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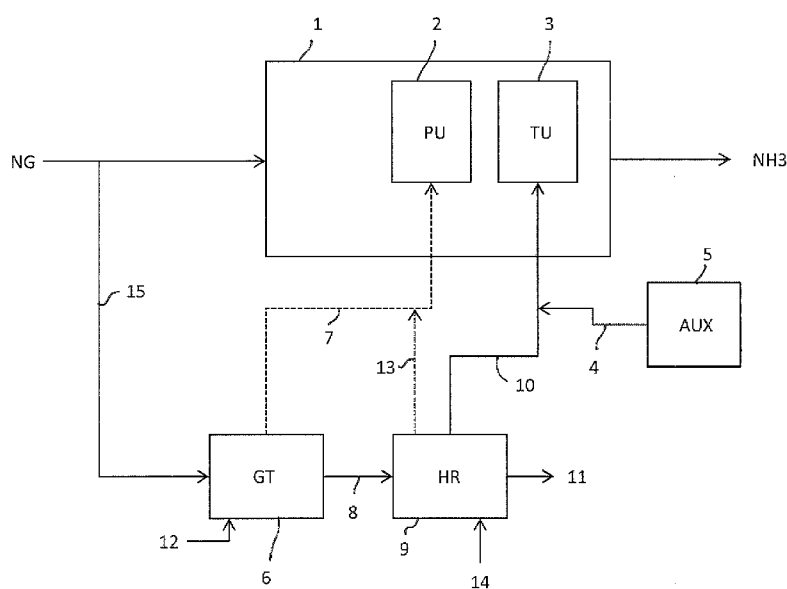
(54) **Title:** PROCESS FOR PRODUCTION OF AMMONIA AND DERIVATIVES, IN PARTICULAR UREA

FIG. 1

(57) **Abstract:** A process for producing ammonia and a derivative of ammonia from a natural gas feed comprising conversion of natural gas into a make-up synthesis gas; synthesis of ammonia; use of said ammonia to produce said derivative of ammonia, wherein a portion of the natural gas feed is used to fuel a gas turbine; power produced by said gas turbine is transferred to at least one power user of the process, such as a compressor; heat is recovered from exhaust gas of said gas turbine, and at least part of said heat is recovered as low-grade heat available at a temperature not greater than 200 °C, to provide process heating to at least one thermal user of the process, such as CO₂ removal unit or absorption chiller; a corresponding plant and method of modernization are also disclosed.

Process for production of ammonia and derivatives, in particular urea

DESCRIPTION

Field of application

The invention concerns a method for producing ammonia and derivatives of
5 ammonia, particularly urea, starting from natural gas. The invention also
discloses a method of modernizing an ammonia-urea plant.

Prior Art

The integrated production of ammonia and derivatives of ammonia is known
in the fertilizer industry. For example the production of ammonia and urea is
10 known.

Ammonia production, usually from a natural gas feed, involves conversion
the natural gas into a synthesis gas in a front-end section and the conversion
of said synthesis gas into ammonia in a synthesis loop. The conversion of the
natural gas feed into synthesis gas usually involves two-stage steam
15 reforming, although autothermal reforming and partial oxidation are feasible
options, followed by purification including shift conversion of CO to CO₂,
removal of CO₂ and optionally methanation. The resulting purified gas is
termed ammonia synthesis gas. A process for producing ammonia synthesis
gas is described for example in EP 2 065 337.

In a so-called ammonia-urea plant, at least part of the synthesized ammonia is reacted with carbon dioxide to produce urea.

A plant for the production of ammonia and its derivatives comprises also a
5 complex steam system including both steam producers and steam users.
The steam producers recover process heat from various process streams, mostly from conversion of the natural gas feed into generation of raw synthesis gas (usually by steam reforming) and from its subsequent purification. The steam users include for example one or more steam
10 turbines to drive equipment such as compressors and pumps.

The main steam users of an ammonia-urea plant are the driving turbines of large gas compressors such as the synthesis gas compressor which raises the pressure of the generated make-up gas to the pressure of the synthesis loop, and other compressors for process air, ammonia, carbon dioxide or
15 natural gas.

