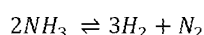


TITLE: AMMONIA CRACKING FOR GREEN HYDROGEN

BACKGROUND

[0001] Global interest in renewable energy and using this renewable energy to generate green hydrogen has driven the interest in converting the green hydrogen to green ammonia, as ammonia is simpler to transport over distance of hundreds or thousands of miles. Particularly, shipping liquid hydrogen is not commercially possible currently but shipping ammonia, which is in a liquid state, is currently practiced.

[0002] For use in a commercial fuel cell, the ammonia must be converted back to hydrogen according to the reaction.



[0003] This is an endothermic process, i.e., a process that requires heat, and is performed over a catalyst. This process is known as cracking. The gas produced (or "cracked gas") is a combination of hydrogen (H₂) and nitrogen (N₂). Since the cracking reaction is an equilibrium reaction, there is also some residual ammonia. In most applications of crackers currently, the hydrogen + nitrogen mixture is utilised as is. However, as ammonia can be a poison to fuel cells, this stream, with ammonia suitably removed such as by scrubbing with water, can be used directly in a fuel cell. However, if the hydrogen is to be used in vehicle fueling, the nitrogen present provides a penalty to the process. The fuel to a vehicle fueling system is compressed to significant pressure - up to 900 bar. This means that the nitrogen, which is merely a diluent in the process, is also compressed, taking power, and taking storage volume and increasing anode gas purge requirement, decreasing efficiency. It is therefore beneficial where hydrogen is to be used in vehicle fueling, for the hydrogen + nitrogen to be purified.

[0004] Small scale cracking reactors, or "crackers", typically use pressure swing adsorption ("PSA") devices to separate the cracked gas and recover the hydrogen and generate a PSA tail gas (or offgas). However, these crackers are generally heated electrically and the PSA tail gas is typically vented to atmosphere.

[0005] As is common in hydrogen production from a steam methane reforming (SMR) reactor, a PSA can be used to purify the nitrogen + hydrogen. The cracking reaction is performed in tubes packed with catalyst which are externally heated by a furnace (see GB1142941).

[0006] GB1142941 discloses a process for making town gas from ammonia. The ammonia is cracked and the cracked gas scrubbed with water to remove residual ammonia. The residual ammonia is recovered using a distillation column, and recycled to the cracking process. The purified hydrogen/nitrogen mixture is then enriched with propane and/or butane vapor to produce the town gas for distribution.

[0007] US6835360A discloses an endothermic catalytic reaction apparatus for converting hydrocarbon feedstock and methanol to useful gases, such as hydrogen and carbon monoxide.

The apparatus comprises a tubular endothermic catalytic reactor in combination with a radiant combustion chamber. The resultant cracked gas is used directly in a fuel cell after passing through a gas conditioning system.

5 [0008] GB977830A discloses a process for cracking ammonia to produce hydrogen. In this process, the hydrogen is separated from the nitrogen by passing the cracked gas through a bed of molecular sieves which adsorbs nitrogen. The nitrogen is then driven off the bed and may be stored in a holder.

10 [0009] JP5330802A discloses an ammonia cracking process in which the ammonia is contacted with an ammonia decomposition catalyst at a pressure of 10 kg/cm² (or about 9.8 bar) and a temperature of 300 to 700°C. Hydrogen is recovered from the cracked gas using a PSA device. The reference mentions that the desorbed nitrogen may be used to boost the upstream process but no details are provided.

15 [0010] US2007/178034A discloses a process in which a mixture of ammonia and hydrocarbon feedstock is passed through a fired steam reformer at 600°C and 3.2 MPa (or about 32 bar) where it is converted into a synthesis gas containing about 70 vol. % hydrogen. The synthesis gas is enriched in hydrogen in a shift reaction, cooled and condensate removed. The resultant gas is fed to a PSA system to generate a purified hydrogen product having 99 vol. % hydrogen or more. The offgas from the PSA system is fed as fuel to the fired steam reformer.

20 [0011] CN111957270A discloses a process in which ammonia is cracked in a tubular reactor within a furnace. The cracked gas is separated by adsorption to produce hydrogen gas and a nitrogen-rich offgas. The fuel demand of the furnace appears to be satisfied using a combination of cracked gas, hydrogen product gas and/or offgas.

25 [0012] US2020/123006 discloses a process for cracking ammonia using heat generated by the non-catalytic partial oxidation of ammonia with an oxygen containing gas. The residual ammonia is separated from the process gas and recycled for use in the oxidation process.

