prior art references before, during, and after prosecution of the '168 Patent. 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.

116. 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.

117. 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.

118. 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.

119. 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.

120. 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.

121. 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.

122. 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.

123. 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.

124. 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.

125. Intentional nondisclosure of material prior art during prosecution of a patent application constitutes inequitable conduct.

126. Inequitable conduct during prosecution of a patent application renders any resultant patent unenforceable.

127. 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.

128. At least attorney Simon, inventors Baratto and Ostuni, and Marco Zardi 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.

129. Casale's, Casale's attorneys, attorney Simon's, and Casale's employees' and '168 Patent inventors' Baratto and Ostuni 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.

130. 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.

131. 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)

132. Topsoe incorporates by reference the allegations set forth in this Complaint as though fully set forth herein.

133. "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).

134. 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 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.

135. 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.

136. 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 liability under the Lanham Act. Casale has acted with malice and specific intent, as it had knowledge of the falsehood of its 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.

137. 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.

138. 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.

139. 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.

140. 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. Additionally, Casale has caused its blue ammonia technology products to enter interstate commerce, including through its proposals to customers in the U.S.

141. 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.

142. 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.

143. 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.

144. 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.

145. 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.

146. 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)

147. Topsoe incorporates by reference the allegations set forth in this Complaint as though fully set forth herein.

148. 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.

149. 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 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 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.

150. 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.

151. 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: January 31, 2024

Respectfully submitted

By: */s/ Robert Riddle*

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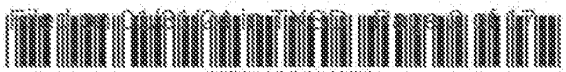
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Counsel for Plaintiff

Exhibit 1



US011286168B2

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

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

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

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

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

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

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

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

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

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

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

(65) **Prior Publication Data**

US 2020/0055738 A1 Feb. 20, 2020

(30) **Foreign Application Priority Data**

Feb. 15, 2017 (EP) 17156256
Oct. 6, 2017 (EP) 17195305

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

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

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

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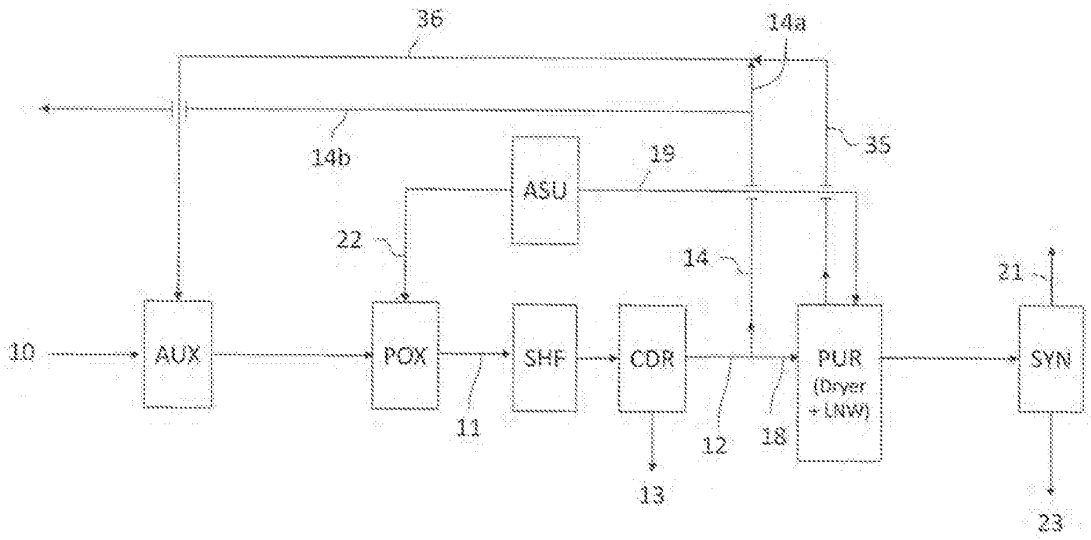
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(Continued)

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

(57) **ABSTRACT**

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

23 Claims, 4 Drawing Sheets



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

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

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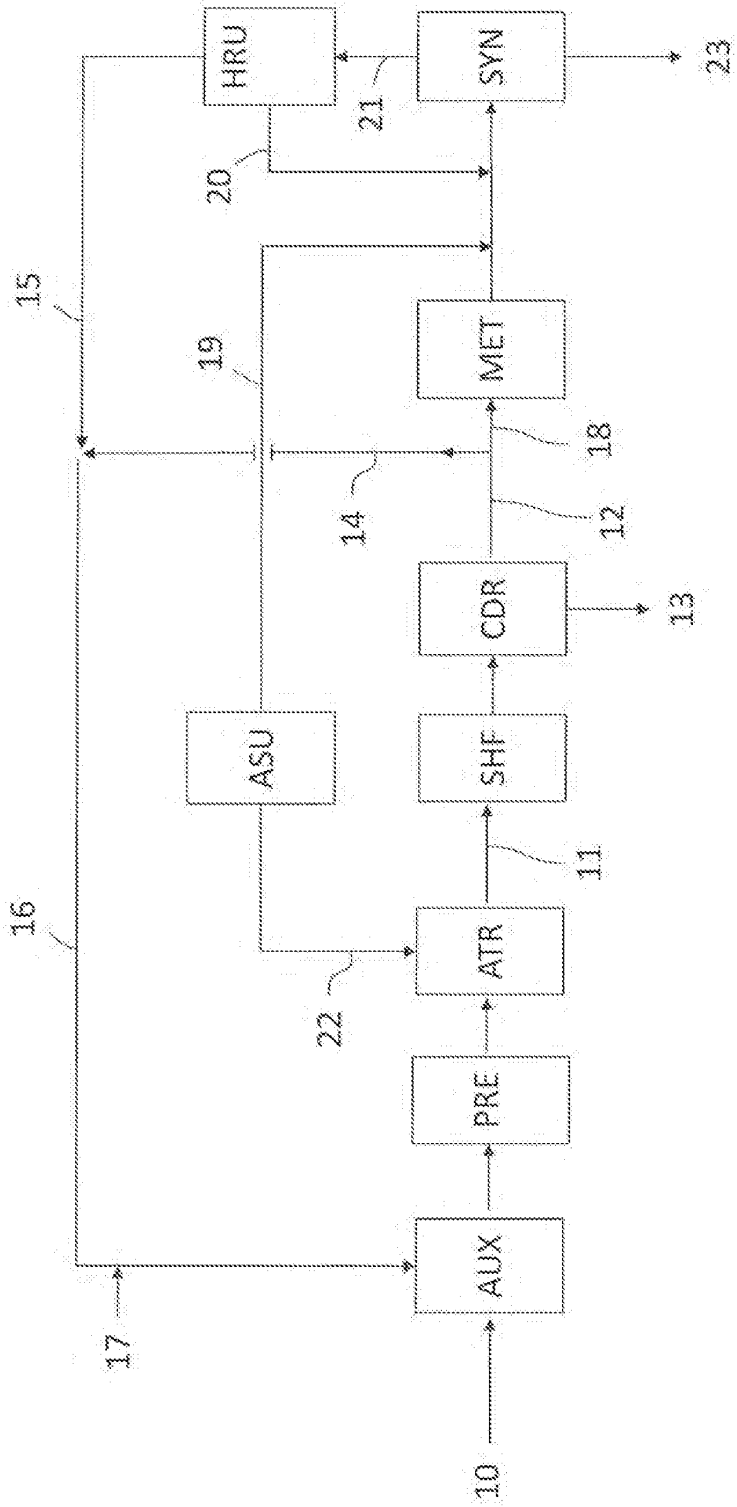

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FIG. 1

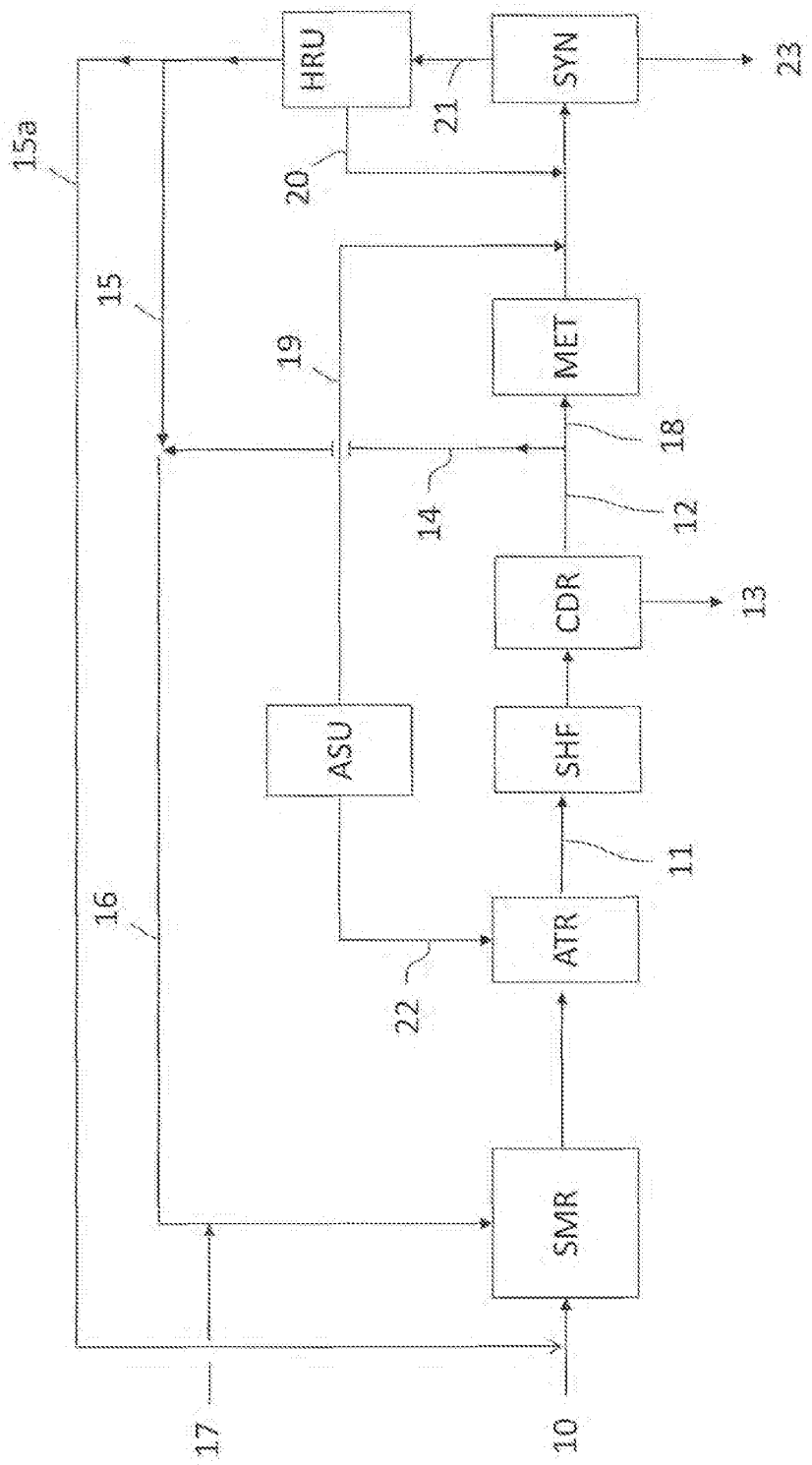

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FIG. 2

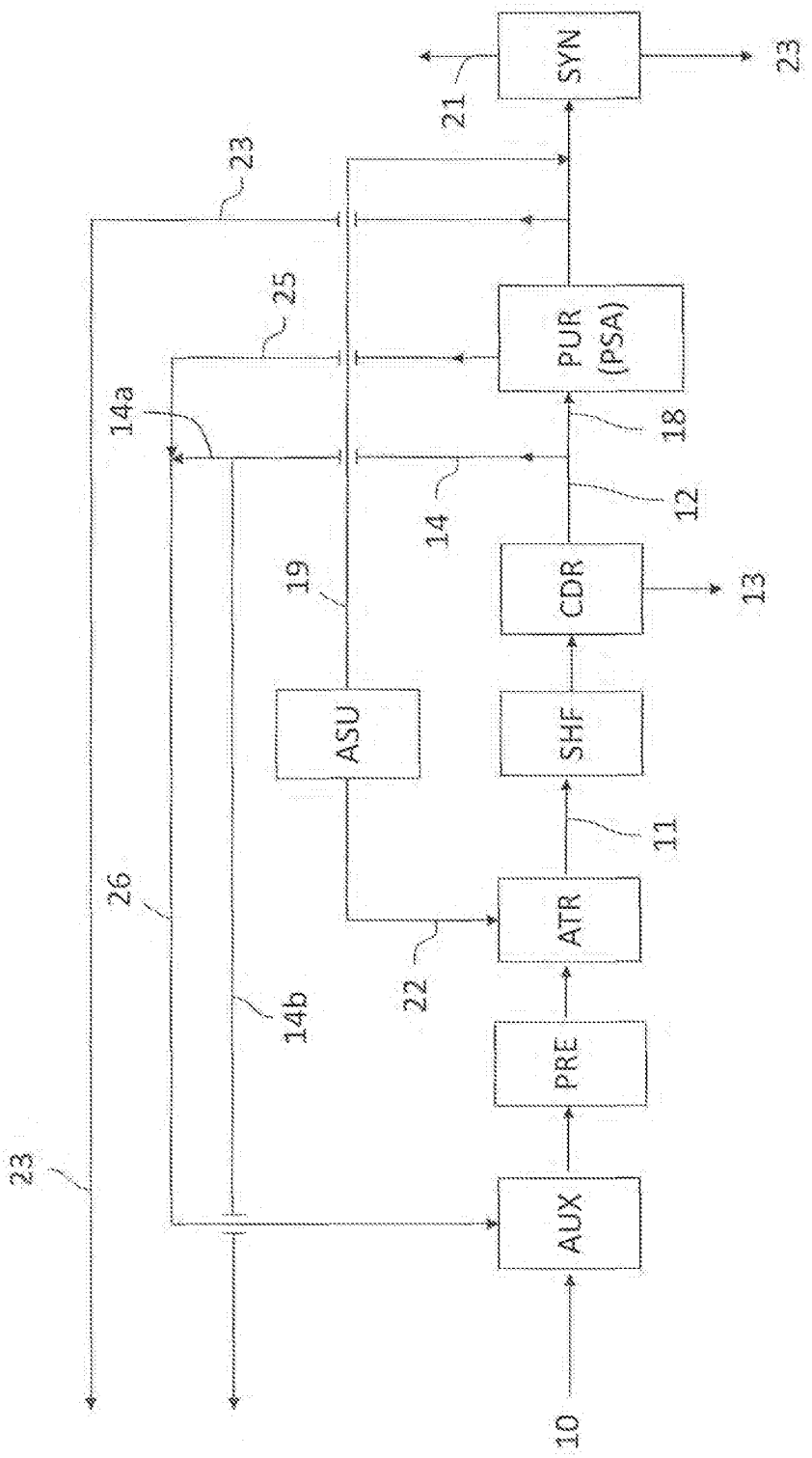

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FIG. 3

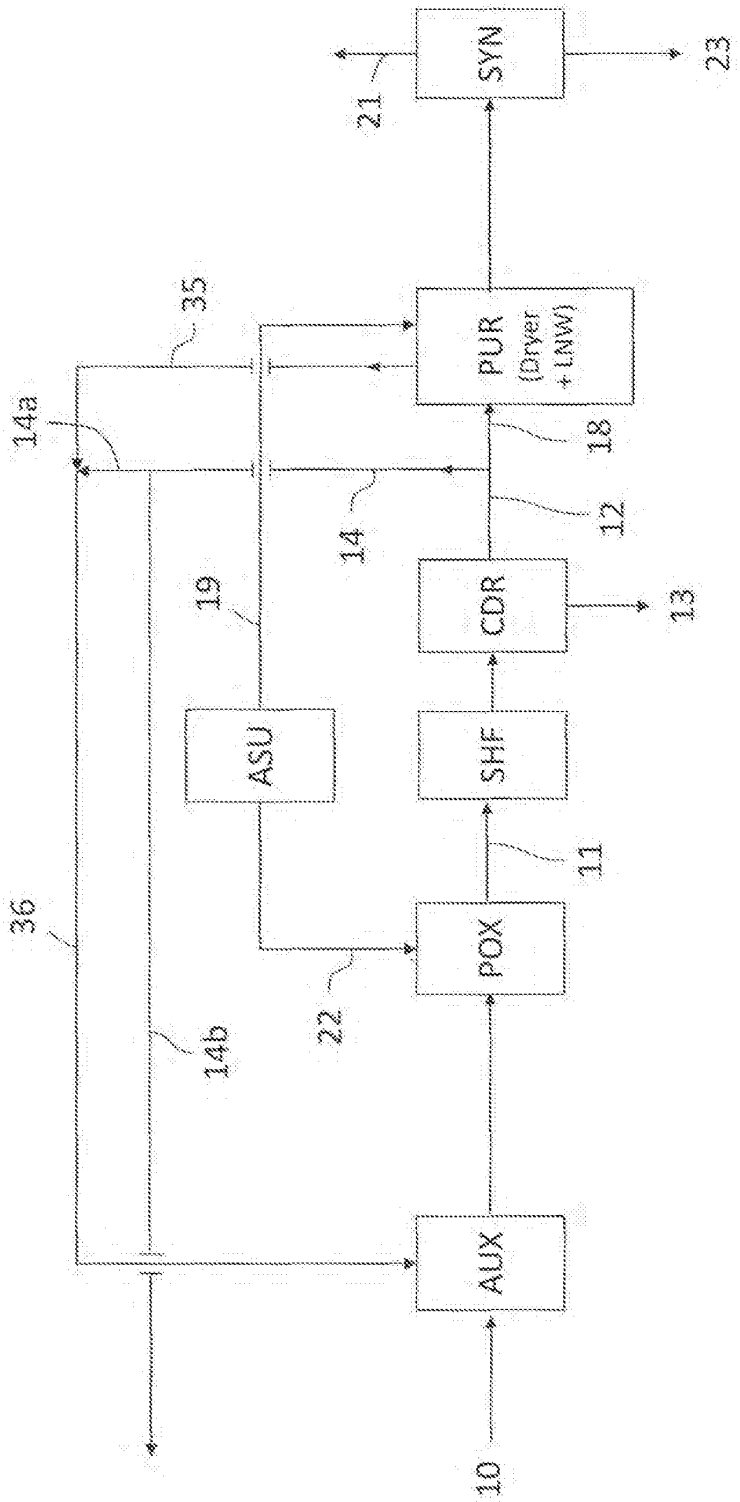

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FIG. 4

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

FIELD OF APPLICATION

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

PRIOR ART

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

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

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

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

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

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

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

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

SUMMARY OF THE INVENTION

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

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

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

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

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

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

characterized by:

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

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

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

separating a part of the synthesis gas downstream of decarbonation;

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

In some embodiments of the invention, in order to reduce also this source of CO2 (i.e. the emissions caused by the presence of residual carbon monoxide of the synthesis gas), the process comprises a catalytic purification which selectively converts the CO into CO2 upstream of decarbonation. Selective conversion of the carbon monoxide may be obtained, for example, using the process known as Selectoxo™ which operates with the reaction CO+½O2→CO2. The oxygen for selective oxidation of the CO may be a part of the mentioned enriched-air or oxygen flow.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

For example, the surplus may be:

- exported as a further product (for example as hydrogen or as CO2-depleted fuel for consumption outside the ammonia plant) or
- conveyed to a storage buffer, or
- flared.