The steam system uses typically a Hirn cycle (or superheated steam Rankine cycle) to produce power. Said cycle as applied in ammonia plants however is relatively inefficient, with less than 30% efficiency and typically only 26-27% even for relatively modern and large plants. Hence, less than 30% of the heat
20 used to raise/superheat the steam is converted into mechanical power, with more than 70% lost mainly to air/water cooling in the steam condenser and in other inefficiencies.

A part of the steam produced in the steam system is also used in the reforming process. This fraction of steam is called process steam. A relevant parameter of the reforming process is the steam-to-carbon ratio which is the molar ratio between steam and carbon introduced in the process. Said ratio
5 is normally around 3.

The steam generated by process heat recovery is generally not enough to cover all requirements, and the shortfall is covered in the prior art by inclusion of a gas-fired auxiliary boiler to generate the additional steam required. Said boiler introduces however an additional consumption of natural
10 gas, increasing the overall consumption for a given capacity in terms of ammonia which is synthesized. Said additional consumption is a drawback especially in a location where the natural gas is expensive and/or is available in a limited amount.

Existing and new plants in these areas of high natural gas cost must
15 minimize the consumption of natural gas to be competitive on the global fertilizer market. Moreover, where the total natural gas available for fertilizer production is limited, any reduction in the specific gas consumption of the plant enables a corresponding increase of the fertilizer production capacity.

The main natural gas consumer of a fertilizer complex for the production of a
20 derivative of ammonia, such as urea, is the ammonia plant. Although many efforts have been made to reduce the energy consumption of ammonia plants, the processes available today are not efficient enough, or are too

expensive to operate, where gas costs are high. Even more so, the existing methods for revamping existing ammonia plants are not competitive as they generally address the requirement to increase the capacity of existing units rather than minimizing the gas consumption.

- 5 In recent times, limitations of quantity of natural gas available for the ammonia plants have emerged. Such limited availability may comprise a physical gas shortage due to the reduction of the production of the gas fields, or may be due to commercial and/or economic reasons like running out of the contractual share of gas available to the plant and/or a different scenario of
10 price and demand for natural gas.

Summary of the invention

The problem faced by the invention is to reduce the energy consumption of the above mentioned ammonia plants based on natural gas feed. In particular, a purpose of the invention is to reduce the amount of natural gas
15 which is consumed in gas-fired boilers to generate steam required by the power users such as the gas compressors of the plant.

The idea underlying the invention is to furnish at least part of the power demanded by the large power users, such as gas compressors, by means of a gas turbine. Power produced by the gas turbine can be transferred to the
20 users, typically said compressors, in mechanical form (direct coupling) or in electrical form. Hence, for example, a gas compressor can be mechanically coupled to said gas turbine or driven by an electric motor using electricity

produced by the turbine. At least some of the heat contained in the exhaust of said gas turbine is recovered as a low-grade heat for use in the thermal users of the plant.

Accordingly, the above problem is solved by a process for producing
5 ammonia and a derivative of ammonia from a natural gas feed, according to claim 1.

The process is characterised in that a portion of said natural gas feed is used to fuel a gas turbine; the power produced by said gas turbine is transferred to at least one of the power users involved in the process; heat is recovered
10 from exhaust gas of said gas turbine; at least part of said heat is recovered as low-grade heat to provide process heating to at least one of the thermal users involved in the process.

The term of low-grade heat denotes heat which is made available to the thermal users at a temperature of 200 °C or less. According to the invention,
15 said low grade heat is recovered by means of a suitable heat exchange medium which is indirectly heated by the exhaust gas to a temperature which is not greater than 200 °C. Said heat exchange medium may be, for example, water which is heated or partially or completely evaporated.

The term of gas turbine denotes an internal combustion engine which
20 operates according to the Brayton Cycle and includes at least a compressor, a burner and an expansion turbine.

The term of low-grade heat denotes that said heat is transferred to a suitable heat sink fluid, such as a boiling medium for example, with the temperature of the said heat sink being not greater than 200 °C.