[0013] There is a need generally for improved processes for the production of hydrogen from ammonia and specifically for processes that are more efficient in terms of energy consumption and/or that have higher levels of hydrogen recovery and/or that reduce or eliminate the need to combust fossil fuels.

30 [0014] In the following discussion of embodiments of the present invention, the pressures given are absolute pressures unless otherwise stated.

BRIEF SUMMARY OF THE INVENTION

35 [0015] According to a first aspect of the present invention, there is provided a method for producing hydrogen from ammonia, comprising:

pressurizing liquid ammonia feed comprising water as a trace impurity to produce pressurized liquid ammonia feed;

combusting a primary fuel in a furnace to heat catalyst-containing reactor tubes and to form a flue gas;

supplying heated ammonia to the catalyst-containing reactor tubes to cause cracking of the ammonia into a cracked gas containing hydrogen gas, nitrogen gas and residual ammonia;

5 cooling the cracked gas by heat exchange to produce cooled cracked gas;

scrubbing ammonia from the cooled cracked gas using water in a scrubbing column to produce ammonia-depleted cracked gas and an aqueous ammonia solution;

10 stripping ammonia from the aqueous ammonia solution in a distillation column system to produce water-depleted ammonia feed vapour and an aqueous ammonia-depleted bottoms liquid;

heating the water-depleted ammonia feed vapour by heat exchange with one or more hot fluids to produce the heated ammonia;

purifying the ammonia-depleted cracked gas in a first PSA device to produce a first hydrogen product gas and a first PSA tail gas;

15 characterised in that the pressurised liquid ammonia feed is heated and vaporised by heat exchange against the one or more hot fluids to produce ammonia feed vapour which is fed to the distillation column system to remove water from the ammonia feed vapour, wherein the one or more hot fluids comprises the cracked gas and/or the flue gas.

[0016] The liquid ammonia feed is typically pressurized to a pressure that is greater than 1.1 bar, 20 e.g. at least 5 bar or at least 10 bar. In some embodiments, the liquid ammonia is pressurized to a pressure in a range from about 5 bar to about 50 bar, or in a range from about 10 to about 45 bar, or in a range from about 30 bar to about 40 bar.

[0017] Typically the liquid ammonia feed has small quantities of water added to it to prevent stress corrosion cracking in vessels during shipping and storage. The liquid ammonia feed 25 contains water as a trace impurity, for example in an amount in the range from about 0.1 wt. % to about 0.5 wt. %, typically in an amount of about 0.2 wt. %. The water should be removed from the feed ammonia to prevent damage to the ammonia cracking catalyst. Some catalysts, for example iron based catalysts are water intolerant and are less compatible with feedstock containing water.

30 [0018] The liquid ammonia feed is heated and vaporised to produce ammonia feed vapour. The temperature of ammonia feed vapour being fed to the distillation column system is typically in a range from about 25°C to about 90°C which ensures that the water was also carried through to the distillation system with the vaporised ammonia. The actual temperature is determined by the boiling point of ammonia at the pressure to which it has been pumped. The vaporized ammonia 35 entering the column may contain a small (e.g. 1 to 2 %) water-rich liquid phase that will be carried through to the distillation system. Alternatively, the water-containing ammonia stream may be vaporized leaving a water-rich liquid stream that may be fed to the distillation system separately.

[0019] The water is removed from the ammonia feed vapour using the distillation column system. As the ammonia feed is already vapourised it can be introduced near the top of the distillation column system. The water-depleted ammonia feed vapour produced typically contains less than 5 ppm, preferably less 2 ppm, more preferably less than 1 ppm water.

- 5 [0020] The water-depleted ammonia feed vapour is typically heated to produce heated ammonia at a temperature greater than about 250°C, e.g. in a range from about 350°C to about 800°C, or from about 400°C to about 600°C.

- [0021] The temperature is ultimately determined by the identity of the catalyst, the operating pressure and the desired "slip", i.e. the amount of ammonia that passes through the cracking reactor without being cracked. In this regard, the process is typically operated with no more than about 4% slip which would be the amount of slip if the cracking process were operated 5 bar and 350°C with a close approach to equilibrium. Problems may arise with some construction materials at any appreciable pressure at temperatures above about 700°C.