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

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

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

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

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

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

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

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

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

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

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

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

The main advantages of the invention are listed below.

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

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

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

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

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

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

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

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

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

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

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

DESCRIPTION OF THE FIGURES

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

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

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

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

DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

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

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

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

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

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

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

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

Preferably the synthesis gas **12** has the following composition: 68% H2, 1% CO+CH4, 0.1% CO2, Ar+N2 0.9%.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

EXAMPLE

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

Table 1 compares the following options:

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

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

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

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

TABLE 1

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

TABLE 1-continued

		Option			
		(1) Prior art	(2) Prior art	(3) Inv.	(4) Inv.
CO2 captured in process	MTD	3600	3600	5200	5100
CO2 to atmosphere (contained in flue gas)	MTD	2300	280	300	200
CO2 to atmosphere (contained in flue gas)	vs NB1	0.7	0.1	0.1	0.1
Main foreground sizes					
Total fired heater duty (reformer/fired heater + auxiliary boiler)	%	100	120	75	105
Process CO2 removal capacity	%	100	110	145	140
ASU O2 capacity	%	100	95	100	60
Flowrate of front end (secondary output/ATR)	%	100	150	120	97

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

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

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

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

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

Table 2 compares the following options:

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

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

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

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

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

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

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

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

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

TABLE 2

	1a: SMR + ATR	1b SMR + ATR	2a ATR	2b ATR	3a POX	3b POX
Daily production of NH3, MTD	3000	3000	3000	3000	3000	3000
Daily throughput of sequestered CO2, MTD	5800	5800	5160	5360	5350	5800
%st consumption of natural gas (for Example 1a), dimensionless	100%	100%	93%	93%	88%	95%

TABLE 2-continued

	1a: SMR + ATR	1b: SMR + ATR	2a: ATR	2b: ATR	3a: POX	3b: POX
CO2 emissions into atmosphere per unit of ammonia produced, t CO2/t NH3	0.15	0.075	0.12	0.10	0.15	0.05
Distribution of the CO2 emissions						
trim fuel	80%	zero	20%	zero	20%	zero
CH4 slip in the process gas	15%	20%	40%	70%	30%	65%
CO slip in the process gas	34%	60%	39%	18%	49%	34%
CO2 slip in the process gas	1%	2%	1%	2%	1%	1%

In Table 2:

"Trim fuel" as defined in the patent;

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

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

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

Several comments may be made in view of Table 2:

In the case of SMR+ATR in option 1a, the trim fuel provides the greatest percentage of the CO2 emissions; avoiding the trim fuel by exporting surplus fuel enables the emissions to be significantly reduced to less than 0.1 t/t, as shown in the Table for option 1b; at the same time, the quantity of sequestered CO2 increases from 5800 to 5800 MTD.

In the case of SMR+ATR, the CO slip in the process gas provides the second greatest percentage of the CO2 emissions in option 1a, and provides the greatest percentage in option 1b; application of the Selectoxo process to option 1a or 1b would significantly reduce the CO2 emissions; the CH4 slip in the process gas and the CO2 slip in the process gas provides a smaller percentage of the CO2 emissions.

The overall energy consumption of the options based on ATR and POX+purification (2 and 3) is decidedly lower than that of the options based on SMR+ATR (1a and 1b); this is mainly due to the synthesis gas purification (which improves the efficiency of the synthesis section and avoids the purge); the quantity of CO2 sequestered in these options (2a, 3a; or 2b, 3b) is consequently less than in options 1a or 1b.

The emissions due to the use of the trim fuel in options 2a (ATR) and 3a are of about 20% of the total emissions, much less than in option 1a, by way of confirmation of the fact that the heat required by the furnace in these two options is much less than in option 1a.

In the embodiments with ATR or POX, the residual CO and CH4 are of higher relevance owing to the lower S/C ratio at which ATR and POX operate compared to SMR+ATR; POX operates at a higher temperature than ATR, which results in a smaller residual amount of CH4, but in a greater residual amount of CO.

In both the options 2b and 3b, the improvement achieved by selective oxidation of CO, in order to reduce the CO slip, and by avoiding trim fuel, is evident.

It should be noted that both POX and ATR achieve very low emissions—as low as 0.05 for POX and 0.1 for ATR—comparable with those achieved by SMR+ATR, but with lower energy consumption, and therefore preferable.

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

The invention claimed is:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

17. The process of claim 1, wherein

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

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

18. The process of claim 1, wherein:

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

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

19. The process of claim 1, wherein:

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

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

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

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

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

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

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

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

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

* * * * *

CIVIL COVER SHEET

The JS 44 civil cover sheet and the information contained herein neither replace nor supplement the filing and service of pleadings or other papers as required by law, except as provided by local rules of court. This form, approved by the Judicial Conference of the United States in September 1974, is required for the use of the Clerk of Court for the purpose of initiating the civil docket sheet. *(SEE INSTRUCTIONS ON NEXT PAGE OF THIS FORM.)*

I. (a) PLAINTIFFS

Topsoe, Inc.

(b) County of Residence of First Listed Plaintiff _____
(EXCEPT IN U.S. PLAINTIFF CASES)

(c) Attorneys *(Firm Name, Address, and Telephone Number)*
Robert Riddle / Reed Smith LLP
1221 McKinney Street, Suite 2100
Houston, Texas 77010, 713-469-3881

DEFENDANTS

Casale US, Inc. and Casale SA

County of Residence of First Listed Defendant _____
(IN U.S. PLAINTIFF CASES ONLY)
NOTE: IN LAND CONDEMNATION CASES, USE THE LOCATION OF THE TRACT OF LAND INVOLVED.

Attorneys *(If Known)*

II. BASIS OF JURISDICTION *(Place an "X" in One Box Only)*

- ☐ 1 U.S. Government Plaintiff
- ☒ 3 Federal Question *(U.S. Government Not a Party)*
- ☐ 2 U.S. Government Defendant
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III. CITIZENSHIP OF PRINCIPAL PARTIES *(Place an "X" in One Box for Plaintiff and One Box for Defendant)*
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- ☐ 835 Patent - Abbreviated New Drug Application
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- ☐ 870 Taxes (U.S. Plaintiff or Defendant)
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V. ORIGIN *(Place an "X" in One Box Only)*

☒ 1 Original Proceeding ☐ 2 Removed from State Court ☐ 3 Remanded from Appellate Court ☐ 4 Reinstated or Reopened ☐ 5 Transferred from Another District *(specify)* ☐ 6 Multidistrict Litigation - Transfer ☐ 8 Multidistrict Litigation - Direct File

VI. CAUSE OF ACTION

Cite the U.S. Civil Statute under which you are filing *(Do not cite jurisdictional statutes unless diversity)*:
35 U.S.C. §§ 271, et seq and 15 U.S.C. § 1125

Brief description of cause:
declaratory judgment of patent unenforceability under Patent Law and unfair competition and false advertising under the Lanham Act

VII. REQUESTED IN COMPLAINT:

☐ CHECK IF THIS IS A CLASS ACTION UNDER RULE 23, F.R.Cv.P.

DEMAND $

CHECK YES only if demanded in complaint:
JURY DEMAND: ☒ Yes ☐ No

VIII. RELATED CASE(S) IF ANY *(See instructions)*:

JUDGE _____ DOCKET NUMBER _____

DATE
Jan 31, 2024

SIGNATURE OF ATTORNEY OF RECORD
/s/ Robert Riddle

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INSTRUCTIONS FOR ATTORNEYS COMPLETING CIVIL COVER SHEET FORM JS 44

Authority For Civil Cover Sheet

The JS 44 civil cover sheet and the information contained herein neither replaces nor supplements the filings and service of pleading or other papers as required by law, except as provided by local rules of court. This form, approved by the Judicial Conference of the United States in September 1974, is required for the use of the Clerk of Court for the purpose of initiating the civil docket sheet. Consequently, a civil cover sheet is submitted to the Clerk of Court for each civil complaint filed. The attorney filing a case should complete the form as follows:

I.(a) Plaintiffs-Defendants. Enter names (last, first, middle initial) of plaintiff and defendant. If the plaintiff or defendant is a government agency, use only the full name or standard abbreviations. If the plaintiff or defendant is an official within a government agency, identify first the agency and then the official, giving both name and title.

(b) County of Residence. For each civil case filed, except U.S. plaintiff cases, enter the name of the county where the first listed plaintiff resides at the time of filing. In U.S. plaintiff cases, enter the name of the county in which the first listed defendant resides at the time of filing. (NOTE: In land condemnation cases, the county of residence of the "defendant" is the location of the tract of land involved.)

(c) Attorneys. Enter the firm name, address, telephone number, and attorney of record. If there are several attorneys, list them on an attachment, noting in this section "(see attachment)".

II. Jurisdiction. The basis of jurisdiction is set forth under Rule 8(a), F.R.Cv.P., which requires that jurisdictions be shown in pleadings. Place an "X" in one of the boxes. If there is more than one basis of jurisdiction, precedence is given in the order shown below.
United States plaintiff. (1) Jurisdiction based on 28 U.S.C. 1345 and 1348. Suits by agencies and officers of the United States are included here.
United States defendant. (2) When the plaintiff is suing the United States, its officers or agencies, place an "X" in this box.
Federal question. (3) This refers to suits under 28 U.S.C. 1331, where jurisdiction arises under the Constitution of the United States, an amendment to the Constitution, an act of Congress or a treaty of the United States. In cases where the U.S. is a party, the U.S. plaintiff or defendant code takes precedence, and box 1 or 2 should be marked.
Diversity of citizenship. (4) This refers to suits under 28 U.S.C. 1332, where parties are citizens of different states. When Box 4 is checked, the citizenship of the different parties must be checked. (See Section III below; **NOTE: federal question actions take precedence over diversity cases.**)

III. Residence (citizenship) of Principal Parties. This section of the JS 44 is to be completed if diversity of citizenship was indicated above. Mark this section for each principal party.

IV. Nature of Suit. Place an "X" in the appropriate box. If there are multiple nature of suit codes associated with the case, pick the nature of suit code that is most applicable. Click here for: Nature of Suit Code Descriptions.

V. Origin. Place an "X" in one of the seven boxes.
Original Proceedings. (1) Cases which originate in the United States district courts.
Removed from State Court. (2) Proceedings initiated in state courts may be removed to the district courts under Title 28 U.S.C., Section 1441.
Remanded from Appellate Court. (3) Check this box for cases remanded to the district court for further action. Use the date of remand as the filing date.
Reinstated or Reopened. (4) Check this box for cases reinstated or reopened in the district court. Use the reopening date as the filing date.
Transferred from Another District. (5) For cases transferred under Title 28 U.S.C. Section 1404(a). Do not use this for within district transfers or multidistrict litigation transfers.
Multidistrict Litigation – Transfer. (6) Check this box when a multidistrict case is transferred into the district under authority of Title 28 U.S.C. Section 1407.
Multidistrict Litigation – Direct File. (8) Check this box when a multidistrict case is filed in the same district as the Master MDL docket.
PLEASE NOTE THAT THERE IS NOT AN ORIGIN CODE 7. Origin Code 7 was used for historical records and is no longer relevant due to changes in statute.

VI. Cause of Action. Report the civil statute directly related to the cause of action and give a brief description of the cause. **Do not cite jurisdictional statutes unless diversity.** Example: U.S. Civil Statute: 47 USC 553 Brief Description: Unauthorized reception of cable service.

VII. Requested in Complaint. Class Action. Place an "X" in this box if you are filing a class action under Rule 23, F.R.Cv.P.
Demand. In this space enter the actual dollar amount being demanded or indicate other demand, such as a preliminary injunction.
Jury Demand. Check the appropriate box to indicate whether or not a jury is being demanded.

VIII. Related Cases. This section of the JS 44 is used to reference related pending cases, if any. If there are related pending cases, insert the docket numbers and the corresponding judge names for such cases.

Date and Attorney Signature. Date and sign the civil cover sheet.

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

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.

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 to Topsoe 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.

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 at Zardi & Co. SA in an attempt to enforce its improperly obtained and unenforceable 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 located in the state of Texas to dissuade that customer from installing Topsoe's ammonia technology at its

facilities in Texas. 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 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). 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.

19. 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.

20. Venue is proper in the Southern District of Texas pursuant to 28 U.S.C. §§ 1391(b) and (c), and 1400(b), at least because Casale is incorporated in the State of Texas, has its principal place of business in the Southern District of Texas and Defendants have committed acts of false advertising in the Southern District of Texas and attempted to enforce their unenforceable patent in the Southern District of Texas.

FACTUAL ALLEGATIONS

Topsoe's Contributions to the Field of Low Carbon Ammonia Technology

21. 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.

22. 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.

23. 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.

24. 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.

25. 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.

26. 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.

27. 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."

28. 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

29. Casale has long been aware of Topsoe's low carbon ammonia technology.

30. 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.

31. Casale also gained access to the IFFCO plant in India described above 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.

32. 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.

33. 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").

34. 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

35. 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.

36. The '168 Patent issued on March 29, 2022.

37. 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.

38. Attorneys of Dorsey & Whitney LLP, including Marcus S. Simon (Reg. No. 50,258) represented Casale in the prosecution of the '168 patent.

39. 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.

40. 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.[1] 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.

41. 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

[1] 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.

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.

42. 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.

43. 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

44. As noted above, the European counterpart to the '168 Patent, is the '067 Patent.

45. 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.

46. 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.

47. Both the '067 Patent and the related '770 patent were prosecuted on behalf of Casale by European law firm M. Zardi & Co. SA ("Zardi").

48. Zardi was founded in 1999 by Marco Zardi and is a Swiss law firm specializing in intellectual property.

49. Both the US and European patents are based on the same PCT application filed by Zardi, and specifically, Marco Zardi.

50. Zardi also is representing Casale in the European Opposition.

51. Zardi, including Marco Zardi and Riccardo Biazzi, also were substantively involved in the prosecution of the '168 Patent.

52. The current Chief Executive Officer of Casale is Frederico Zardi.

53. On information and belief, Marco Zardi and Federico Zardi are blood relatives.

54. 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

55. 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.

56. 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.

57. 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.

58. 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."

59. 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.

60. 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.

61. 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.

62. 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.

63. 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.

64. 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.

65. Casale knew that its patent was invalid and unenforceable but engaged in these communications regardless.

66. Casale's statements were also false and misleading 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

67. 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.

68. 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]."

69. 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."