A preferred feature of the invention is a regulation of the global steam-to-carbon ratio (SC ratio) of the front-end section to a value lower than
5 conventional. Preferably said SC ratio is regulated to a value of less than 2.7 and more preferably in the range 2.3 to 2.6. Although lowering the SC ratio has certain advantages for the ammonia production process as outlined below, it has the disadvantage of determining a reduction in the quantity of
10 steam available from heat recovery for power generation; this shortfall is however compensated in the present invention by the provision of said gas turbine. Hence, the advantages of a lower SC can be fully exploited.

Beneficial effects of a low SC ratio include: the steam required for the reforming process is reduced; the heat duty of the steam reformer for
15 preheating and reforming the mixed feed is reduced for a given ammonia production, and so is the reformer fuel consumption; less heat is rejected to cooling water / air at the end of the heat recovery train in the front end, after recovering the valuable heat from the syngas (steam is in fact added in large excess of steam the requirements for the reforming and CO shift, and the
20 excess steam is substantially all condensed before the synthesis); and the mass flow rate in the front end is lower.

Preferred ways of facilitating a reduction in the SC ratio include provision of a pre-reformer and use of improved catalysts in the steam reformer and CO shift reaction stages.

According to the invention, low-grade heat is recovered from exhaust of said gas turbine. Said heat can be used for a number of purpose including, but not limited to, the following examples: heating of a heat transfer medium such hot water or thermal oil, the regeneration of a CO₂-rich solution in a CO₂ removal unit, the heating of the reboiler of an absorption refrigeration chiller, the distillation of an ammonia-rich aqueous ammonia solution, and/or the initial preheating of natural gas, process air , combustion air.

According to different embodiments, said low-grade heat as defined above constitutes only a portion of the total heat that can be recovered from the exhaust of the gas turbine. Heat recovered from the gas turbine exhaust at a higher temperature, for example an exhaust temperature greater than around 250 °C, may be used for example for the generation or superheating of steam suitable to drive a turbine. One embodiment of the invention provides that: a first portion of heat recovered from exhaust of said gas turbine is used in a heat recovery steam generator to produce superheated steam and said steam is expanded in a backpressure or extraction steam turbine producing further mechanical power, thus forming a combined cycle, and a second portion of heat recovered from exhaust of said gas turbine is used to provide said low-grade heat. More preferably, a steam flow taken from said

backpressure or extraction steam turbine can be further used to provide heating to at least one of said thermal users.

Part of the steam produced can also be exported if an external user is available.

- 5 The invention is synergistic in particular with carbon dioxide removal techniques which require a low-grade heat For example, removal of carbon dioxide by chemical or chemical-physical absorption needs a heat input used for regeneration of a CO₂ removal solution. Said solution may include amine or potassium carbonates or similar.
- 10 The above mentioned derivative of ammonia may be, for example, one or more of urea, phosphates or nitric acid. Preferably said derivative is urea. A preferred application of the invention relates to ammonia-urea processes and plants, where some or all of the synthesized ammonia is reacted with carbon dioxide to produce urea.
- 15 Another aspect of the invention is a method of modernizing a plant for producing ammonia and a derivative of ammonia, particularly urea, according to the attached claims.

- Said method is characterized by the provision of: at least one gas turbine; suitable power transfer means to transfer the power produced by said turbine
- 20 to at least one of the power users; heat recovery means for recovering low-grade heat from the exhaust gas of said gas turbine, and also comprises the

provision of said low-grade heat to at least one of the thermal users of the plant, or to at least one newly-installed thermal user.

In some embodiments, the modernization comprises the installation of new thermal users. A newly-installed thermal user, in some embodiments, may
5 replace an existing power user. For example, the ammonia section normally comprises a vapour compression refrigerator for condensation of the produced ammonia, and the invention may comprise the replacement of said cycle with an absorption refrigerator which uses low-grade heat instead of mechanical power.

10 Hence, an aspect of the invention is to provide a suitable low-grade heat sink, to exploit the heat recovered from the gas turbine exhaust. This may be done by lowering the steam-to-carbon ratio, as stated above, and/or by installing new thermal users.