- 10 [0022] The cracking reaction takes place in catalyst-filled reactor tubes that are heated by a furnace. However, in theory any heterogeneously catalysed gas reactor could potentially be used for the conversion.

- [0023] There are a large number of catalysts known in the art as useful for the ammonia cracking reaction and any of these conventional catalysts may be used in this invention. Iron-based catalysts are commonly used in the Haber-Bosch process for the manufacture of ammonia and so, since both processes are the same equilibrium-limited reaction, it is expected that such an iron-based catalyst could be utilised for the ammonia cracking process. However, it is well-known in ammonia production processes that the catalyst is poisoned by ppm levels of water and oxygen present in the feed. Therefore, it is expected that if iron-based catalysts are used, the water in the feed ammonia would need to be removed.

- 20 [0024] The primary fuel for the furnace typically comprises hydrogen, ammonia, cracked gas and/or PSA tail gas although the primary fuel preferably comprises methane. The fuel may be pure methane but is more likely natural gas or biogas.

- [0025] The PSA device may operate a PSA cycle or a vacuum swing adsorption (VSA) cycle. Suitable PSA cycles include any of the cycles disclosed in US9381460, US6379431 and 30 US8778051, the disclosures of which are incorporated herein by reference.

- [0026] In a normal PSA system with a single PSA device, the recovery of hydrogen is typically in the range of about 75% to 85%. However, there are two options for increasing recovery. First, the PSA tail gas may be recycled to the first PSA. In such embodiments, the first PSA tail gas may be compressed and the compressed PSA tail gas recycled to the first PSA device. Recycling in this way can achieve an overall hydrogen recovery of about 94% to about 96%.

35 [0027] Alternatively, two PSA devices may be used in series and the first PSA tail gas is further processed in the second PSA device. In these embodiments, the process comprises

compressing the first PSA tail gas to produce a compressed PSA tail gas; and purifying the compressed PSA tail gas in a second PSA device to produce a second PSA tail gas and a second hydrogen product gas. Further processing in this way can achieve an overall hydrogen recovery of about 95% to about 97%. For example, if the first PSA device achieves 83% recovery and the
5 second PSA achieves 80% recovery, then the overall recovery is 96.6%.

[0028] In these embodiments, the second hydrogen gas may be combined with the first hydrogen product gas to form a combined hydrogen product gas.

[0029] Similarly to the first PSA device, the second PSA device may operate a PSA cycle or a vacuum swing adsorption (VSA) cycle. Suitable PSA cycles include any of the cycles disclosed
10 in US9381460, US6379431 and US8778051.

[0030] The PSA tail gas from either the first PSA device or the second PSA device may be fed as a secondary fuel for combustion in the furnace. Preferably, the PSA tail gas is warmed by heat exchange against the one or more hot fluids and/or optionally mixed with the primary fuel before being fed to the furnace.

15 **[0031]** The PSA tail gas, or a gas derived therefrom, can be separated using a membrane separator to discharge a nitrogen-rich retentate gas and recycle a hydrogen-rich permeate gas for further processing in the PSA device and/or for mixing into the hydrogen product gas,

[0032] Like hydrogen, ammonia is a "fast gas" that readily permeates across membranes used for gas separation. Some membranes, such as those constructed of polyamide or polysulfone
20 polymers, are more tolerant of ammonia. However, some membranes, such as those constructed of polyimide polymers, are less tolerant of ammonia. Therefore, ammonia is typically removed, or its concentration is at least reduced, upstream of the membrane separator.

[0033] The cooled cracked gas is typically produced by heat exchange against the pressurised liquid ammonia feed and the water-depleted ammonia feed vapour, and optionally against the
25 primary fuel source, air supply to the furnace, and/or PSA tail gas.

[0034] Ammonia is removed from the cooled cracked gas by absorption in water, e.g. by washing the gas with water in a scrubbing column. The resultant ammonia-depleted gas and aqueous ammonia solution are separated so the ammonia-depleted gas can be further processed without the ammonia causing any difficulties. Ammonia is recovered from the aqueous ammonia solution
30 by stripping in the distillation column system. Preferably, the aqueous ammonia solution is pumped from the scrubbing column to the distillation column system. Such a process may be also be applied to the PSA tail gas prior to being supplied to the membrane separator.

[0035] Recovering the ammonia from the cracked gas not only simplifies the hydrogen purification steps but, as the recovered ammonia is recycled to the ammonia feed, it may increase
35 the recovery of hydrogen from the ammonia. It also removes ammonia from the feed to the burners, reducing concerns over production of oxides of nitrogen (NO_x) caused by combusting ammonia.