70. 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:

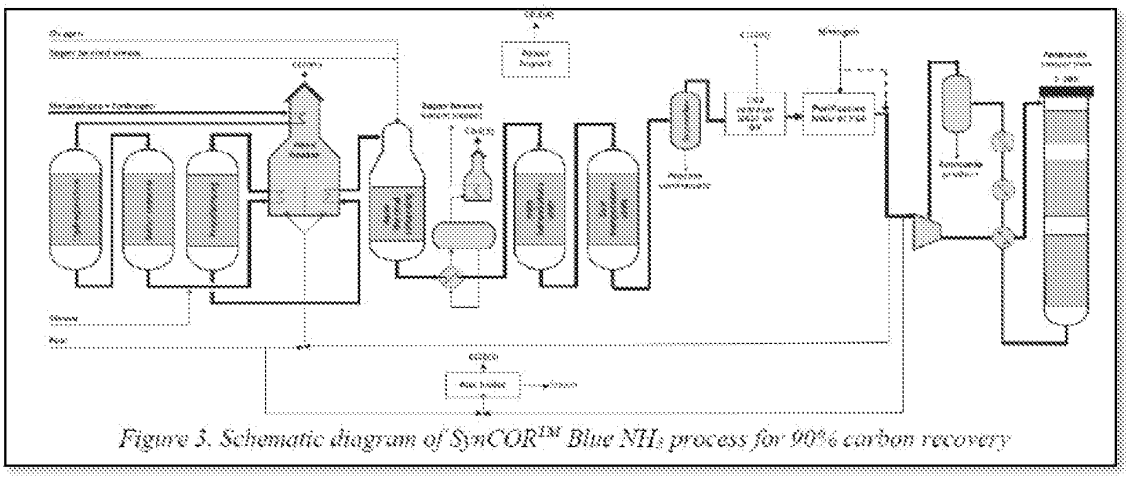


Figure 3. Schematic diagram of SynCOR™ Blue NH₃ process for 90% carbon recovery

71. 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."

72. 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.

73. 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 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.

74. 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

75. 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.

76. 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. 3583067B1) to U.S. Patent No. 11,286,168 was challenged via two Notices of Opposition both filed before the European Patent Office on June 8, 2022. These opposition proceedings remain pending before the European Patent Office, with the Patent Owner having filed a reply to the Notice of Opposition on November 3, 2022. Out of an abundance of caution, the Patent Owner is submitting this Request, which includes as the items of information to be considered the references cited in the Notice of Opposition.

Corrected Request for Supplemental Examination dated April 16, 2023.

77. 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.

78. 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.

79. 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.

80. 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.

81. 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.

82. 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."

83. Casale has never retracted any of its statements to Topsoe's customers regarding the Disputed Patents and their enforceability, despite knowing that the US PTO has now 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)

84. Topsoe incorporates by reference the allegations set forth in this Complaint as though fully set forth herein.

85. An actual and justiciable controversy exists between Topsoe and Casale concerning the '168 patent.

86. 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.

87. 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.

88. 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"). These individuals deliberately and knowingly withheld and/or omitted material information from Topsoe prior art in connection with the prosecution 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 and was withheld and omitted with an intent to deceive the PTO and/or '168 patent examiner, as described below.

89. The '168 Patent lists two inventors, Francesco Baratto and Raffaele Ostuni.

90. 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.

91. As a registered patent attorney for Casale, Simon was aware, or should have been aware, of his duty of candor to the US PTO.

92. 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.

93. 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.

94. Both Ostuni and Simon have been actively involved in communications regarding Casale's assertion of claims of infringement against Topsoe. Ostuni and Simon were both present during the September 15, 2023, call between Casale and Topsoe.

95. The '168 Patent has an effective filing date of January 31, 2018.

96. Prior to the effective filing date of the '168 Patent, Casale had access to and knowledge of 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.

97. 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 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.

98. On information and belief, Ostuni also had direct, firsthand knowledge of at least one 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.

99. In addition, Topsoe has published and presented frequently on its low carbon ammonia process and it is used commercial in many facilities worldwide. Casale and Topsoe are direct competitors and aware of one another generally in the industry.

100. The '168 Patent is directed towards a process for synthesis of ammonia from natural gas. The '168 Patent includes two independent claims.

101. 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.

Ex. 1 at col. 18, ll. 38-57.

102. 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.

Ex. 1 at col. 20, ll. 22-38.

103. 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.

104. 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.

105. 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, <u>said first and second streams having the same composition</u>." 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.[2]

106. 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 information from the Examiner in order to secure allowance of the patent.

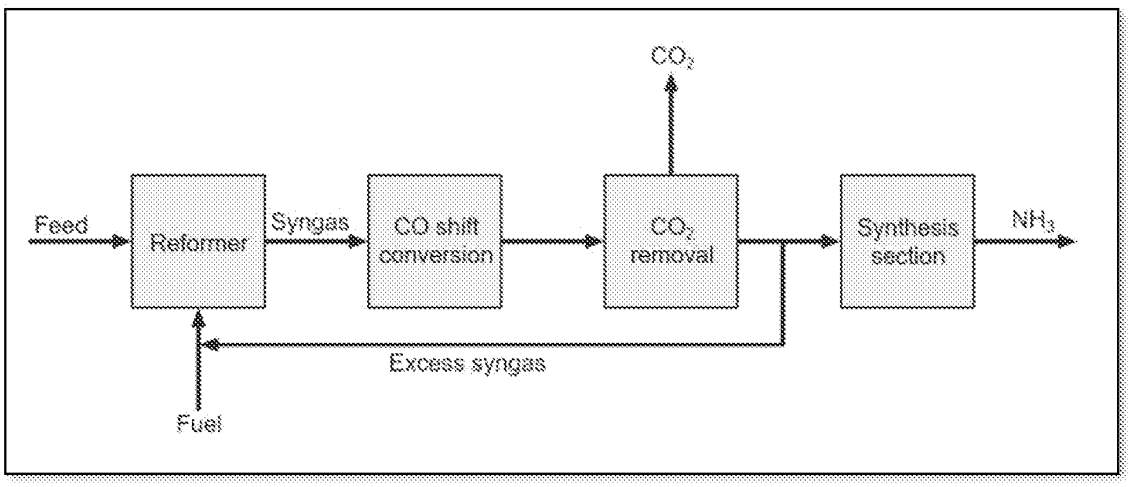
107. Casale's concealment strategy worked, and the Examiner withdrew the rejection. The reason the Examiner gave for allowing the claims was the "distinguishing feature of the first and second streams having the same composition." Notice of Allowance dated Nov. 18, 2021. As a result, the claims were 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.

108. 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

[2] 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 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.

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, this reference is highly material to the patentability of the '168 Patent and should have been disclosed during prosecution.

109. 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.



110. 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.

111. 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.

112. 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.

113. 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.

114. 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 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.

115. Casale knew of the materiality of the Topsoe prior art references before, during, and after prosecution of the '168 Patent. 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.

116. 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.

117. 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.

118. 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.

119. 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.

120. 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.

121. 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.

122. 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.

123. 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.

124. 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.

125. Intentional nondisclosure of material prior art during prosecution of a patent application constitutes inequitable conduct.

126. Inequitable conduct during prosecution of a patent application renders any resultant patent unenforceable.

127. 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.

128. At least attorney Simon, inventors Baratto and Ostuni, and Marco Zardi 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.

129. Casale's, Casale's attorneys, attorney Simon's, and Casale's employees' and '168 Patent inventors' Baratto and Ostuni 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.

130. 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.

131. 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.

Topsoe, Inc. – EX1003
Page 1074 of 1210

SECOND COUNT

(UNFAIR COMPETITION AND FALSE ADVERTISING UNDER THE LANHAM ACT)

132. Topsoe incorporates by reference the allegations set forth in this Complaint as though fully set forth herein.

133. "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).

134. 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 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.

135. 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.

136. 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 liability under the Lanham Act. Casale has acted with malice and specific intent, as it had knowledge of the falsehood of its 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.

137. 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.

138. 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.

139. 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.

140. 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. Additionally, Casale has caused its blue ammonia technology products to enter interstate commerce, including through its proposals to customers in the U.S.

141. 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.

142. 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.

143. 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.

144. 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.

145. 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.

146. 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)

147. Topsoe incorporates by reference the allegations set forth in this Complaint as though fully set forth herein.

148. 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.

149. 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 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 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.

150. 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.

151. 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: January 31, 2024

Respectfully submitted

By: */s/ Robert Riddle*

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Exhibit 1



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

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

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

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

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

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

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

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

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

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

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

(65) **Prior Publication Data**

US 2020/0055738 A1 Feb. 20, 2020

(30) **Foreign Application Priority Data**

Feb. 15, 2017 (EP) 17156256
Oct. 6, 2017 (EP) 17195305

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

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

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

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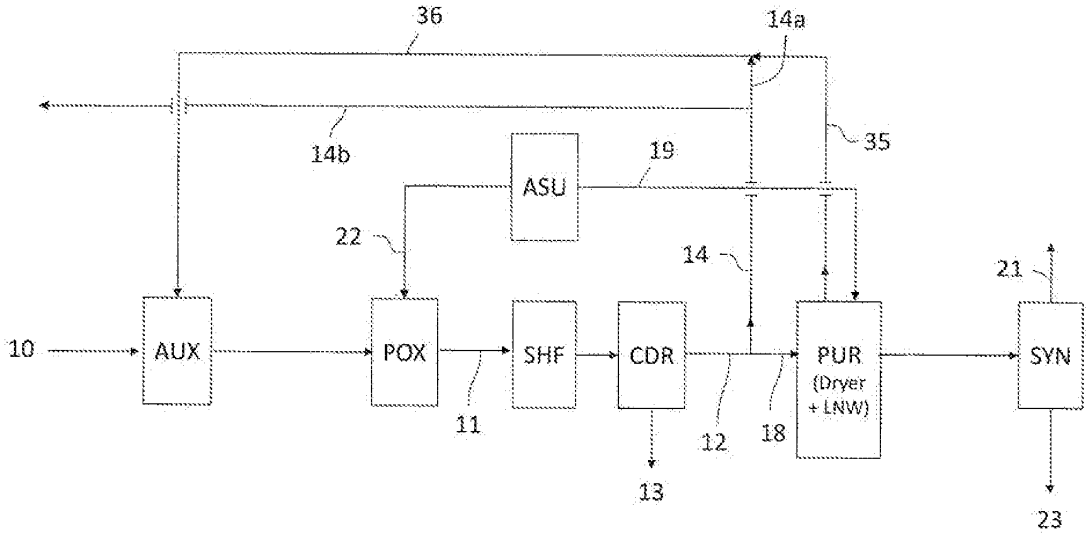
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(57) **ABSTRACT**

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

23 Claims, 4 Drawing Sheets



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CPC *C01B 2203/0244* (2013.01); *C01B 2203/0283* (2013.01); *C01B 2203/042* (2013.01); *C01B 2203/0445* (2013.01); *C01B 2203/0475* (2013.01); *C01B 2203/068* (2013.01); *C01B 2203/1241* (2013.01)

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

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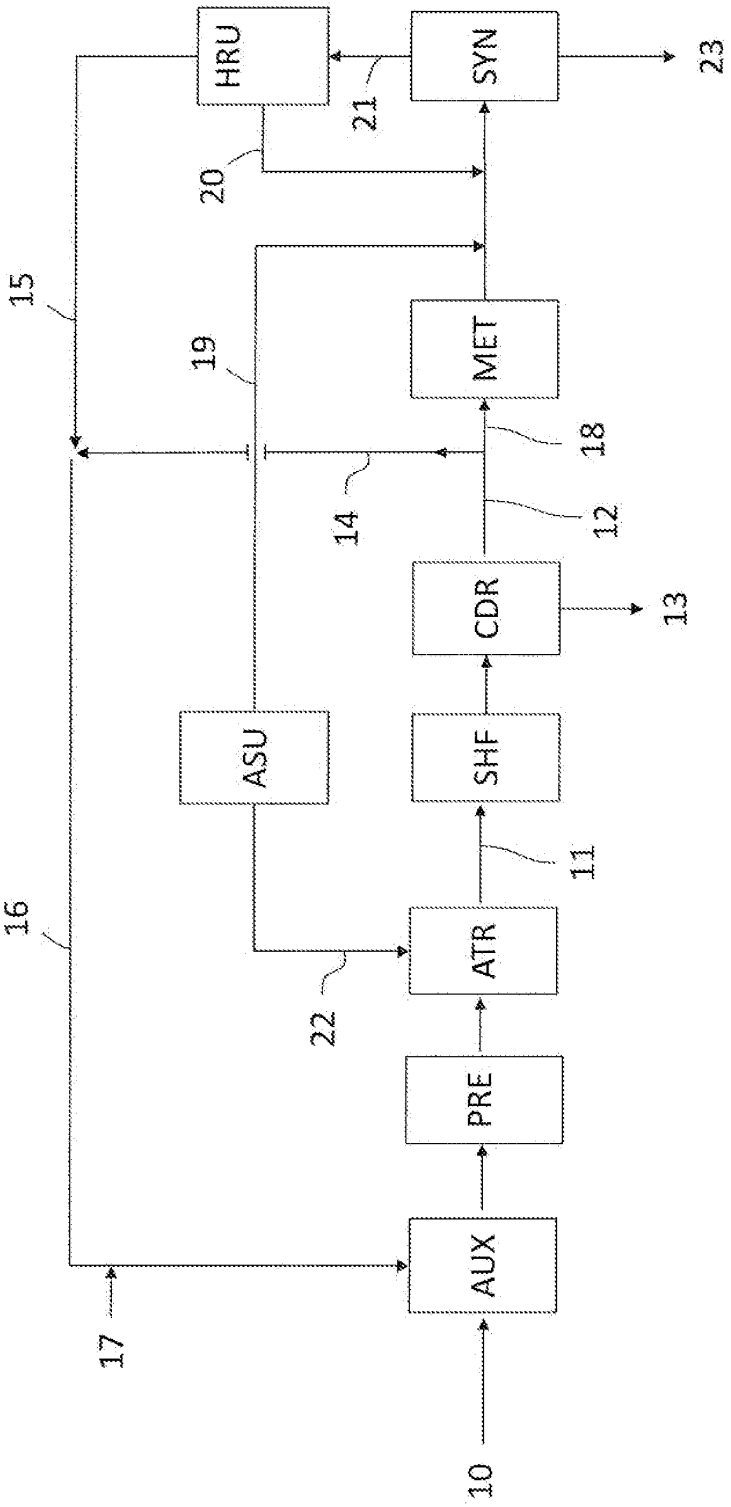