An advantage of the invention is that the gas turbine alone can reach a
15 thermal efficiency of more than 35% on LHV (low heat value of fuel) basis, and an efficiency of over 40% can be achieved when a heat recovery steam generator (HRSG) and associated back-pressure or extraction steam turbine, as described above, are also provided. These efficiency values are considerably higher than the typical efficiency of the steam cycle in an
20 ammonia plant, resulting in a reduction of consumption of natural gas fuel and hence in the total gas consumption of the ammonia plant.

Another advantage is the strong integration and unexpected synergistic effect between the provision of said power unit, the lowering of the SC ratio, and the feeding of low-grade heat to the existing or newly-installed thermal users.

The invention is particularly advantageous in conjunction with chemical or
5 chemical-physical absorption technique for the removal of carbon dioxide. A CO₂ removal unit with chemical or chemical-physical absorption is a major user of low-grade steam; the remaining steam after abstraction of steam needed for CO₂ solvent regeneration can be exported, but the amount exportable is generally limited. Reducing the SC ratio has the effect that less
10 steam (i.e. less amount of low grade heat) is available, which would be perceived as a drawback in the prior art. This drawback could be theoretically solved by implementation of a physical absorption CO₂ removal unit, which would require less heat for solvent regeneration than a chemical or chemical-physical CO₂ removal unit, but this would entail a significant capital cost. The
15 invention overcomes this problem, thanks to the possibility to recover CO₂ removal solvent regeneration heat from exhaust gas of the gas turbine.

The invention will be further elucidated by the following description of an embodiment thereof, given by way of non-limiting example with reference to the attached Fig. 1.

20 Detailed description

Fig. 1 illustrates a scheme of a process for ammonia synthesis from natural gas, according to a preferred embodiment of the invention.

Block 1 denotes an ammonia-urea plant comprising: an ammonia synthesis section, comprising a front end section and a high pressure synthesis loop, and a urea plant where some or all of the ammonia is reacted with carbon dioxide to produce urea.

- 5 Said front end section comprises preferably a steam reforming section and a purification section. Said steam reforming section comprises for example a primary steam reformer and a secondary reformer. Said purification section may include shift converters of CO to CO₂, a CO₂ removal unit and, optionally, a methanator.
- 10 The ammonia-urea plant 1 comprises a number of power users 2 and thermal users 3. Typically, said power users (PU) include large gas compressors such as the synthesis gas compressors and other compressors for process air, ammonia, carbon dioxide or natural gas, and smaller steam consumers such as pumps and fans. Thermal users (TU) typically use steam
- 15 as a source of heat and include for example the CO₂ removal unit where heat is needed for regeneration of a CO₂ removal solution.

A portion 15 of the available natural gas feed NG is used to fire a gas turbine 6. The power produced by said turbine 6 is transferred to one or more of the PUs (line 7) in a mechanical or electrical form, that is via direct mechanical

20 coupling or conversion into electrical energy.

For example, in a first embodiment a PU such as a compressor may be directly coupled to said gas turbine 6; in a second embodiment said gas

turbine 6 is coupled to a generator and a PU is coupled to an electric motor powered at least in part by electrical energy produced by said generator.

The gas turbine 6 hence will replace one or more of the steam turbines of the prior art.

- 5 Exhaust gas flow 8 discharged by said gas turbine 6 is fed to a heat recovery unit 9. Said recovery unit 9 produces a low-grade steam 10 by evaporating a feed water 14. Said steam 10 has a temperature not greater than 200°C, preferably in the range 150 – 200 °C, and is used in at least one of the TUs 3 of the ammonia section 1. The cooled exhaust gas leaves the recovery unit 9
- 10 at line flow 11.

A particularly preferred use for low-grade steam 10 is regeneration of CO₂ removal solution in the CO₂ removal unit of the purification section. Removal of carbon dioxide is preferably carried out with any of the following methods: amines, or activated amines, or potassium carbonate.

- 15 Since the gas turbine exhaust gas 8 is usually at a higher temperature (e.g. 450 - 550 °C), the heat recovery unit may also provide an additional amount of mechanical or electrical power, as indicated by line 13, for example via a heat recovery steam generator (HRSG) and a backpressure or extraction steam turbine.