[0036] The distillation column system typically produces overhead vapour containing ammonia and an aqueous bottoms liquid. Part of bottoms liquid from the distillation column may be purged. Additionally or alternatively, all or part of the bottoms liquid from the distillation column may be reboiled. In this regard, the bottoms liquid in or from the distillation column system may be reboiled by heat exchange against the one or more hot fluids.

[0037] In other embodiments, the bottoms liquid in or from the distillation column system is reboiled using an electrically powered heater. The heater may be powered at least in part by electricity generated from at least one renewable source, such as solar, wind, or tidal energy, as this would reduce the carbon intensity of the process.

[0038] Aqueous bottoms liquid from the distillation column system can be fed to the scrubbing column. Prior to entering the scrubbing column, the aqueous bottoms liquid is preferably cooled by heat exchange with a coolant, preferably the aqueous ammonia solution being fed to the distillation system from the scrubbing column.

[0039] In some preferred embodiments, the overhead vapour in or from the distillation column system is partially condensed by heat exchange against a coolant to produce a condensed stream and the water-depleted ammonia feed vapour. The condensed stream is then used as reflux for the distillation column system.

[0040] According to a second aspect of the present invention, there is provided apparatus for producing hydrogen from ammonia comprising:

a pump for pressurizing liquid ammonia feed comprising water as a trace impurity to produce pressurized liquid ammonia feed;

at least one first heat exchanger in fluid communication with the pump for vaporizing pressurized liquid ammonia by heat exchange with one or more hot fluids to produce ammonia feed vapour;

catalyst-containing reactor tubes in fluid communication with the first heat exchanger(s) for cracking heated ammonia from the first heat exchanger(s) to produce a cracked gas containing hydrogen gas, nitrogen gas and residual ammonia;

a furnace in thermal communication with the catalyst-containing reactor tubes for combustion of a fuel to heat the catalyst-containing reactor tubes and to form a flue gas;

a flue gas conduit for feeding flue gas from the furnace to the at least one first heat exchanger(s);

a cracked gas conduit for feeding cracked gas to the at least one first heat exchanger(s);

a scrubbing column in fluid communication with the at least one first heat exchanger(s) for scrubbing ammonia from cooled cracked gas after passage through the first heat exchanger(s)

using water to produce ammonia-depleted cracked gas and an aqueous ammonia solution;

a distillation column system in fluid communication with the scrubbing column for stripping ammonia from the aqueous ammonia solution to produce water-depleted ammonia feed vapour and an aqueous ammonia-depleted bottoms liquid;

an ammonia feed vapour conduit for feeding ammonia feed vapour from the first heat exchanger(s) to the distillation column system;

a water-depleted ammonia feed vapour conduit for feeding water-depleted ammonia feed from the distillation column system to the first heat exchanger(s) for further heating by heat exchange with one or more of the hot fluids to produce the heated ammonia;

a PSA device in fluid communication with the scrubbing column for purifying the ammonia-depleted cracked gas to produce a hydrogen product gas and a first PSA tail gas; and

a hydrogen product gas conduit for removing hydrogen product gas from the PSA device.

[0041] The furnace may be separate from the catalyst-filled reactor tubes although the furnace and the catalyst-filled reactor tubes are preferably integrated within the same unit. In preferred embodiments, a steam methane reforming (SMR) type reactor is used in which the furnace comprises a radiant section through which pass the catalyst-containing reactor tubes.

[0042] A compressor may be provided downstream of the first PSA device for compressing the first PSA tail gas to produce compressed PSA tail gas. The compressor may consist of one or more stages and cooling will take place between each stage and after the final stage. Water will typically condense out of the compressed PSA tail gas at the interstages or at the aftercooler stage. The aqueous condensate is typically removed after each cooling stage of the compressor and a small amount of ammonia will come out of the first PSA tail gas with this condensate.

[0043] In some preferred embodiments, the apparatus comprises:

a compressor in fluid communication with the first PSA device for compressing the first PSA tail gas to produce compressed PSA tail gas; and

a recycle conduit for recycling the compressed PSA tail gas to the first PSA device.