HRU
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FIG. 1

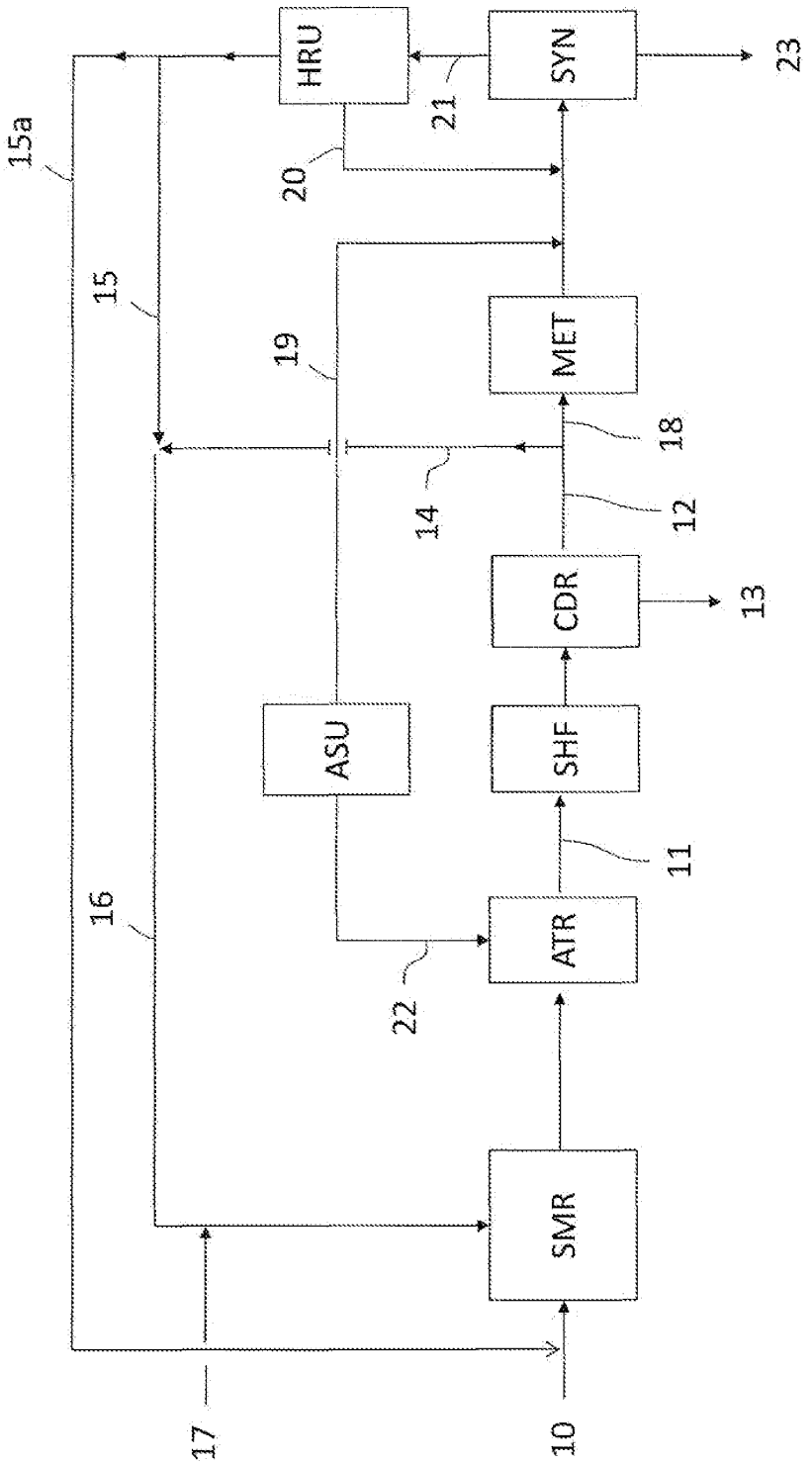

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FIG. 2

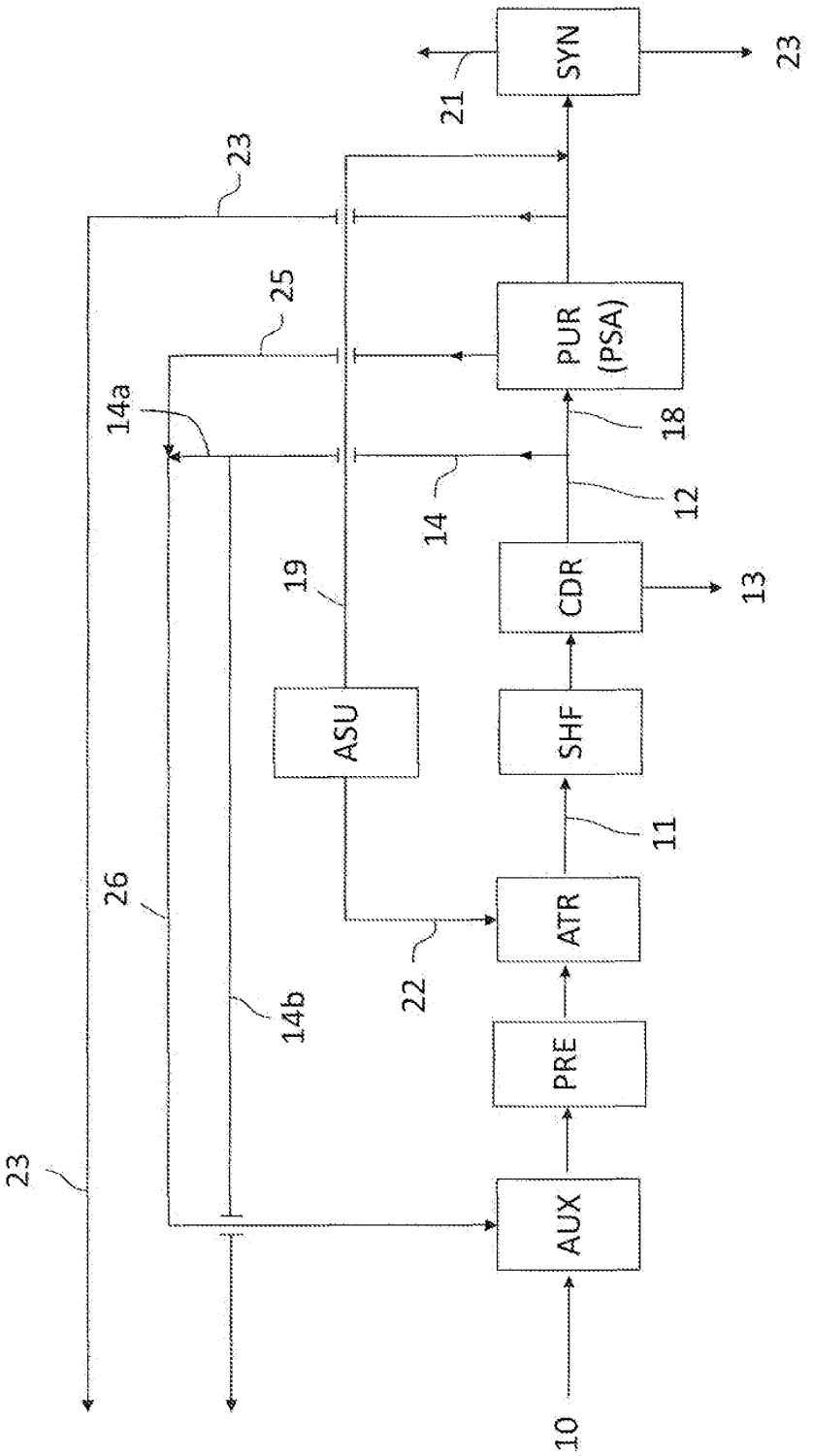

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PUR (PSA)
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ATR
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14b
PRE
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AUX
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FIG. 3

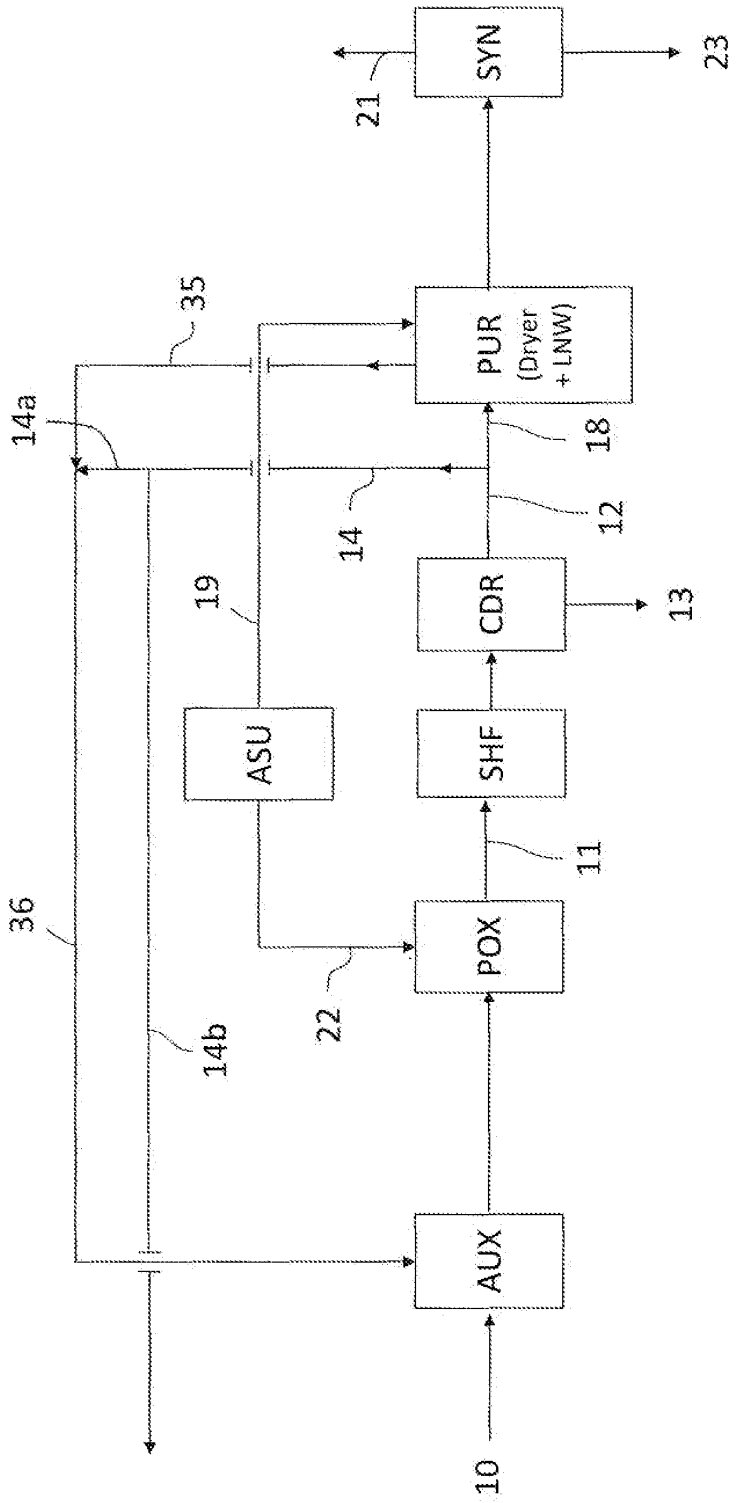

SYN
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PUR
(Dryer
+ LNW)
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CDR
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ASU
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POX
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14b
AUX
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FIG. 4

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

FIELD OF APPLICATION

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

PRIOR ART

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

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

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

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

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

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

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

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

SUMMARY OF THE INVENTION

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

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

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

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

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

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

characterized by:

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

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

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

separating a part of the synthesis gas downstream of decarbonation,

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

For example, the surplus may be:

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

conveyed to a storage buffer, or

flared.

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

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

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

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

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

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

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

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

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

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

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

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

The main advantages of the invention are listed below.

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

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

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

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

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

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

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

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

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

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

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

DESCRIPTION OF THE FIGURES

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

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

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

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

DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

EXAMPLE

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

Table 1 compares the following options:

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

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

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

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

TABLE 1

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

TABLE 1-continued

		Option			
		(1) Prior art	(2) Prior art	(3) Inv.	(4) Inv.
CO2 captured in process	MTD	3600	3600	5200	5106
CO2 to atmosphere (contained in flue gas)	MTD	2100	200	200	206
CO2 to atmosphere (contained in flue gas)	t/t NH3	0.7	0.1	0.1	0.1
Main Equipment size					
Total fired heater duty (reformer/fired heater + auxiliary boiler)	%	100	120	75	105
Process CO2 removal capacity	%	100	100	145	140
ASU O2 capacity	%	n/a	n/a	100	60
Flowrate of front end (secondary output/ATR)	%	100	100	120	97

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

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

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

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

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

Table 2 compares the following options:

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

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

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

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

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

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

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

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

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

TABLE 2

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

TABLE 2-continued

	1a: SMR + ATR	1b: SMR + ATR	2a ATR	2b ATR	3a POX	3b POX
CO2 emissions into atmosphere per unit of ammonia produced, t CO2/t NH3	0.15	0.975	0.17	0.10	0.15	0.05
Distribution of the CO2 emissions						
trim fuel	59%	zero	20%	zero	20%	zero
CH4 slip in the process gas	15%	29%	40%	79%	30%	63%
CO slip in the process gas	34%	69%	39%	19%	49%	34%
CO2 slip in the process gas	1%	2%	1%	2%	1%	3%

In Table 2:

"Trim fuel" as defined in the patent;

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

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

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

Several comments may be made in view of Table 2:

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

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

The invention claimed is:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

17. The process of claim 1, wherein

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

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

18. The process of claim 1, wherein:

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

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

19. The process of claim 1, wherein:

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

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

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

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

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

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

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

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

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

* * * * *

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(EXCEPT IN U.S. PLAINTIFF CASES)

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DEFENDANTS

Casale US, Inc. and Casale SA

County of Residence of First Listed Defendant _____
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PERSONAL INJURY
- ☐ 365 Personal Injury - Product Liability
- ☐ 367 Health Care/ Pharmaceutical Personal Injury Product Liability
- ☐ 368 Asbestos Personal Injury Product Liability

PERSONAL PROPERTY
- ☐ 370 Other Fraud
- ☐ 371 Truth in Lending
- ☐ 380 Other Personal Property Damage
- ☐ 385 Property Damage Product Liability

CIVIL RIGHTS
- ☐ 440 Other Civil Rights
- ☐ 441 Voting
- ☐ 442 Employment
- ☐ 443 Housing/ Accommodations
- ☐ 445 Amer. w/Disabilities - Employment
- ☐ 446 Amer. w/Disabilities - Other
- ☐ 448 Education

PRISONER PETITIONS

Habeas Corpus:
- ☐ 463 Alien Detainee
- ☐ 510 Motions to Vacate Sentence
- ☐ 530 General
- ☐ 535 Death Penalty

Other:
- ☐ 540 Mandamus & Other
- ☐ 550 Civil Rights
- ☐ 555 Prison Condition
- ☐ 560 Civil Detainee - Conditions of Confinement

FORFEITURE/PENALTY
- ☐ 625 Drug Related Seizure of Property 21 USC 881
- ☐ 690 Other

LABOR
- ☐ 710 Fair Labor Standards Act
- ☐ 720 Labor/Management Relations
- ☐ 740 Railway Labor Act
- ☐ 751 Family and Medical Leave Act
- ☐ 790 Other Labor Litigation
- ☐ 791 Employee Retirement Income Security Act

IMMIGRATION
- ☐ 462 Naturalization Application
- ☐ 465 Other Immigration Actions

BANKRUPTCY
- ☐ 422 Appeal 28 USC 158
- ☐ 423 Withdrawal 28 USC 157

INTELLECTUAL PROPERTY RIGHTS
- ☐ 820 Copyrights
- ☒ 830 Patent
- ☐ 835 Patent - Abbreviated New Drug Application
- ☐ 840 Trademark
- ☐ 880 Defend Trade Secrets Act of 2016

SOCIAL SECURITY
- ☐ 861 HIA (1395ff)
- ☐ 862 Black Lung (923)
- ☐ 863 DIWC/DIWW (405(g))
- ☐ 864 SSID Title XVI
- ☐ 865 RSI (405(g))

FEDERAL TAX SUITS
- ☐ 870 Taxes (U.S. Plaintiff or Defendant)
- ☐ 871 IRS—Third Party 26 USC 7609

OTHER STATUTES
- ☐ 375 False Claims Act
- ☐ 376 Qui Tam (31 USC 3729(a))
- ☐ 400 State Reapportionment
- ☐ 410 Antitrust
- ☐ 430 Banks and Banking
- ☐ 450 Commerce
- ☐ 460 Deportation
- ☐ 470 Racketeer Influenced and Corrupt Organizations
- ☐ 480 Consumer Credit (15 USC 1681 or 1692)
- ☐ 485 Telephone Consumer Protection Act
- ☐ 490 Cable/Sat TV
- ☐ 850 Securities/Commodities/ Exchange
- ☐ 890 Other Statutory Actions
- ☐ 891 Agricultural Acts
- ☐ 893 Environmental Matters
- ☐ 895 Freedom of Information Act
- ☐ 896 Arbitration
- ☐ 899 Administrative Procedure Act/Review or Appeal of Agency Decision
- ☐ 950 Constitutionality of State Statutes

V. ORIGIN *(Place an "X" in One Box Only)*

☒ 1 Original Proceeding ☐ 2 Removed from State Court ☐ 3 Remanded from Appellate Court ☐ 4 Reinstated or Reopened ☐ 5 Transferred from Another District *(specify)* ☐ 6 Multidistrict Litigation - Transfer ☐ 8 Multidistrict Litigation - Direct File

VI. CAUSE OF ACTION

Cite the U.S. Civil Statute under which you are filing *(Do not cite jurisdictional statutes unless diversity)*:
35 U.S.C. §§ 271, et seq and 15 U.S.C. § 1125

Brief description of cause:
declaratory judgment of patent unenforceability under Patent Law and unfair competition and false advertising under the Lanham Act

VII. REQUESTED IN COMPLAINT:

☐ CHECK IF THIS IS A CLASS ACTION UNDER RULE 23, F.R.Cv.P.

DEMAND $

CHECK YES only if demanded in complaint:
JURY DEMAND: ☒ Yes ☐ No

VIII. RELATED CASE(S) IF ANY *(See instructions)*:

JUDGE _____ DOCKET NUMBER _____

DATE
Jan 31, 2024

SIGNATURE OF ATTORNEY OF RECORD
/s/ Robert Riddle

FOR OFFICE USE ONLY

INSTRUCTIONS FOR ATTORNEYS COMPLETING CIVIL COVER SHEET FORM JS 44

Authority For Civil Cover Sheet

The JS 44 civil cover sheet and the information contained herein neither replaces nor supplements the filings and service of pleading or other papers as required by law, except as provided by local rules of court. This form, approved by the Judicial Conference of the United States in September 1974, is required for the use of the Clerk of Court for the purpose of initiating the civil docket sheet. Consequently, a civil cover sheet is submitted to the Clerk of Court for each civil complaint filed. The attorney filing a case should complete the form as follows:

I.(a) Plaintiffs-Defendants. Enter names (last, first, middle initial) of plaintiff and defendant. If the plaintiff or defendant is a government agency, use only the full name or standard abbreviations. If the plaintiff or defendant is an official within a government agency, identify first the agency and then the official, giving both name and title.

(b) County of Residence. For each civil case filed, except U.S. plaintiff cases, enter the name of the county where the first listed plaintiff resides at the time of filing. In U.S. plaintiff cases, enter the name of the county in which the first listed defendant resides at the time of filing. (NOTE: In land condemnation cases, the county of residence of the "defendant" is the location of the tract of land involved.)

(c) Attorneys. Enter the firm name, address, telephone number, and attorney of record. If there are several attorneys, list them on an attachment, noting in this section "(see attachment)".