- 20 In a preferred embodiment, the global steam-to-carbon ratio in the front-end section of the plant 1 is regulated at a low value of less than 2.7, preferably in

the range 2 – 2.6 and more preferably in the range 2.3 - 2.6. As stated above, the reduction of said ratio has a positive and synergistic effect with the provision of the gas turbine 6 and of the heat recovery unit 9.

The global steam-to-carbon ratio can be reduced in conjunction with one or
5 more of the following: by installing a pre-reformer upstream the primary reformer; bypassing a portion of natural gas (typically more than 10% of the reformer feed) around the steam reformer tubes and sending it directly to the secondary reformer.

In some embodiments, the ammonia-urea plant 1 comprises a hydrogen
10 recovery unit (HRU). The tail gas 12 of said HRU may be used as fuel in the gas turbine 6 as shown in Fig. 1. For a revamp, this is very convenient compared to the recycle in the steam reformer, because it avoids the otherwise typically necessary modification of the steam reformer burners.

Additional steam 4 for the thermal users 3 can be optionally provided by a
15 gas-fired auxiliary boiler 5.

Further preferred aspects of the invention are the following. Energy can be saved by installing a means for recovering reactants (H₂ and N₂) from the synthesis loop purge, while effectively rejecting the inerts (Ar and especially CH₄). Such means may include a membrane, or on adsorbents, or preferably
20 a cryogenic HRU which recovers most of the reactants at a pressure preferably of at least 60 bar and preferably more than 100 bar.

Both reducing the S/C ratio alone and installing a purge gas recovery HRU alone provides some energy saving, but there is synergy in applying both solutions together.

In fact, a lower S/C ratio reduces the methane conversion in the reforming process, increasing the residual methane concentration in the make-up gas and ultimately in the synthesis loop. This offsets saving in process steam consumption. However, coupling an HRU with a lower S/C ratio eliminates the drawbacks of the latter, i.e. the increased methane concentration in the synthesis loop, while retaining the benefits of both: reduced firing, less inerts in the synthesis loop, H₂ and N₂ recovered at high pressure.

Depending on the selected S/C ratio, either a high temperature (HTS) or a medium temperature (MTS) shift may be deployed. A HTS allows recover of a higher level heat, hence ensuring a higher overall efficiency and less gas consumption. However, HTS can be used only down to a global S/C ratio of about 2.6 - 2.7. In some cases it may be useful to reduce the S/C ratio to lower values, hence MTS is then required. The MTS can be adiabatic or isothermal. Isothermal MTS means that the shift converter contains a heat exchanger adapted to keep the temperature of the shift converter product gas within a desired range. Adiabatic MTS can be used when the amount of heat released in the shift converter is limited, for example when the oxidant in the secondary reformer is air and the concentration of CO inlet to the shift is not too high.

CLAIMS

1) A process for producing ammonia and a derivative of ammonia from a natural gas feed comprising:

conversion of natural gas into synthesis gas in a front-end section;

5 synthesis of ammonia from said synthesis gas in a synthesis loop;

use of at least part of said ammonia to produce said derivative of ammonia,

said process being carried out with power users requiring a mechanical power for operation, and thermal users requiring a heat input for

10 operation;

the process being **characterised in that:**

- a portion of said natural gas feed is used to fuel a gas turbine;
- power produced by said gas turbine is used to cover at least partially the power demand of said power users;

15 - heat is recovered from exhaust gas of said gas turbine, and at least part of said heat is recovered as low-grade heat, to provide process heating to at least one of said thermal users,

- said low-grade heat being transferred from said exhaust gas to said at least one of said thermal users via a heat exchange medium, said medium being heated by indirect heat exchange with the exhaust gas to a temperature which is not greater than 200 °C.