[0044] In some alternative preferred embodiments, the apparatus comprises:

a compressor in fluid communication with the first PSA device for compressing the first PSA tail gas to produce compressed PSA tail gas;

a second PSA device in fluid communication with the compressor for purifying the compressed PSA tail gas to produce a second PSA tail gas and a second hydrogen gas;

a second hydrogen gas conduit for removing second hydrogen gas from the second PSA device; and

a second PSA tail gas conduit for removing the second PSA tail gas from the second PSA device.

[0045] In these embodiments, the first and second hydrogen gas conduits combine to form a hydrogen product gas conduit.

[0046] In some preferred embodiments, part or all of the first PSA tail gas and/or second PSA tail gas can be recycled and used as a secondary fuel for combustion in the furnace. In these embodiments, the apparatus comprises a conduit for feeding first PSA tail gas and/or second PSA tail gas to the furnace. Preferably, the conduit is in fluid communication with the first heat exchanger(s) for heating by heat exchange against the one or more hot fluids prior to combustion in the furnace.

[0047] The invention will now be described by way of example only with reference to the following drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0048] Fig. 1 is a process flow diagram of a first reference example of an ammonia cracking process to produce hydrogen;

[0049] Fig. 2 is a process flow diagram of another reference example based on the ammonia cracking process of Fig. 1 in which no hydrogen product is used as fuel

[0050] Fig. 3 is a process flow diagram of a further reference example based on the ammonia cracking process of Figs. 1 & 2 in which only PSA tail gas is used as fuel;

[0051] Fig. 4 is a process flow diagram of an ammonia cracking process including recovery of residual ammonia from the cracked gas; and

[0052] Fig. 5 is a process flow diagram of an embodiment of an ammonia cracking process to produce hydrogen wherein water is removed from the feed ammonia according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

[0053] A process is described herein for producing hydrogen by cracking ammonia. The process has particular application to producing so-called "green" hydrogen which is hydrogen created using renewable energy instead of fossil fuels. In this case, the ammonia is typically produced by electrolyzing water using electricity generated from renewable energy, such as wind and/or solar energy, to produce hydrogen which is then reacted catalytically with nitrogen (Haber process) to produce the ammonia which is more easily transported than hydrogen. After reaching its destination, the ammonia is then cracked to regenerate the hydrogen.

[0054] In this inventive process, heat required for the reaction is typically provided by combustion of PSA tail gas (which usually contains some amount of residual hydrogen and ammonia) in the furnace. If the PSA tail-gas has insufficient heating value than either vaporised ammonia, a portion of the product hydrogen, or another fuel may also be used.

[0055] In practice, natural gas could be used as a fuel, together with the PSA tail gas, as is practiced in SMRs for hydrogen. However, with the desire to maintain the "green" or renewable credentials of the hydrogen so produced, there is an incentive to use a "renewable fuel". This

can be the cracked "renewable" ammonia, the ammonia itself, or another renewable energy source, such as biogas, or indeed electric heating whether the electricity is itself from a renewable source, in this case local to the cracking process as opposed to the renewable electricity used to generate the hydrogen which has been transported in the form of ammonia.

5 [0056] A reference example of the process is shown in Fig. 1. The process takes liquid ammonia from storage (not shown). The ammonia to be cracked (line 2) is pumped (pump P201) as liquid to a pressure greater than the desired cracking pressure (see GB1142941). The reaction pressure is a compromise between operating pressure and conversion according to Le Chatelier's principle. There is an incentive to operate the reactor (8) at higher pressure because
10 pumping liquid ammonia requires less power and capital than compressing the product hydrogen.

[0057] The pressurised liquid ammonia (line 4) is then heated, vaporised (if it is below its critical pressure) and heated further, up to a temperature of greater than 250 °C via a heat exchanger (E101) using the heat available in the cracked gas leaving the reaction tubes and the flue gas from the furnace. In the figure, the heat exchanger (E101) is shown as one heat exchanger but,
15 in practice, it will be a series of heat exchangers in a network.

[0058] The initial heating and vaporization of the pressurized liquid ammonia may alternatively take place against an alternative heat source, such as cooling water or ambient air. Typical reaction temperatures are greater than 500 °C (see US2601221), palladium-based systems can run at 600 °C and 10 bar, whereas RenCat's metal oxide-based system runs at less than 300 °C
20 and 1 bar. (See <https://www.ammoniaenergy.org/articles/ammonia-cracking-to-high-purity-hydrogen-for-pem-fuel-cells-in-denmark/>). The operating pressure of the cracker is typically an optimization of several factors. Cracking of ammonia into hydrogen and nitrogen is favored by low pressure but other factors favor higher pressure, such as power consumption (which is minimized by pumping the feed ammonia rather than compressing the product hydrogen), and
25 the PSA size (which is smaller at higher pressure).