II. Jurisdiction. The basis of jurisdiction is set forth under Rule 8(a), F.R.Cv.P., which requires that jurisdictions be shown in pleadings. Place an "X" in one of the boxes. If there is more than one basis of jurisdiction, precedence is given in the order shown below.
United States plaintiff. (1) Jurisdiction based on 28 U.S.C. 1345 and 1348. Suits by agencies and officers of the United States are included here.
United States defendant. (2) When the plaintiff is suing the United States, its officers or agencies, place an "X" in this box.
Federal question. (3) This refers to suits under 28 U.S.C. 1331, where jurisdiction arises under the Constitution of the United States, an amendment to the Constitution, an act of Congress or a treaty of the United States. In cases where the U.S. is a party, the U.S. plaintiff or defendant code takes precedence, and box 1 or 2 should be marked.
Diversity of citizenship. (4) This refers to suits under 28 U.S.C. 1332, where parties are citizens of different states. When Box 4 is checked, the citizenship of the different parties must be checked. (See Section III below; **NOTE: federal question actions take precedence over diversity cases.**)

III. Residence (citizenship) of Principal Parties. This section of the JS 44 is to be completed if diversity of citizenship was indicated above. Mark this section for each principal party.

IV. Nature of Suit. Place an "X" in the appropriate box. If there are multiple nature of suit codes associated with the case, pick the nature of suit code that is most applicable. Click here for: Nature of Suit Code Descriptions.

V. Origin. Place an "X" in one of the seven boxes.
Original Proceedings. (1) Cases which originate in the United States district courts.
Removed from State Court. (2) Proceedings initiated in state courts may be removed to the district courts under Title 28 U.S.C., Section 1441.
Remanded from Appellate Court. (3) Check this box for cases remanded to the district court for further action. Use the date of remand as the filing date.
Reinstated or Reopened. (4) Check this box for cases reinstated or reopened in the district court. Use the reopening date as the filing date.
Transferred from Another District. (5) For cases transferred under Title 28 U.S.C. Section 1404(a). Do not use this for within district transfers or multidistrict litigation transfers.
Multidistrict Litigation – Transfer. (6) Check this box when a multidistrict case is transferred into the district under authority of Title 28 U.S.C. Section 1407.
Multidistrict Litigation – Direct File. (8) Check this box when a multidistrict case is filed in the same district as the Master MDL docket.
PLEASE NOTE THAT THERE IS NOT AN ORIGIN CODE 7. Origin Code 7 was used for historical records and is no longer relevant due to changes in statute.

VI. Cause of Action. Report the civil statute directly related to the cause of action and give a brief description of the cause. **Do not cite jurisdictional statutes unless diversity.** Example: U.S. Civil Statute: 47 USC 553 Brief Description: Unauthorized reception of cable service.

VII. Requested in Complaint. Class Action. Place an "X" in this box if you are filing a class action under Rule 23, F.R.Cv.P.
Demand. In this space enter the actual dollar amount being demanded or indicate other demand, such as a preliminary injunction.
Jury Demand. Check the appropriate box to indicate whether or not a jury is being demanded.

VIII. Related Cases. This section of the JS 44 is used to reference related pending cases, if any. If there are related pending cases, insert the docket numbers and the corresponding judge names for such cases.

Date and Attorney Signature. Date and sign the civil cover sheet.

Experience of Energy Saving and Naphtha to Gas Conversion Projects at IFFCO

IFFCO (Indian Farmers Fertiliser Cooperative Limited) is continually striving to be the most efficient energy consumer in the fertilizer industry. To achieve its goal, a number of energy saving schemes have been successfully implemented and envisaged savings are achieved. IFFCO-Phulpur Unit, the world's largest naphtha based Urea complex, consuming one full naphtha rake (2200 t) daily has been modified from costly feedstock of naphtha to re-gasified liquefied natural gas (RLNG). There shall be national saving in Government subsidy of about US $ 220 millions per year due to conversion of Phulpur Unit to Re-gasified Liquefied Natural Gas. This paper highlights the schemes implemented under Energy Saving Projects and modifications carried out under the RLNG Conversion Job. It describes in detail the experiences gained during both project execution and implementation.

M. Rajashekhariah,
IFFCO-Phulpur, Allahabad, India
Yogesh Narula
IFFCO-Phulpur, Allahabad, India

Introduction

The Indian Fertilizer Industry has come a long way since the establishment of the first Super-Phosphate factory in 1906 at Ranipet (Tamil Nadu). The turning point in the Indian Agriculture Sector was the introduction of HYV (High Yielding Varieties) seeds of wheat and rice in mid-sixties. The expansion in area of land under cultivation and switch-over to HYVs seeds led to a remarkable growth in fertilizer use and crop production.

Subsequently, with the aid of government policies for fertilizer production, India became self-sufficient in food grain production. Today, fertilizers have become an essential input to Indian Agriculture for meeting the food grain requirements of the growing population of the country. Fertilizer Industries have a mammoth task of providing essential nutrients to Indian farmers so that the growth in the agricultural sector is sufficient for meeting the domestic food requirements.

Implications of Feedstock and Energy

Main feed stocks used for manufacture of Urea in India are Natural Gas (65%), Naphtha (25%) and Fuel Oil (FO) 10%). Because of shortage of gas supplies to gas-based Urea plants, many units are operating on mixed feed options wherein naphtha is used along with gas through a pre-reformer system, which results in higher cost of production.

Improving Reliability of Ammonia-Urea Plants

The most significant factor in improving productivity is plant reliability. Plant reliability is measured in terms of improvement in on-stream days. All other parameters in operation of plant meet, finally at reliability. Plant

Topsoe, Inc. – EX1003
Page 1101 of 1210

reliability determines directly profitability, safety and environmental performance.
The Ammonia-Urea complex is a high energy and capital intensive industry. Therefore, higher reliability and better energy efficiency is the key to its competitiveness.

Use of Cheaper and Better Feedstock

Type of feedstock has a major influence on energy consumption in an Ammonia-Urea Plant. Hydrogen to carbon ratio increases as we move from liquid hydrocarbons (naphtha or fuel oil) to gaseous hydrocarbons (natural gas). Besides, associated impurities namely sulphur, etc. are present only in traces in case of gas.

With the steep rise in the cost of liquid hydrocarbons in the last five-to-six years, Ammonia-Urea production from liquid hydrocarbons plants has become very costly. Keeping this in view, one of the main guidelines provided under the Government of India's New Policy was that all such plants should switch-over to Natural Gas or Re-gasified -Liquid Natural gas (RLNG) so that they can also become viable and compete in the business of Urea manufacturing.

Use of Modern Process Technologies and Advanced Instrumentation

Developments in science and engineering helped technologists to design and construct plants that are more reliable and energy efficient. There have been several developments in the past which have been adopted as part of the modernizations in old plants. Some of these measures are:

- Addition of S-50 (Synthesis Converter) in the Synthesis Loop of the Ammonia Plant to reduce operating pressure and thus save energy.
- Highly active and sturdy catalysts in reformer/shift, etc. are giving higher conversion efficiency and longer periods of operation.
- Improving performance of the CO_2 removal section by selecting better solvent and installing or modifying equipments.
- Installation of molecular sieves or ammonia wash for the purification of synthesis gas.
- Installation of Purge Gas Recovery (PGR) Unit to recover hydrogen and ammonia from purge gas.
- Installation of pre-reformer to overcome gas shortage through the use of naphtha.
- Change of material of construction of critical heat exchangers from carbon steel to stainless steel.
- Use of additional Urea trays in the Urea Reactor for higher efficiency.
- Increasing CO_2 feed temperature to the Urea Reactor by recovering heat in an exchanger from the third stage of the CO_2 Compressor.
- Replacement of old HP Stripper with new Bi-metallic Stripper in Urea Plant.
- Installation of pre-concentrator in the Urea Plant.
- Installation of Urea MP Pre-decomposer in case excess low pressure steam is available in the complex.
- Better integration of the steam network and preparation of Boiler Feed water for Utility Boiler in Ammonia Plant by recovering heat from low level of energy.
- Installation of variable speed drives for electric motors to optimize power consumption with variable speeds.
- Recovery of waste heat particularly from reformer furnace flue gases.
- Installation of Carbon Dioxide Recovery Plant in gas plant for meeting the requirement of CO_2 to balance ammonia and Urea production. This will save the

Topsoe, Inc. – EX1003
Page 1102 of 1210

costly naphtha fuel being used by various natural gas based plants.

- Upgrading Plant and Instrument Air System by installing HOC (Heat of Compression) type dryers.
- Installation of efficient moving machineries.
- Upgrading Instrumentation System by switching over from pneumatic to DCS.
- Increase in Capacity of existing plants by way of retrofitting & modification.

The Indian Ammonia-Urea Plants have kept pace with the developments taking place around the world. There is a marked improvement in the energy consumption and increase in on-stream days. In the last fifteen years, the energy consumption for manufacturing of ammonia has been reduced by more than 25% while the average on-stream days of ammonia plants based on reforming process has improved from 290 days (1987-90) to around 320 days at present.

Fertilizer Policy in India

To increase self sufficiency in fertilser production, the Government of India (GOI) started the Retention Pricing Scheme in late 70's. The retention price varied from unit to unit depending upon vintage, location of the plant, feedstock, technology used, etc. This led to an increase in fertilizer production. Many new plants were setup and the country became self sufficient in food production. However, there was an increase in the subsidy burden. To emphasize international competitiveness, global marketing, import liberalization, import price parity and free trade, the plant-specific Retention Price Scheme was phased out. The Government of India (GOI) has implemented a new pricing policy for urea manufacturing industries in effect as of April 2003. The new pricing policy is in the form of a group based concession scheme. The key objective of the new pricing policy for urea units is to gradually move in the direction of parity with international prices based on the use of the most efficient feedstock and the state-of-the-art technology.

Strategies Adopted at IFFCO-Phulpur in Meeting the Challenges

Indian Farmers Fertiliser Cooperative Limited (IFFCO), globally acclaimed cooperative in fertilizer production and marketing has been striving for socio-economic upliftment of the rural population of India since inception. To ensure timely availability of quality fertilizers to the farmers, IFFCO came into being on 3rd November, 1967. Initially, IFFCO commissioned Kalol and Kandla plants in Gujarat in early 1975. Subsequently, the society expanded its base by building two more plants at Phulpur and Aonla in U.P. in the years 1981 and 1988 respectively. Subsequently the capacity of all these four units has been increased, either by installing new plants at the existing site or by revamping the existing plants. Last year, it acquired the DAP/NPK unit at Paradeep in Orissa having an annual capacity to produce 1.9 million tonne of NPK/DAP. The marketing of IFFCO's products – NPK/DAP/UREA – are channeled through 37,500 member cooperative societies and 158 Farmers Service Centers in over 28 States / Union Territories in the country. IFFCO along with a joint venture partner, Oman Oil India Company (OOC) has set up Oman India Fertiliser Company (OMIFCO) at Sur in Oman with annual capacity of producing 1.65 million tonne, of Urea. IFFCO launched another company Indo-Egyptian Fertiliser Company (IEFC), a joint venture with El Nasr Mining Company (ENMC), for setting up a Phosphoric Acid Plant in Egypt.

IFFCO-Phulpur Unit, is located at Phulpur, Allahabad in the state of Uttar Pradesh. It has been the world's largest naphtha based Urea complex, consuming one full naphtha rake (2200 t) daily. Both of its units have been performing well since beginning. Unit –I started its commercial production in March,1981 and

Topsoe, Inc. – EX1003
Page 1103 of 1210

has a 977 metric tonne per day (MTPD) ammonia plant, 1670 MTPD Urea plant, three coal fired boilers having 125 MT/hr capacities each and 12.5 MW Turbo-Generator.

The Second Unit started commercial production in December, 1997 and consists of a 1520 MTPD ammonia plant, two streams of 1310 MTPD Urea plants, a FO fired boiler of 200 MT/hr and 18 MW Turbo-Generator along with other offsite facilities

The Ammonia-Urea complex at Phulpur has been based on naphtha since inception when cost of naphtha was quite low. The Phulpur Unit has been performing well with the help of effective and efficient operation and maintenance practices. Specific energy consumption per MT of ammonia produced in Unit-I was initially at 42.6 GJ/MT (36.6 mmBTU LHV/short ton) and was being operated at 38.4 GJ/MT (33.0 mmBTU LHV /ton) later. Specific energy consumption per MT of ammonia in Unit-II was 32.7 GJ/MT (28.1 mmBTU LHV /ton). The energy difference was due to technological difference of vintage as earlier plant was 1976 year based and later plant of 1994 year based.

Realizing the importance of improving the productivity of the complex, IFFCO had initiated the following main projects in the year 2004 to 2006 in a phased manner:

A. **Energy Saving Projects (ESP) in all 5 Ammonia Plant**
B. **Re-gasified Liquid Natural Gas (RLNG) Conversion at Phulpur (Naphtha to Gas Conversion).**
C. **Installation of a Carbon Dioxide Recovery (CDR) plant at Phulpur & Aonla**

All activities pertaining to Energy Saving Projects, RLNG Conversion, and Installation of CDR have already been successfully completed.

All the above steps were in line with the new policy of the Government of India on fertilizer to improve the productivity of plants by way of reduced energy consumption, and change over to cheaper feed stock RLNG to reduce the cost of production and thereby reducing the subsidy.

A) Energy Saving Projects (ESP)

A study was carried out in all the three units to find out the possibility of improving plant performance in order to make the Unit more energy efficient. It was observed that in ammonia plants, significant energy loss occurs in the form of dumping heat to the cooling water system through coolers and condensers. Schemes were finalized for individual plant under Energy Saving Projects (ESP) with the help of Consultant and in-house studies: The schemes common for all the three Units and all 5 Ammonia Plant are as follows:

1. New LT Shift Guard, BFW Preheater and Separator
2. Installation of S-50 radial flow synthesis converter and HP / MP Boiler.

Schemes other than above common schemes installed at Phulpur Plant are shown in the table below:

Sl. No.	Description
	Phulpur –I
1.0	Reduction in pressure drop of LT shift converter.
2.0	Revamp of CO_2 Removal System to a modern 2-stage M/s Giammarco-Vetrocoke (GV) Process layout.
3.0	Drying of make-up gas and synthesis loop re-piping.
4.0	Synthesis gas compressor LP and HP case internal replacement.
5.0	Installation of final gas chiller.
	Phulpur –II
6.0	Installation of final gas chiller.

Phulpur-II being the latest generation plant with already low specific consumptions, had limited options for further improvement. More information on the Phulpur-I and II project is given in then next paragraphs.

Topsoe, Inc. – EX1003
Page 1104 of 1210

Phulpur-I

1. Improvement in outlet systems for LT shift converter

The outlet system of LT Shift reactor was changed to decrease the pressure drop across the Reactor. The elephant stool design outlet system provided by Kellogg was modified to M/s Haldor Topsoe A/S (HTAS) outlet system. This lowered pressure drop by 39 kPa (5.66 psi) and resulted in a higher suction pressure at the synthesis compressor, thereby reducing the steam consumption of the synthesis compressor turbine.

2. New LT Shift Guard

A new LT Shift Guard Reactor has been installed with 10 m^3 (353.15 ft^3) of catalyst. CO slip at the outlet of LT Shift Converter, is lowered to 0.15% compared to the earlier 0.25-0.30%. Lower CO slip has resulted in additional ammonia production due to reduction in consumption of hydrogen in the methanator.

3. Revamp of the CO_2 Removal System to a Modern 2-Stage GV process Layout

Originally, Benfield System was provided as the CO_2 Removal System with design regeneration energy of 4414 KJ/Nm^3 of CO_2 (0.0425 mmBTU/ lb-mole CO_2). In 1993, it was modified to Low-Heat Benfield System by employing a multistage flash tank and steam ejectors with design regeneration energy of 4012 KJ/Nm^3 of CO_2 (0.0387 mmBTU/lb-mole CO_2).

For further reduction of energy consumption, a revamp of the CO_2 removal system to a 2-Stage GV Process Layout was the best available option in the existing system, as it did not involve much modification.

The main features of a 2-Stage M/s Giammarco Vetrocoke (GV) Italy, Process are the operation of the two strippers at different pressures, i.e. one at high pressure (107.9 kPa i.e.15.65 psig) and the other at low pressure (13.7 kPa i.e. 1.99 psig) using the same Benfield solution with activator ACT-1. Rich CO_2 loaded solution is introduced to both HP & LP Strippers and semi-lean and lean solution from HP stripper passes to LP Stripper before going to respective circulation pump suctions. In order to compress, the CO_2 generated from the LP Stripper, a blower has been provided. Packing of the absorber bottom bed was replaced with Intalox Metal Tower Packing – 40 mm (IMTP 40) and the discharged packing (Hy-Pak No.2) was utilized to replace the bottom of HP Stripper. The above modification has enabled to achieve the lower CO_2 regeneration energy with higher purity.

4. Installation of S-50 radial flow synthesis converter and MP Boiler

In Phulpur-I, The original design Ammonia concentration at the outlet of the synthesis converter was only 15.5 % whereas the new generation plants are designed with ammonia concentration as high as 24 %. In order to increase ammonia conversion, a new S-50 converter with a lower heat exchanger and internal electrical start-up heater was installed down-stream of existing ammonia Synthesis converter. As a result ammonia conversion per pass has increased and the Gas circulation in the synthesis loop has decreased, thereby reducing the overall steam consumption of the synthesis compressor turbine. A new MP Boiler has been installed down-stream of S-50 converter to recover heat and produce medium pressure steam to optimize the overall steam balance of the plant.