20

- 2) A process according to claim 1, said power being transferred from said gas turbine to at least one of said power users in a mechanical or electrical form.
- 3) A process according to any preceding claims, wherein said conversion of natural gas into synthesis gas in said front-end section is carried out by steam reforming with a global steam-to-carbon molar ratio not greater than 2.7 and preferably in the range 2.3 to 2.6.
- 4) A process according to any of the previous claims, wherein said heat recovered from said gas turbine is used to provide heat to one or more of the following thermal users:
- heating of a heat transfer medium such hot water or hot oil,
 - the regeneration of a CO₂-rich solution in a CO₂ removal unit,
 - the powering of an absorption refrigeration chiller,
 - the distillation of an ammonia-rich aqueous ammonia solution,
 - heating of natural gas or other fuel,
 - heating of process air,
 - heating of combustion air.
- 5) A process according to any of the previous claims, wherein:

- a first portion of heat recovered from exhaust of said gas turbine is used in a heat recovery steam generator to produce steam and said steam is expanded in a backpressure or extraction steam turbine producing further mechanical power, thus forming a combined cycle, and
- 5 a second portion of heat recovered from exhaust of said gas turbine is used to provide said low-grade heat.
- 6) A process according to claim 5, wherein a steam flow taken from said backpressure or extraction steam turbine is used to provide heating to at least one of said thermal users.
- 10 7) A process according to any of the previous claims, wherein said conversion of natural gas into synthesis gas comprises a primary steam reformer and a secondary reformer, or a pure autothermal reformer, or a partial oxidation reactor, obtaining a raw synthesis gas, and a purification of said raw synthesis gas, comprising at least a shift reaction and
- 15 removal of carbon dioxide from the shifted gas.
- 8) A process according to claim 7, said shift conversion being a high temperature shift (HTS) on iron-based catalyst, or a medium temperature shift (MTS) on copper-based catalyst.

- 9) A process according to claim 7 or 8, said removal of carbon dioxide being carried out with any of the following methods: amines, or activated amines, or potassium carbonates.
- 10) A process according to any of the previous claims, said derivative of ammonia being urea.
- 11) A process according to any of the previous claims, in which said power users are one of CO₂, air, ammonia, natural gas compressors.
- 12) A plant for producing ammonia and a derivative of ammonia, particularly urea, from a natural gas feed, said plant comprising:
- a front-end section for generation of ammonia make-up synthesis gas;
 - a synthesis loop for synthesis of ammonia from said make-up synthesis gas;
 - a section for the conversion of at least part of the synthesized ammonia into said derivative;
 - power user requiring a mechanical power for operation, and at least one thermal user requiring a heat input for operation;
- characterised in that** said plant further comprises:
- at least one gas turbine, the power produced by said gas turbine being transferred to at least one of said power users,

- heat recovery means for recovering low-grade heat from exhaust of said gas turbine, via a heat exchange medium
- said heat recovery means comprising indirect heat exchange means arranged to heat said medium to a temperature not greater than 200 °C , and
- means arranged to transfer said low-grade heat to at least one of said thermal users.

13) A method of modernizing a plant for producing ammonia and a derivative of ammonia, particularly urea, wherein:

said plant comprises a front-end section for generation of ammonia make-up synthesis gas; a synthesis loop for synthesis of ammonia from said make-up synthesis gas; a section for the conversion of at least part of the synthesized ammonia into said derivative;

the plant also comprising power users and thermal users;

the method being **characterized by:**

the provision of at least one gas turbine, and the provision of suitable power transfer means to transfer the power produced by said turbine to at least one of said power users,

the provision of heat recovery means for recovering a low-grade heat from exhaust gas of said gas turbine, by indirect heat exchange with a

medium, said medium being heated by the exhaust gas to a temperature not greater than 200 °C,

the provision of the so recovered low-grade heat to at least one of said thermal users of the plant, or to at least one newly-installed thermal user.

5 14) A method according to claim 12, wherein the provision of said power transfer means includes: the provision of an electrical motor and the provision of an electrical generator coupled to said gas turbine.

15) A method according to claim 12 or 13, said newly-installed thermal user being one of the following: a reboiler of a CO₂-rich solution in a CO₂
10 removal unit, a reboiler of an absorption refrigeration chiller, a reboiler of an ammonia-rich aqueous ammonia solution distillation system, a preheater of a natural gas or fuel gas, a preheater of process air, a preheater of combustion air.

16) A method according to any of claims 12 to 14, further comprising the step
15 of reducing the global steam-to-carbon ratio of the front-end section to a value lower than the original, and preferably lower than 2.7.