[0059] The hot ammonia (line 6) enters reaction tubes of a reactor (8) at the desired pressure where additional heat is provided by the furnace (10) to crack the ammonia into nitrogen and hydrogen. The resulting mixture of residual ammonia, hydrogen and nitrogen exits (line 12) the reaction tubes of the reactor (8) at the reaction temperature and pressure. The reaction products
30 are cooled in a heat exchanger (E101) against a combination of feed ammonia (from line 4), furnace fuel (in this case pumped ammonia from line 14, pump P202 and line 16; PSA tail gas from line 18; and product hydrogen to be used as fuel in line 20) and combustion air (from line 22, fan K201 and line 24) to reduce the temperature as close as possible to that required for the inlet of a PSA device (26). Any residual heat in the cracked gas mixture (line 28) is removed in
35 a water cooler (not shown) to achieve an inlet temperature to the PSA device (26) of in a range from about 20°C to about 60°C, e.g. about 50°C.

[0060] The PSA product (line 30) is pure hydrogen compliant with ISO standard 14687 - Hydrogen Fuel Quality - with residual ammonia < 0.1 ppmv and nitrogen < 300 ppmv - at approximately the reaction pressure. The product hydrogen (line 30) is further compressed (not shown) for filling into tube trailers (not shown) for transport or it may be liquefied in a hydrogen liquefier (not shown) after any required compression. The PSA tail gas (line 18) or "purge gas" from the PSA device (26) is shown as being heated via the heat exchanger E101, using the cracked gas (line 12) leaving the reaction tubes of the reactor (8) or furnace flue gas (line 32), before being sent (in line 36) to the furnace as a combustion fuel. However, the PSA tail gas (line 18) may be fed directly to the furnace (10) without heating.

[0061] The resultant warmed ammonia fuel (line 34) and warmed hydrogen (line 40) are depicted as combined with the (optionally) warmed PSA tail gas (line 36) in a mixer (42) to produce a combined fuel which is fed (line 44) to the furnace (10) for combustion to generate the flue gas (line 32 and, after cooling in E101, line 48). However, it should be noted that one or more of the fuels could be fed directly to the furnace without prior mixing. The warmed air (for combustion of the fuel) is fed to the furnace (10) in line 46.

[0062] One of the aims of preferred embodiments of the present process is to maximise the amount of hydrogen generated by cracking the renewable ammonia. That means minimising the amount of hydrogen used as fuel, or ammonia if ammonia were to be used as a fuel directly. Therefore, heat integration is important so as to use the hot flue gas and cracked gas appropriately, for instance to preheat air (line 24) and ammonia (line 4) to the cracker as this reduces the amount of "fuel" to be used in the burners of the furnace (10). This leads to higher hydrogen recovery as less of the hydrogen is lost in the furnace flue gas (lines 32 & 48) as water. Therefore, steam generation, for instance, should be minimised in favour of intra-process heat integration.

[0063] Fig. 1 shows ammonia provided as fuel (lines 34 & 44) and feed (line 6) and it also shows product hydrogen as fuel (lines 40 & 44) – in practice, it is likely only one of these streams would be used as fuel. In this regard, Fig. 2 depicts a similar process to that of Fig. 1 in which ammonia is used as a fuel (line 34) but not product hydrogen. All other features of the process depicted in Fig. 2 are the same as in Fig. 1 and the common features have been given the same reference numerals.

[0064] The inventors are aware that stable combustion of ammonia is facilitated if hydrogen is also used as a fuel, particularly at start-up and warm-up.

[0065] Fig. 3 depicts a process similar to that depicted in Fig. 2. In this process, the recovery of hydrogen (line 30) from the PSA may be adjusted to provide a tail gas (line 18) which, when burned, will provide all the heat required by the process, thus eliminating the need for a trim fuel. All other features of the process depicted in Fig. 3 are the same as in Fig. 1 and the common features have been given the same reference numerals.

[0066] Should there be a viable alternative source of renewable energy for the cracking reactions, as discussed above, one could consider recovering hydrogen from the PSA tail gas to increase the net hydrogen production from the process in addition to the hydrogen produced from the PSA. Such a process could use membranes in series or in parallel to separate hydrogen
5 from the nitrogen rich PSA tail gas stream.