5. Drying of make-up gas and synthesis loop re-piping

It was observed that refrigeration load in Ammonia-I was very high in comparison to that of Ammonia-II due to high circulation rate in the synthesis loop. The piping around the synthesis compressor recycle was rearranged in such a manner that ammonia present in the converter effluent got condensed and separated before going to recycle stage of the compressor. This system had a disadvantage because oxides of carbon present in the make-up gas were

Topsoe, Inc. – EX1003
Page 1105 of 1210

getting fed to synthesis converter directly. After loop re-piping work, a new kick back cooler was installed at the discharge of synthesis compressor, as the existing water cooler was not being used to cool kick back gases.

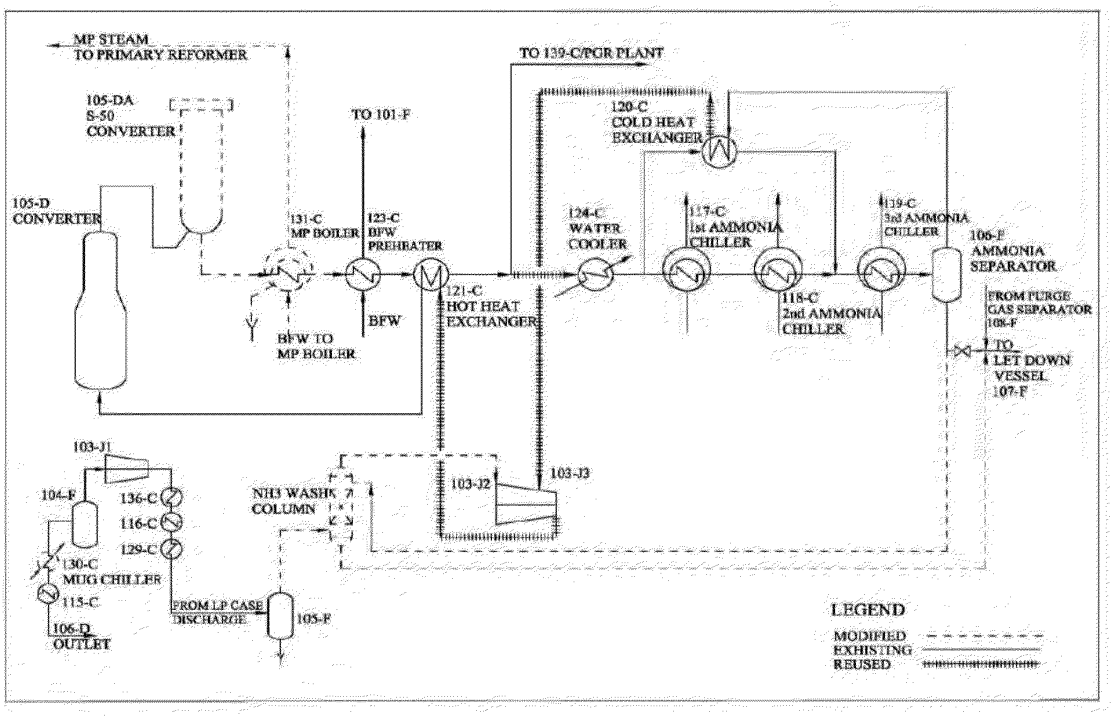
In order to send oxide-free make-up gas directly to the converter, an ammonia wash unit has been installed between LP & HP case of the synthesis compressor. The make-up gas is being washed with ammonia stream from the ammonia separator to remove the oxides. Installation of ammonia wash unit and synthesis loop re-piping has reduced the circulation rate thereby reducing the power consumption in the synthesis compressor.

6. Synthesis gas compressor LP and HP case internal replacement

The original compressor is of mid-1970 design and the operating conditions have changed largely after the synthesis converter retrofit in which Kellogg design 4-bed axial flow quench type reactor was modified to Casale design axial-radial flow reactor. Moreover, after the installation of S-50 converter and loop re-piping, operating condition, particularly circulation rate, was expected to change drastically and would have decreased the operating pressure of the synthesis loop. The new internals of LP and HP case were designed to meet the new operating condition and with better efficiency. The combined efforts of matching the system and operating conditions, and the improvement in efficiency led to less steam consumption in the synthesis compressor turbine.

7. Installation of Final Gas Chiller

After the installation of S-50 converter and ammonia wash unit, synthesis and ammonia wash unit, synthesis converter effluent gas is being cooled and chilled successively in three ammonia chillers. Due to higher loop pressure and higher ammonia concentration, vapour generated in the first chiller, which is operated at a pressure corresponding to 3rd stage suction of regeneration compressor, will be high.



Schematic Diagram of modified back-end of the ammonia plant Phulpur-I

Topsoe, Inc. – EX1003
Page 1106 of 1210

This would have caused improper distribution of ammonia vapor among the different stages of the refrigeration compressor, which would have resulted in operation very close to the surge limit, even with a small kickback flow.

Adding load on the 1st stage and subsequent stages of the refrigeration compressor will improve its operation and reduce the wastage of power by the kickback flow.

With the intention to increase load on the 1st stage of the refrigeration compressor, a final gas chiller has been introduced to cool down the make-up gas to 6 °C (42.8 °F). This increased volumetric efficiency due to lower inlet temperature of make-up gas has led to reduction in steam consumption in the synthesis gas compressor for the same work output.



Ammonia -I plant Energy Saving Project Scheme: S-50Converter and MP Boiler



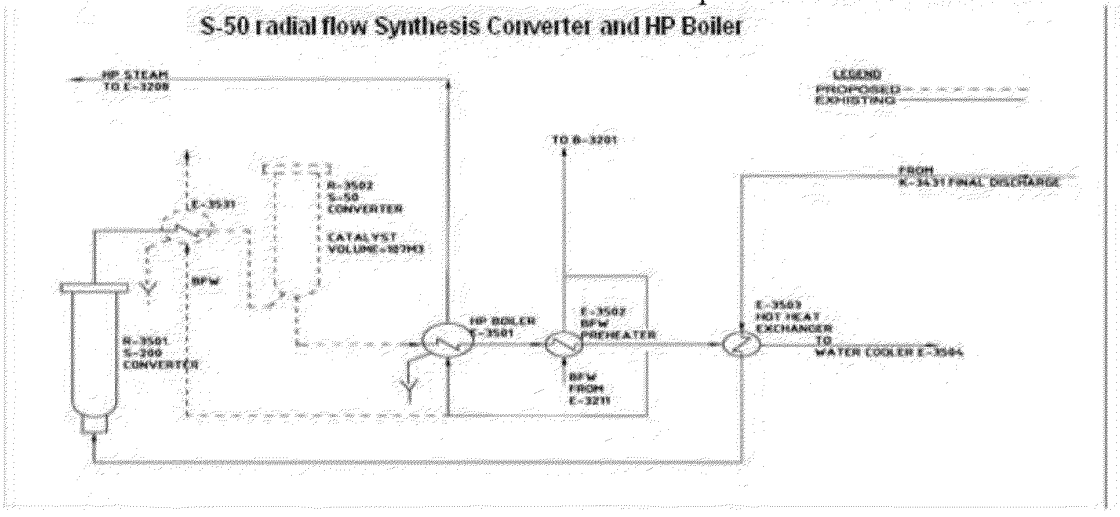
Ammonia-I plant Energy Saving Project Scheme: Dehydrator Column

Phulpur-II

1. Installation of S-50 Radial Flow Synthesis Converter and HP Boiler

For energy reduction in the ammonia synthesis loop, installation of a M/s Haldor Topsoe A/S (HTAS) S-50 ammonia synthesis converter and a new HP-WHB was found to be the most beneficial option. The S-50 converter and New HP boiler have been located in series in between the existing converter and existing HP synloop boiler. The S-50 converter increased the conversion and reduced the circulation rate, thereby reducing the pressure drop in the loop. Furthermore, to make an optimum overall steam balance, high pressure steam is being generated from the waste heat boiler to control the inlet temperature to the new converter.

S-50 radial flow Synthesis Converter and HP Boiler



Topsoe, Inc. – EX1003
Page 1107 of 1210

2. New LT Shift Guard and BFW Preheater

The purpose of installing a LT Shift Guard before the LT Shift Reactor was to reduce CO slippage from shift section on a consistent basis without increasing the pressure drop. A new BFW preheater was installed at down stream of new LT shift Guard to control the inlet temperature of the LT Shift Reactor and to recover the exothermic heat of reaction. After its installation, CO slip from LT Shift Converter has come down from 0.20% to 0.12%.

3. Installation of Final Gas Chiller

In the earlier system, make-up gas was being cooled to 35 °C (95 °F) before being compressed in the synthesis gas compressor. The final gas chiller will be introduced to cool down the make-up gas to 6 °C (42.6 °F) from the present level of 35 °C. This will increase the volumetric efficiency due to lower inlet temperature of make-up gas leading to a reduction in steam consumption in the synthesis gas compressor for the same work output.

Schemes installed at Kalol Plant apart from the schemes installed at Phulpur plant are as follows:

Sl. No.	Description
1.0	Revamp of CO_2 Removal System to a 2-stage a-MDEA system.
2.0	Revamp of Synthesis Gas Compressor
3.0	Condensing mode operation of ID Fan Turbine and reduction in Steam/Carbon ratio to the reformer.
4.0	Installation of new BFW Coil in convection section of Primary Reformer

Schemes installed in Aonla Unit to reduce energy consumption other than the schemes installed at Phulpur Unit are as follows:

Sl. No.	Description
	Aonla - I
1.0	Revamp of CO_2 Removal System
2.0	Replacement of Cooling Water Pump Turbine and GV Booster Pump Turbine to Motor.
	Aonla –II
1.0	Replacement of Cooling Water Pump Turbine and GV Booster Pump Turbine to Motor.
2.0	Additional Process Condensate Exchanger
3.0	New Combustion Air Module



Ammonia-II plant Energy Saving Project Scheme: S-50 Converter and HP Boiler



Energy Saving Project Kalol : Two Stage aMDEA CO2 Removal System

Topsoe, Inc. – EX1003
Page 1108 of 1210

Benefits achieved from Energy Saving Project: As a result of Energy Saving, steam consumption in both Ammonia plant has reduced which in turn has saved costly fuel. The Investment made in the Project of 36 million USD has a pay-back of 4 years. Additional advantage of installing S-50 Converter has been in terms of extra capacity availability in back-end of Ammonia plants. This margin has been appropriately utilized in Capacity Enhancement Project.

B) Re-gasified Liquefied Natural Gas (RLNG) Conversion at IFFCO-Phulpur

IFFCO-Phulpur initiated the task of executing RLNG conversion along with Energy Saving Project. As the availability of indigenous natural gas was limited, the only possible alternative was to go for RLNG which was to be sourced from outside and made available to Phulpur as per the requirement. IFFCO held discussions with the concerned parties and finally an agreement was reached between M/s Gas Authority of India Ltd. (GAIL) and IFFCO on August 25, 2004. A separate 140 km pipeline was laid from Thulendi of District RaiBarelly to the Phulpur Unit from the existing HBJ gas pipeline.

Important Technical Aspects in RLNG Conversion

The most significant differences between naphtha and natural gas based ammonia plants are in the desulphurization section. Since natural gas does not contain much sulphur, unlike naphtha, hence a pre-desulphurization section need not be operated. Other important aspect is in the ratio of hydrogen to carbon ratio, which is high in case of gas. As a result, less steam is consumed in the reforming section and less CO_2 is generated. After the reforming section, plants operating on naphtha or gas are identical except in the quantity of generated CO_2.

Major technical aspects that have to be looked into are:

a) To allow operation on RLNG, the main equipment / section which required addition or modification in existing sections were catalyst for the desulphuriser and the Primary Reformer, burners and their control systems, Convection zone Coils, ID & FD Fans capacities, Gas Turbine & CO_2 removal system.

b) Since the carbon content in RLNG feed is less compared to Naphtha, CO_2 production would also be less. Conversion of all ammonia into urea was desired, so modifications would be needed to re-balance the CO2 production with the ammonia production.

c) To provide flexibility in operation during any eventual shortage of RLNG, the new / modified equipment shall be designed to handle either 100 percent Naphtha or 100 percent RLNG or any mixture there-of.

d) As the conversion required additional equipment, layout of new equipment posed challenges in the case of the old naphtha based plant where space is a major constraint. Maintaining 100 % Naphtha facilities along with new RLNG facilities was going to be very difficult.

e) New generation Naphtha based plants generally include a pre-reformer as an additional feature. For smooth operation with Mixed Feed, plants having Pre-reformers may be chosen for implementing Mixed Feed operation facilities ranging from zero to 100 % percent of Naphtha

f) For RLNG Conversion of a FO Fired Boiler, the performance of the economizer & superheater needs to be examined, as they may be affected due to a change in flue gas composition. This

Topsoe, Inc. – EX1003
Page 1109 of 1210

could result in higher tube metal temperature for the superheater coils and thereby lower capacity of the boiler itself.

Necessary modifications have been carried out in the following areas for RLNG Conversion Job:

- Ammonia-I Plant: Complete Feed System and Complete Fuel System.
- Ammonia –II Plant: Feed System and Complete Fuel System with provision for using100% Feed on naphtha.
- Boiler-4: RLNG Modification with provision for 100% FO firing system.
- Boiler-1, 2 & 3: Support fuel on RLNG in place of FO and usage of coal to continue as main fuel.

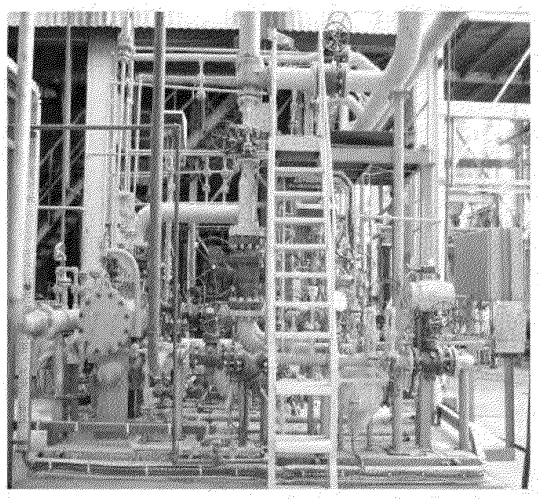
After finalizing the road map for RLNG conversion, M/s Haldor Topsoe A/S (HTAS) Denmark, was awarded the responsibility of basic engineering for RLNG conversion along with energy saving projects for Ammonia Plants. M/s PDIL was engaged for the detailed engineering, procurement and M/s Thermax Babcock & Wilcox (TBW) Pune, India was awarded the contract for Boiler modification ,engineering and supply of all related items of burners and gas stations.

Modifications / Jobs carried out

A gas receiving and metering station to supply the gas to IFFCO-Phulpur was installed and is being operated by GAIL (India) Ltd. The gas metering station has the required facilities of metering, filtration, gas chromatograph for composition analysis and Gross Calorific Value (GCV) / Net Calorific Value (NCV) determination, pressure regulation, etc. A common header has been laid from metering station to ammonia-I, ammonia-II and boilers. Additional structural and pipe racks were provided for the gas and utility pipelines.

Ammonia-I: Major modifications are listed below-

- Burners and Fuel Control Station: All liquid fuel burners; 162 top arch, 9 tunnel burners, 4 hydrocarbon preheater and 5 auxiliary boiler burners were replaced with new RLNG burners of John Zink.
- A New RLNG Coil and RLNG preheater coil was installed in between the LT superheater and the combustion air preheater.
- Primary Reformer Catalyst: New gas reforming catalyst, supplied by M/s Sud-chemie was loaded in primary reformer tubes.
- DCS & ESDS System: Control logic, emergency shut down system and annunciation system were modified as per the requirement.
- Pre-Desulphurization Section: This section decommissioned and kept idle.



RLNG Control station in Amm.-1 plant

Ammonia-II: Major modifications are listed below-

- Pre-desulphurization section has been retained for operation with naphtha in case of RLNG shortage.
- Installation of new RLNG Coils: Two

Topsoe, Inc. – EX1003
Page 1110 of 1210

RLNG heating coils have been installed in the waste heat section of primary reformer.

- Modification of Primary reformer Burners: All existing 576 burners were modified by replacing air mixing nozzle and gas nozzle of the burners with suitable dimensions which were fabricated in the workshop.
- Fuel system for GT including Skid, Nozzle and Control System: Necessary modification in fuel nozzles and combustion chamber liners were carried out. A new fuel skid along with control and safety system was installed.
- Modification in Heat Recovery Unit (HRU) Burners and its Control system: Naphtha burners were modified to dual firing burners with facilities of on-line change over.
- RLNG Fuel Preheater: RLNG is supplied at battery limit at 3923 kPa (569 psig) pressure let down station and a fuel preheater has been installed. The old naphtha vaporizer has been modified and is being used as fuel preheater.
- DCS and ESD Modification: DCS control system has been modified to handle either 100% naphtha and 100% RLNG or any mixture thereof with on-line switch-over facility.

Steam Generation Plant: It was decided that the Coal fired boilers-1, 2 & 3 would continue to operate on Coal as main fuel, however, the support fuel would be changed from FO to RLNG. Boiler-4, originally on FO firing was to be modified to have dual firing facility of FO as well as RLNG.