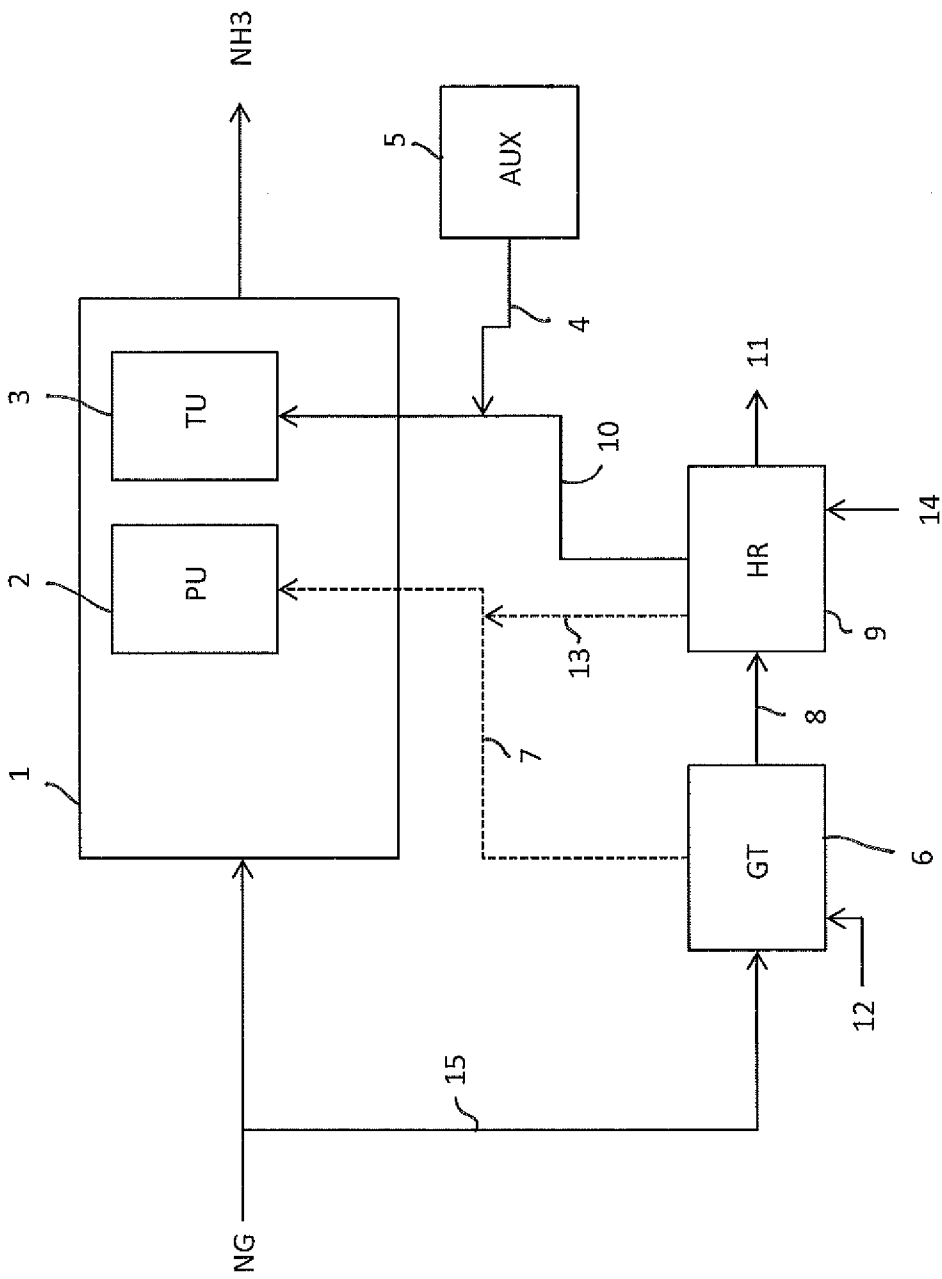


FIG. 1

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2015/062329

A. CLASSIFICATION OF SUBJECT MATTER

INV. C01C1/04 B01J19/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C01C B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	EP 0 595 100 A1 (LINDE AG [DE]) 4 May 1994 (1994-05-04) abstract -----	9
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Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/062329

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2015/062329

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