[0067] The cracked gas (line 12) contains residual amounts of ammonia which can be removed and recycled to the cracking process. This has two benefits; first, it simplifies the adsorption process and secondly, it allows recovery of uncracked ammonia back to the process by stripping the ammonia from the water in a distillation system. Ammonia may need to be removed
10 particularly but not exclusively if membranes are being used as part of the separation process since membrane material can be intolerant of ammonia and ammonia is a fast gas and would permeate with the hydrogen so would accumulate in the process if not removed. NH₃ may be removed for instance by a water wash or other well-known technology for ammonia removal, upstream of the membrane. The ammonia recovered in the ammonia removal step can be
15 recovered to the feed to the cracking process using a distillation system to recover the ammonia from the water used to absorb the ammonia from the cracked gas. This could theoretically increase the hydrogen recovery from the process up to 100%. Recovering NH₃ from the cracked gas simplifies the hydrogen purification steps, may increase the recovery of hydrogen from the ammonia if the separated ammonia is recovered as feed, and also removes ammonia from the
20 feed to the burners, at least reducing and possibly eliminating concerns over production of NO_x caused by burning NH₃.

[0068] Fig. 4 depicts a process involving a conventional means of recovering residual ammonia from the cracked gas and recycling the recovered ammonia to the catalyst-containing reactor tubes for cracking. The features of the process in Fig. 4 that are common to the processes of
25 Figs. 1 to 3 have been given the same reference numerals. The following is a discussion of the new features in Fig. 4.

[0069] A fuel (line 50) is warmed in the heat exchange (E101). The resultant warmed fuel (line 52) is combined with the warmed PSA tail gas (line 36) in a mixer (42) to produce a combined fuel which is fed (line 44) to the furnace (10) for combustion to generate the flue gas (line 32 and,
30 after cooling in E101, line 48). However, it should be noted that one or more of the fuels could be fed directly to the furnace without prior mixing. The warmed air is fed to the furnace (10) in line 46.

[0070] The cracked gas is cooled in a heat exchanger (E101) against a combination of feed ammonia (from line 4), furnace fuel (in this case fuel in line 50; PSA tail gas from line 18) and
35 combustion air (from line 22, fan K201 and line 24) to reduce the temperature as close as possible to that required for the inlet of a scrubbing column (60). The inlet temperature to the scrubbing column (60) is preferably in a range from about 5°C to about 30°C, e.g. about 10°C.

[0071] The cooled cracked gas (line 28) is fed to a scrubbing column (60) where water (line 61) is used to recover the residual ammonia from the cracked gas to produce ammonia-depleted cracked gas and an aqueous ammonia solution. The aqueous ammonia solution is (line 70) transferred to the distillation column system (72) using a pump (P301). IN some embodiments, there may be no need to use a pump for this purpose.

[0072] The distillation column system (72) removes the water from the aqueous ammonia solution to produce water-depleted ammonia feed vapour and an aqueous ammonia-depleted bottoms liquid. The water-depleted ammonia feed vapour is recycled via line 76 to the catalyst-containing reactor tubes for cracking. The overhead vapour containing ammonia is partially condensed by a condenser (82) and the two-phase fluid is phase separated in separator (80) to produce condensed liquid which is fed (line 78) to the column system (72) as reflux, and the water-depleted ammonia feed vapour (line 76).

[0073] The aqueous bottoms liquid from the column system (72) can be purged (line 86) or reboiled. In this regard, the aqueous bottoms liquid (line 88) can be warmed and partially vaporized in the heat exchanger (E101) before being fed via line 90 to a separator (92). Alternatively, or in addition, the aqueous bottoms liquid (line 88) can be warmed and partially vaporized using an electrically powered heater (not shown). The separator (92) separates the liquid and vapour portions of the reboiled aqueous bottoms liquid. The vapour portion is fed back to the distillation column system (72) via line 94 to provide vapour for the column system. The liquid portion of the reboiled liquid, now a water-rich liquid with the majority of the ammonia stripped out, is fed to the scrubbing column (60) via line 96. Alternatively, the warmed and partially vaporized aqueous bottoms liquid (line 90) can be fed directly back to the distillation system (72) (not shown).