Boilers-1, 2 & 3: These are corner fired boilers with inclining (tilt) arrangement. Previously, FO was used as support fuel to support Coal firing. New RLNG burners have been installed along with igniters and scanners.

Boiler-4: Dual fuel burners suitable for 100% FO or 100 % gas or combination of both, were installed. Modification in the boiler front panel to accommodate the new burners was carried out. The newly installed burners have igniters and scanners. Wind box, air duct, and atomizing valves were modified. A new fuel control station, new burner management system and block/bleed arrangement for safety have also been provided.

Benefits after RLNG Conversion: Natural gas is the ideal feedstock for ammonia production. It has several advantages besides being cheaper and easy to handle. Now there is an easy and shorter start-up of the plant, thereby reducing unproductive consumption. The reformer burners' choking phenomena is completely solved and CO_2 emission from the furnace has been reduced. The loading in CO_2 section has been reduced, therby giving extra margin in the front-end of Ammonia plant The plant also runs trouble free and the catalyst life has also increased. The savings due to switching over from costly Naphtha and FO to RLNG on annual basis is 240 million USD.

C) Carbon Dioxide Recovery (CDR) Plant

The major disadvantage of RLNG conversion is less CO_2 production due to lower C/H ratio in RLNG as compared to naphtha. The CO_2 generated with lean RLNG is not adequate to convert all ammonia produced to urea. To overcome the problem, the possible options are as follows:

a. Use of costlier fuel i.e. naphtha along with RLNG in feed to the extent necessary to offset the CO_2 deficit required for total conversion of ammonia to urea.
b. Recycle of synthesis gas to the primary reformer as fuel which has the following bottlenecks.
    - Recycle of synthesis gas to the primary reformer as fuel would strain the front end. The reforming section, CO_2 removal section etc. which may not be designed to handle the required increased load.

Topsoe, Inc. – EX1003
Page 1111 of 1210

- Recycle capacity may not be sufficient to satisfy the total CO_2 deficit, thus requiring front end modification and incurring capital expenditure
- Using the existing additional front end capacity for recycling synthesis gas may be less economical than making additional ammonia and urea and getting benefits under new policy.

c. Recovery of CO2 from flue gas from various furnaces.

Among all the above options available, CO_2 recovery from flue gases was found most economical and viable. Therefore IFFCO-Phulpur has installed a Carbon Dioxide Recovery (CDR) Plant to recover CO_2 from flue gases of Ammonia-II plant primary reformer furnace.

Similarly at the Aonla Unit, the feed stock for the ammonia plant since inception was natural gas. There also, in order to meet CO_2 deficit, naphtha along with gas was fed to the primary reformer in Ammonia-I Plant. To meet the CO_2 deficit with 100% Gas operation, a CDR plant has been installed to recover CO_2 from the flue gases of Ammonia-I plant primary reformer furnace.

The capacity of the plant in both the units at Phulpur and Aonla is 450 MTPD of CO2 and M/s Mitsubishi Heavy Industries Ltd. (MHI) Japan, has provided the basic engineering for it. M/s Tecnimont ICB Pvt. Ltd. (TICB) Mumbai India, was engaged as turnkey contractor for detailed engineering, procurement, erection and commissioning. The use of naphtha in the feed for ammonia plant is going to be completely stopped as the shortfall quantity of CO_2 is being made available by recovery of CO_2 from flue gases of the primary reformer. This is going to save the Government Subsidy outgo substantially and would also reduce the emission of Green House Gases (GHG) to the atmosphere thereby providing cleaner environment.

The CDR plant is basically a low pressure CO_2 removal section in which CO_2 present in flue gases is absorbed and then regenerated to produce CO_2 having 99.93 % purity. CO_2 recovery from flue gases is a new concept in fertilizer industries.

Basic steps involved in CDR plant are:

a) Flue gas Pretreatment,
b) Low pressure CO_2 absorption in special solution KS-1,
c) CO_2 regeneration and
d) CO_2 compression to desired level.

Though regeneration energy is very high in comparison to that of any normal CO_2 removal section in ammonia plants, the cost effectiveness of the plant is very attractive because the use of costlier Naphtha as feed to balance the CO_2 for Urea production shall be stopped completely.

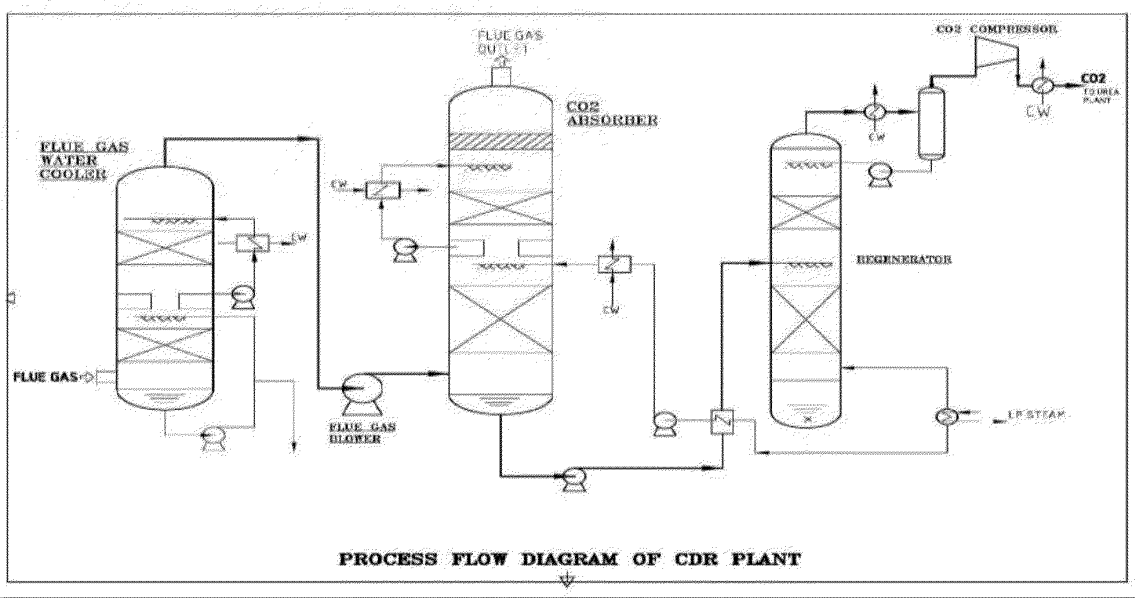
Brief Description of the Process

Flue gas at a temperature of 180 °C (356 °F) is cooled down in a Water Cooler, a packed column using structured packing, by direct contact with water supplied from the top and then compressed in flue gas blower. Compressed flue gas is fed to a CO_2 Absorber.
The CO_2 Absorber is a packed bed column using structured packing and having two sections, bottom for CO2 absorption and top for washing section. In this column, CO_2 is absorbed in a special solution (KS-1) supplied from the top of the absorption section. Flue gas after washing is then exhausted at a sufficient height.

Rich KS-1 solution is regenerated in the regenerator by supplying heat through LP steam (at 42.7 psig pressure) re-boiler. Lean solution from the bottom of the tower is cooled in Lean solution cooler against cooling water and re-circulated back to the CO2 Absorber. Overhead vapour is condensed and separated condensate is returned back to the top of the regenerator.

Topsoe, Inc. – EX1003
Page 1112 of 1210

Sulphur in RLNG fuel being not traceable, there is no contamination in CO_2 product which is compressed and then sent to the Urea Plant.



PROCESS FLOW DIAGRAM OF CDR PLANT

Commissioning Experience

Level of top section of CO2 Absorber

The CO_2 Absorber in CDR plant is divided in 3 section 1st wash section, 2nd wash section and the bottom CO_2 absorber section. Flue gas from flue gas cooler is introduced in the bottom section of the CO_2 absorber through flue gas blower while the CO_2 lean KS-1 solution is introduced from the top of the absorption section onto the packing. Here the CO_2 is absorbed in KS-1 solution. The flue gas then moves upward into the treated flue gas washing section where the flue gas comes in contact with water for washing of amine content in it. At the top of washing section, a chimney tray is provided. The level of each section is maintained by circulation pumps. Overflow of each section comes to the adjacent lower sections.

During initial filling of column with DM water for starting circulation, there was a problem of level build up in top section of the column. Since there was no gas flow, the water was pouring down through the chimney tray and packing to the bottom section of absorber, leading to an increase in level of the bottom section and a decrease in top section. To overcome this problem a 2" line was connected from the discharge of the rich solution pump to the suction of 1st wash water circulation pump.

Low flow through Flue Gas Blower

During the start of the plant, the desired flow of flue gas from flue gas blower was not obtained at full opening of dampener provided at the inlet of blower. Although the indication at DCS was showing 100% full opening, it was found in the field that dampener was stuck at 90% opening, resulting in restriction of flow through blower. The dampener was opened and the problem was rectified.

Final Shut-down Valve in CO2 Line

Final Shut-down Valve (USV-01) is installed in CO_2 product line connected to main CO_2 header, which is closed in case the CO_2 blower is not in

Topsoe, Inc. – EX1003
Page 1113 of 1210

operation. Due to this, the CO_2 blower was kept running even if it was not required at lower plant load. Now the closing of USV- 01 is connected to the flue gas blower trip and now the plant can be run without the CO2 blower running.

Steam Flow Measurement
During commissioning of the plant, the reboiler temperature was going high, although the steam flow indication was well within limits. The steam flow meter was checked and it was found that the tube connected to LP tapping was blocked partially with foreign particles. The tube was cleaned and thereafter the steam flow was OK.

Tripping of Condensate Pump (P-3710)
During commissioning of plant the steam condensate pump was tripping frequently on low suction pressure. The suction line was checked and it was found badly choked with the scaffolding clamps. The line was cleaned and again connected to pump suction. Since then it has been running normally.

Temperature Control of LP steam for reboiler
LP steam to the CDR plant is available at 294.2 kPa pressure (42.7 psig) and 240 °C (464 °F). Before being introduced to the reboiler, this steam is brought down to 194.2 kPa (28.2 psig) pressure and 133 °C (271.4 °F) temp. by pressure let down and desuperheating. For quenching, steam condensate from the reboiler was used which was cooled to 70 °C (158 °F) from 133 °C (271.4 °F) in a plate type cooler. However, the temperature of the steam was higher than required during commissioning of the plant which is not at all recommended due to KS-1 solution degradation at temperatures higher than 135 °C (275 °F). It was found that the temperature of condensate for quenching was higher, resulting in high temperature steam to the reboiler. The system was modified to use a separate Demineralized (DM) water line which is at around 40 °C (104 °F) at the inlet to the cooler, is connected with the condensate line to get the specified temperature of steam.



The Carbon Dioxide Recovery plant: A view of all three towers

Reduction in CO_2 Emissions after Implementation of Energy Saving Project, RLNG Changeover and CDR plant

Reduction in Steam Consumption through Revamping of Ammonia Plant:

After implementation of schemes under the Energy Saving Project, reduction in HP steam consumption to a tune of 35 MT/hr in Ammonia Plants at Phulpur alone has been achieved, which has resulted in lesser firing of Coal and Fuel Oil in Steam generation facilities, thereby CO_2 generation from these furnaces has reduced to a great extent.

Fuel Switchover from Naphtha / FO to Natural Gas in Furnaces:

On burning gas in place of Naphtha, Fuel oil in furnaces CO_2 emissions are much less since these fuels contains higher carbon content than natural gas.

Topsoe, Inc. – EX1003
Page 1114 of 1210

Feed Switchover from Naphtha to Natural Gas in Ammonia Plants

Naphtha, being rich in carbon, produces more carbon dioxide than required for Urea production. This excess CO_2 is being vented to the atmosphere. At IFFCO Phulpur unit, feed switchover from naphtha to NG was carried out. NG being lower in carbon, produces less carbon dioxide thereby venting of CO_2 has been eliminated.

Installation of CDR Plant

With natural gas as feedstock, less CO_2 is generated than required for Urea production. This requires use of additional naphtha / natural gas as feed stock.

In Ammonia -II plant, flue gases from the Primary Reformer furnace contain sufficient, recoverable CO_2 to meet the requirement of CO_2 for Urea production. Being impure, hot and corrosive, it is not possible to use this CO_2 directly in the Urea plant. Therefore, a Carbon Dioxide Recovery plant was installed to recover CO_2 from flue gases, which was previously going to the atmosphere.

The annual reduction in CO_2 Emission for all IFFCO Projects is estimated to be more than 0.9 million tons.

Future Action Plan

Presently the demand of Urea is met by imports which are very costly. Keeping this in view, IFFCO is going ahead with the Capacity Enhancement Projects (CEP) at Phulpur and Aonla to bridge the gap to some extent in demand of Urea by Indian farmers. The following capacities are being aimed in the project:

Plant	Present Ammonia / Urea Capacity	Enhanced Ammonia / Urea Capacity
Phulpur–I Plant	970 / 1670 MTPD	1215 / 2115 MTPD
Phulpur–II Plant	1520 / 2620 MTPD	1740 / 3030 MTPD
Aonla –I Plant	1520 / 2620 MTPD	1740 / 3030 MTPD
Aonla–II Plant	1520 / 2620 MTPD	1740 / 3030 MTPD

This will enable an additional Urea production of 553,000 MT on yearly basis. It may be noted here that the expenditure involved in increasing the capacity of existing plants by debottlenecking works out to be around one-fourth that of installing a grass root plant, besides saving significant subsidy of the government by cutting down costly imports.

Various jobs have been identified in different plants with the help of consultants and in-house studies. Some of the main schemes in Ammonia Plant are: Modifications in Air and Synthesis Compressors and their turbines, replacement of exchangers, including the methanator effluent cooler, Secondary Reformer burner modification, one additional cooling water cell, etc. Major jobs identified in the Urea plants: CO_2 Compressor replacement, additional HP Ammonia and HP Carbamate Pumps, MP Pre-decomposer, Prill Cooling System, additional Ammonia Condenser & Preheater and an additional Cooling Tower Cell.
Engineering and commercial activities for procurement have been completed. The Prill Cooling System has already been installed and commissioned in Phulpur Urea-I Plant. Most of the above activities shall be completed in the year 2007.

Topsoe, Inc. – EX1003
Page 1115 of 1210

Conclusion

The business of indigenous Urea manufacturing is a very important industry for food security and national pride. Today it is facing stiff challenges from many quarters, like high input cost, delay in late disbursement of subsidy, etc. However, if the fertilizer industry works in a positive frame of mind and the Government brings out encouraging policies, suitable strategies can emerge in meeting these challenges. IFFCO has taken all the required actions in the right direction to overcome these challenges. It has been the first fertilizer plant to have switched over to RLNG from liquid hydrocarbons, implemented Energy Saving projects and Carbon dioxide recovery Plant Project. Also, the Capacity Enhancement Project is under way. All these steps have resulted in more fertilizer at a cheaper price than the imported Urea price, which is the real need of the country at this juncture.

Topsoe, Inc. – EX1003
Page 1116 of 1210

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Filing Date	2023-04-26
First Named Inventor	Francesco Baratto
Art Unit	3991
Examiner Name	JEAN C WITZ
Attorney Docket Number	283386WOUS02_495230-102

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	2	102381717	CN	A	2012-03-21	PETROCHINA COMPANY LIMITED		☐
	3	102502702	CN	A	2012-06-20	PETROCHINA COMPANY LIMITED; CHINA HUANQIU CONTRACT		☐
	4	102533365	CN	A	2012-07-04	AEROSPACE CHANGZHENG ENGINEERING CO.,LTD.		☐
	5	103303863	CN	A	2013-09-18	HUANG JIAHU		☐
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	2	Nitrogen + Syngas Conference in Athens, Number 315, January - February 2012, 40 pages	☐
	3	Complaint: Topsoe, Inc. vs. Casale US, Inc. and Casale SA. Case No.: 3-24-cv-00033, January 31, 2024, 54 pages	☐
	4	First Amended Complaint: Topsoe, Inc. vs. Casale US, Inc. and Casale SA. Case No.: 3-24-cv-00033. Document 28, May 2, 2024, 43 pages	☐
	5	RAJASHEKHARIAH , et al., "Experience of Energy Saving and Naphtha to Gas Conversion Projects and IFFCO", Ammonia Technical Manual, 2007, pp. 57-72	☐
	6	Noelker, et al. "Autothermal Reforming: A Flexible Syngas Route with Future Potential" Preprints of Nitrogen + Syngas 2010 International Conference in Bahrain, February 28, 2010 - March 3, 2010, pp. 1-19	☐

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4. A record in this system of records may be disclosed, as a routine use, to a contractor of the Agency having need for the information in order to perform a contract. Recipients of information shall be required to comply with the requirements of the Privacy Act of 1974, as amended, pursuant to 5 U.S.C. 552a(m).

5. A record related to an International Application filed under the Patent Cooperation Treaty in this system of records may be disclosed, as a routine use, to the International Bureau of the World Intellectual Property Organization, pursuant to the Patent Cooperation Treaty.

6. A record in this system of records may be disclosed, as a routine use, to another federal agency for purposes of National Security review (35 U.S.C. 181) and for review pursuant to the Atomic Energy Act (42 U.S.C. 218(c)).

7. A record from this system of records may be disclosed, as a routine use, to the Administrator, General Services, or his/her designee, during an inspection of records conducted by GSA as part of that agency's responsibility to recommend improvements in records management practices and programs, under authority of 44 U.S.C. 2904 and 2906. Such disclosure shall be made in accordance with the GSA regulations governing inspection of records for this purpose, and any other relevant (i.e., GSA or Commerce) directive. Such disclosure shall not be used to make determinations about individuals.

8. A record from this system of records may be disclosed, as a routine use, to the public after either publication of the application pursuant to 35 U.S.C. 122(b) or issuance of a patent pursuant to 35 U.S.C. 151. Further, a record may be disclosed, subject to the limitations of 37 CFR 1.14, as a routine use, to the public if the record was filed in an application which became abandoned or in which the proceedings were terminated and which application is referenced by either a published application, an application open to public inspections or an issued patent.

9. A record from this system of records may be disclosed, as a routine use, to a Federal, State, or local law enforcement agency, if the USPTO becomes aware of a violation or potential violation of law or regulation.

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Remarks:
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(54) A METHOD FOR MODERNIZING THE SYNTHESIS LOOP OF AN AMMONIA PLANT

(57) A method for modernizing an ammonia synthesis loop (1) with a first converter (10) and a second converter (11) in series, the first converter (10) comprises a cartridge with one or more catalyst beds, the second converter (11) comprises a catalyst bed in direct contact with said vessel, the method comprising the steps of removing the second converter, boosting the first converter by replacing the cartridge with a new cartridge comprising an isothermal catalyst bed, and reducing the concentration of inerts in said first converter.

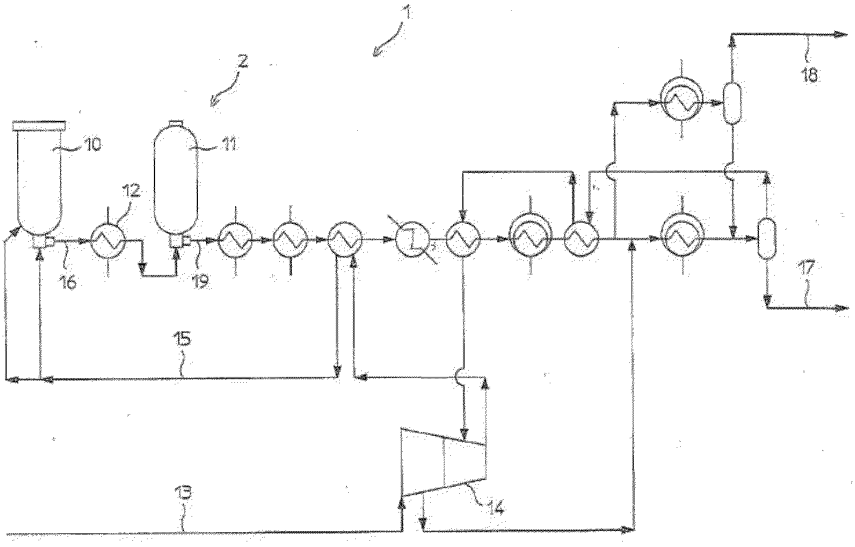


Fig.1

EP 3 067 318 A1

Description

Field of the invention

[0001] The present invention relates to the revamping of ammonia plants. More in detail, the invention relates to a method for revamping an ammonia plant where the ammonia synthesis loop comprises a converter system with a first converter and a second converter, the second converter being adiabatic and operating at a high temperature.

Prior Art

[0002] A prior art layout of the synthesis loop of an ammonia plant comprises a converter system with two converters in series. The first converter receives the fresh ammonia make-up syngas and comprises an internal cartridge containing one or more catalytic beds, possibly with interbed heat exchangers. The second converter is a much simpler and low cost adiabatic unit, where the catalytic bed is in direct contact with the pressure vessel.

[0003] For example, the first converter comprises a cartridge with two radial-flow catalyst beds and an interbed heat exchanger. The second converter is a pressure vessel containing one catalyst bed enclosed in flow panels mounted directly on the inside wall of the vessel, with no cartridge.

[0004] A heat exchanger such as a steam superheater is provided between the first and the second converter. The product stream delivered by the first converter is cooled by said heat exchanger, before entering the second converter. Hence, the working temperature of the second converter is controlled mainly by said heat exchanger, and is typically around 350 - 500 °C.

[0005] The mass of catalyst of the second converter is comparable to the mass of catalyst of the first converter, which means that the second converter may contain around 50% of the total catalyst of the loop.

[0006] Adding the second converter is considered an attractive way to boost the capacity of the loop, and decrease the energy consumption. An example is the S-250 system currently available from Haldor Topsøe. In the past years, some plants have been revamped by adding a second converter to the loop, in accordance with the above.

[0007] There are however some drawbacks. The design of the first converter allows adequate cooling of the shell of the pressure vessel, e.g. by circulating the fresh feed syngas, before entering the converter cartridge, in an annular space around the cartridge. The very simple design of the second converter, however, does not allow any effective cooling of the shell. The lack of a shell cooling medium causes the pressure vessel of the second converter to operate constantly at about the same temperature of the catalyst bed, which means over 350 °C and in some cases close to 500 °C. The combination of high pressure, high temperature and corrosive environment causes a severe stress to the pressure vessel. In particular, it has been noted that under these conditions the pressure vessel is much more exposed to corrosion due to attack of hydrogen and ammonia. Hydrogen and ammonia corrosion causes brittleness of the steel of the vessel and may lead to formation of stress cracks, especially in weak points such as weldings, and/or in points of the shell where some residual stress is found.

[0008] In some cases, serious damages have been observed in the second reactor after some years to an extent that the second reactor was shut down to avoid explosion. In other words, the experience shows that the above layout has a risk of failure of the second reactor.

Summary of the invention

[0009] The aim of the invention is to provide an effective way of modernizing an ammonia synthesis loop of the above disclosed type, in order to avoid the risk of failure of the second reactor.

[0010] This aim is reached with a method for modernizing the ammonia synthesis loop of an ammonia plant, wherein:

- said loop comprises a converter system with at least a first converter and a second converter in series, the second converter receiving a process stream from the first converter,
- said first converter comprises a cartridge with one or more catalyst beds,
- said second converter comprises a pressure vessel and a catalyst bed enclosed in flow distributors associated directly to said vessel,
- a purge rate containing inert gases is taken from the synthesis loop,

the method being characterized in that:

- said second converter is by-passed or removed from the loop;
- the first converter is revamped by at least the step of replacing said cartridge with a new cartridge comprising an isothermal catalyst bed, and
- the purge rate of the loop is increased.

[0011] The invention is based on the very unexpected finding that the combined effect of boosting the first converter with said cartridge comprising an isothermal catalyst bed, and of increasing the inerts purge from the loop, allows the first reactor alone to give substantially the same conversion rate of the former scheme with two reactors. This was surprising because - as stated above - the second reactor hosts a relevant fraction of the cat-

alyst, namely around 50% of the catalyst of the loop.

[0012] The catalyst bed of the second converter is a cartridge-less catalyst bed, for example said catalyst bed is enclosed in flow distribution panels mounted on the inside wall of the pressure vessel of said second converter.

[0013] According to the invention, the original cartridge of the first ammonia converter is replaced with a new cartridge comprising an isothermal catalyst bed. The term of isothermal catalyst bed is used to mean that a heat exchanger is immersed in the catalyst bed, to remove heat and keep the temperature of the bed within a given range. The heat exchanger is fed with a suitable heat exchange medium, e.g. boiling water or any other suitable medium. The heat exchanger may be a tube heat exchanger or plate heat exchanger, according to various embodiments of the invention.

[0014] Preferably, the purge rate is increased by around 30% to 100 %; more preferably by 40% to 80 % or more. The purge rate is preferably increased to obtain a concentration of inerts in the first converter less than 10% molar. The purge rate may consist of one purge stream taken from a suitable point in the ammonia synthesis loop; increase of the purge rate may be achieved by increasing the flow rate of said purge stream or addition of further purge stream(s). The purge stream remove from the loop is preferably send to a unit to recover at least partially the hydrogen contained therein.

[0015] Usually the pressure vessel of the first container can be maintained. If necessary or appropriate, however, the whole converter may be replaced with a new one. The second converter does not need to be physically removed from the loop, it may be sufficient to by-pass it completely.

[0016] The proposed method allows to eliminate the second reactor, which is a source of a possible, dramatic failure of the whole plant, without affecting the performance and, in particular, the concentration of ammonia (% mol) in the product stream at the exit of the synthesis reactor. The method is further advantageous in that the other items of the loop, such as heat exchangers, compressors, etc... need not be modified. In particular, the expensive compression section of the make-up syngas is not affected. The recovery of more hydrogen from the purge stream may involve a little more energy consumption for compression of said hydrogen, this effect being however overcompensated by the advantages of the invention. It should be noted that the invention provides inexpensive and attractive method for making a double-converter ammonia loop more reliable.

[0017] These and still further advantages of the invention will be elucidated with the help of the following description of preferred and non-limiting embodiment.

Brief description of the drawing

[0018] Fig. 1 is a scheme of a known ammonia synthesis loop comprising two ammonia converters.

Detailed description

[0019] Fig. 1 is a scheme of an ammonia synthesis loop such as the S-250 system available from Haldor Topsøe. The ammonia synthesis loop 1 comprises a converter system 2 with a first converter 10 and a second converter 11 in series. A superheater (or other types of gas cooler) 12 is provided on the flow line between the converters.

[0020] The first converter 10 comprises a cartridge with two radial-flow catalyst beds and an interbed heat exchanger. The first converter 10 may be realized e.g. according to one of the embodiments disclosed in US 4181701. The second converter 11 consists of a pressure vessel containing one catalyst bed enclosed in flow panels mounted directly on the inside wall of the vessel.

[0021] The make-up syngas 13 is compressed in inter-refrigerated compression section 14 and is fed to the first converter 10, via line 15. The product gas stream 16 delivered by the first reactor 10 is cooled in the steam superheater 12 and fed to the second reactor 11. The product stream 19 from the second reactor 11 is passed through a series of heat exchanger as shown; the loop delivers a product ammonia stream 17.

[0022] A purge gas stream 18 is removed from the loop in order to avoid accumulation of inerts in the converters. Said purge gas stream 18 may contain hydrogen, nitrogen and a certain amount of inerts, mainly methane and argon. The hydrogen contained in the purge stream 18 is usually recovered in a hydrogen recovery section. It is common that the hydrogen recovery section operates at a lower pressure than the loop, thus requiring a compressor to feed the recovered hydrogen back to the loop itself.

[0023] The temperature of the catalyst bed of the second converter 11 is controlled by the superheater 12 and is usually in the range 350 - 480 °C. Said temperature is also the temperature of the pressure vessel of the converter 11, causing a relevant stress to the vessel, for the above discussed reasons.

[0024] The loop of Fig. 1 is known art and hence it is not described in further details.

[0025] A method for modernizing said ammonia synthesis loop 1 is characterized in that:

said second converter 11 is removed from the loop;

said first converter 10 is revamped by at least the step of replacing said cartridge with a new cartridge comprising an isothermal catalyst bed, and

the purge rate of the loop is increased.

Claims

1. A method for modernizing the ammonia synthesis loop (1) of an ammonia plant, wherein:

- said loop (1) comprises a converter system (2) with at least a first converter (10) and a second converter (11) in series, the second converter receiving a process stream from the first converter,
- said first converter (10) comprises a cartridge with one or more catalyst beds,
- said second converter (11) comprises a pressure vessel and a catalyst bed enclosed in flow distributors associated directly to said vessel,
- a purge rate containing inert gases is taken from the synthesis loop,

the method being **characterized in that**:

- said second converter (11) is removed from the loop;
- the first converter is revamped by at least the step of replacing said cartridge with a new cartridge comprising an isothermal catalyst bed, and
- the purge rate of the loop is increased.

2. A method according to claim 1, said new cartridge comprising an isothermal catalyst bed with a heat exchanger immersed in said bed.

3. A method according to claim 2, said heat exchanger immersed in the bed being a tube or plate heat exchanger.

4. A method according to any of the previous claims, the purge rate containing inerts being increased by at least 30%.

5. A method according to any of the preceding claims, the purge rate containing inerts being increased to obtain a concentration of inerts in the first converter (10) less than 10% molar.

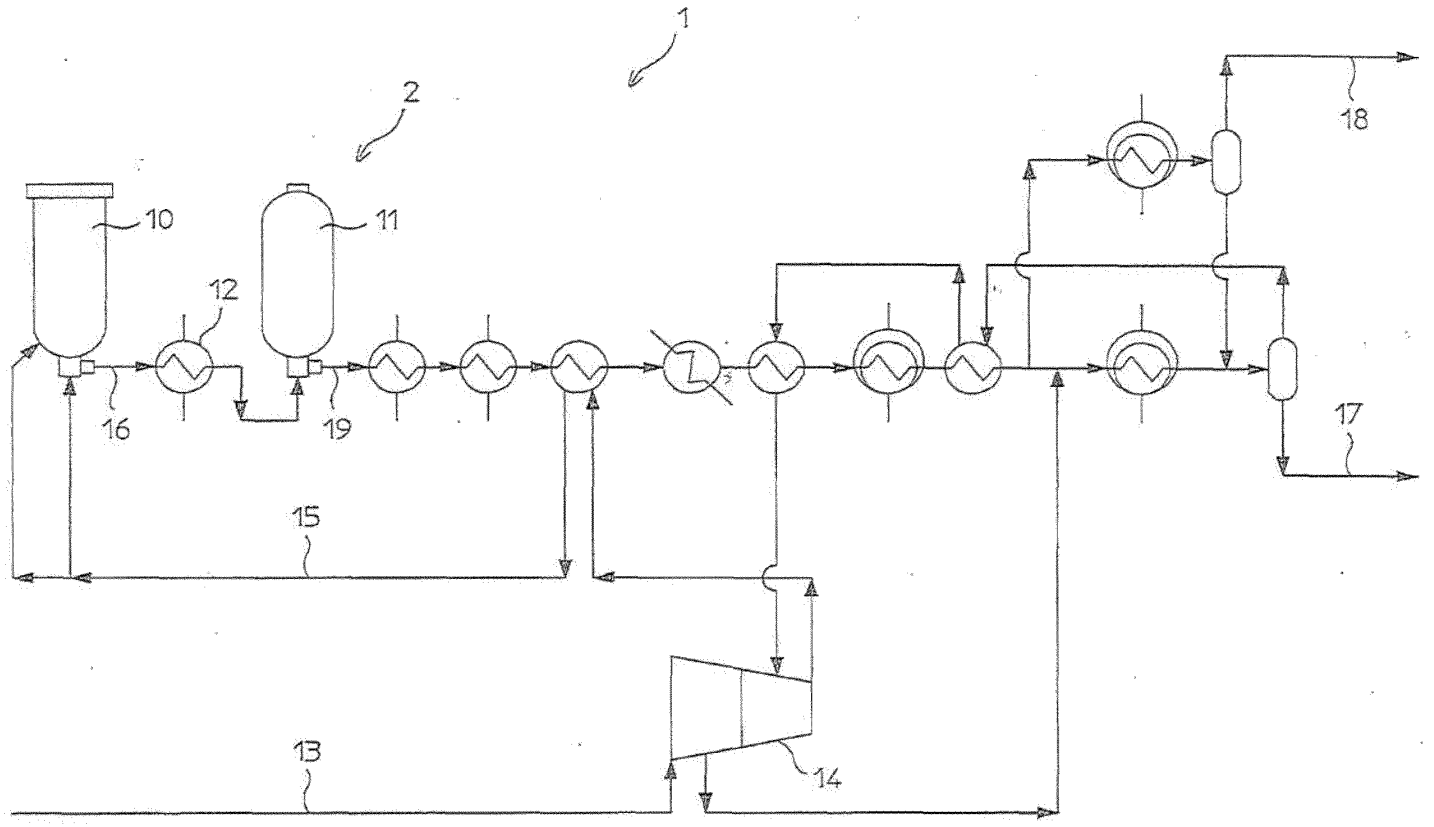


Fig.1

EP 3 067 318 A1

Topsoe, Inc. – EX1003
Page 1126 of 1210

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EUROPEAN SEARCH REPORT

Application Number
EP 16 16 8159

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	EP 0 297 474 A2 (AMMONIA CASALE SA [CH]; ZARDI UMBERTO [CH]) 4 January 1989 (1989-01-04) * the whole document *	1-5	INV. C01C1/04
A	EP 0 994 072 A1 (KELLOGG BROWN & ROOT INC [US]) 19 April 2000 (2000-04-19)	1-5	
A	EP 0 355 259 A1 (SHANNAHAN CORNELIUS E) 28 February 1990 (1990-02-28) * claims 8,9 * * page 2, line 30 - line 45 * * page 5, line 57 - page 6, line 22 *	1-5	
A	"6.4 Synthesis of Ammonia" In: Nielsen A.: "Ammonia Catalysis and Manufacture", 1996, Springer, Berlin, XP002588258, pages 221-251, * pages 221,232 * * page 247 *	1-5	

TECHNICAL FIELDS SEARCHED (IPC)
C01C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	14 July 2016	Gumann, Sina

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 16 16 8159

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14-07-2016

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EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 4181701 A **[0020]**

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.