[0074] The water-rich liquid (line 96) derived from the reboiled aqueous bottoms liquid is cooled prior to entry into scrubbing column (60). Preferably, the cooling is achieved by heat exchange against aqueous ammonia solution (lines 106 & 108) in a heat exchanger (98). The cooled water-rich liquid (line 100) is cooled further by heat exchange against a coolant in heat exchanger (102) prior to being fed into the scrubbing column (60).

[0075] The ammonia depleted cracked gas is fed (line 62) to a first PSA device (26). The cracked gas is separated to form a first hydrogen product gas (line 30) and tail gas (line 54). The tail gas can be fed (line 54) back to the furnace, optionally via heat exchanger (E101) and mixer (42) (not shown).

[0076] In one alternative, as shown in Fig. 4 and Fig. 5, the tail gas (line 54) from the first PSA device (26) is compressed in a compressor (K301) to produce compressed PSA tail gas (line 56) which is fed to a second PSA device (64) to produce a second hydrogen product gas (line 66) and a second PSA tail gas (line 18). The second hydrogen product gas (line 66) is combined with the hydrogen product gas (line 30) from the first PSA device (26) to produce a combined

hydrogen product gas (line 68). The second PSA tail gas (line 18) is warmed by heat exchange against the cracked gas (line 12) and the flue gas (line 32) in the heat exchanger (E101) and then fed as fuel (lines 36 & 44) to the furnace (10).

5 [0077] Optionally, a portion of the first PSA tail gas (from line 54) can be combined with the second PSA tail gas (line 18) to produce a combined PSA tail gas which can then be used as fuel in the furnace (10).

[0078] The second PSA tail gas, or the combined PSA tail gas, may optionally be fed directly to the furnace (10) without heating and/or mixing with the primary fuel (line 50 & 52) (not shown).

10 [0079] In another embodiment with only a single PSA device (26), the compressed PSA tail gas (line 56) can be recycled back to the first PSA device (26) for purification with the cooled ammonia-depleted cracked gas (62) (not shown).

[0080] In further embodiments, a first part of the first PSA tail gas (line 54) can be compressed in a compressor (K301) to produce compressed PSA tail gas (line 56) and further processed as described above. However, a second part (not shown) of the first PSA tail gas can be fed back
15 to the furnace via a flow control valve (not shown). The valve could control the ratio of the PSA tail gas used a fuel to the primary fuel, thereby controlling the carbon intensity of the process.

[0081] Water may need to be removed from the feed ammonia to prevent damage to the ammonia cracking catalyst. Some catalysts, for example iron-based catalysts, are known to be water intolerant and are not compatible with feedstock containing water. Unfortunately, ammonia
20 typically has small quantities of water added to it to prevent stress corrosion cracking in vessels during shipping and storage. If this water is removed, any suitable cracking catalysts may be used, including water intolerant catalysts.

[0082] Water removal can be incorporated into the distillation column system as shown in Fig. 5. The features of the process in Fig. 5 that are common to the processes of Figs. 1 to 4 have been
25 given the same reference numerals. The following is a discussion of the additional features in Fig. 5.

[0083] In Fig. 5, pressurized liquid ammonia feed (line 4) is warmed and at least partially vaporised in the heat exchange (E101). The ammonia is evaporated at the required pressure, to ensure that the water was also carried through to the distillation system with the vaporised
30 ammonia.

[0084] The warmed and vaporised ammonia feed (line 110) is fed to the distillation system (72), usually at an intermediate location of the column. The overhead vapour produced in the column system is substantially free of water (e.g. contains about 1 ppm water) and contains the ammonia from the feed, together with the ammonia recovered from the cracked gas.

35 [0085] The recovered ammonia (line 76) is returned to the heat exchange (E101) to be heated further before being fed (line 6) to the reaction tubes of a reactor (8).

[0086] The invention will now be illustrated with reference to the following Invention Examples and by comparison with the following Reference Examples.

REFERENCE EXAMPLE 1

- 5 [0087] The process depicted in Fig. 2 has been simulated by computer (Aspen Plus, ver. 10, Aspen Technology, Inc.) and the results are depicted in Table 1. This example assumes an equilibrium for the cracking reaction at 11 bar and 500°C.

Fluid Description		Feed Ammonia	Fuel Ammonia	Air	Cracked Ammonia	Cooled Crude Hydrogen to PSA	PSA Offgas	Hydrogen Product	Cooled Flue Gas
Stream number		2	14	22	12	28	18	30	48
Composition									
Hydrogen	mol%	0.0000	0.0000	0.0000	73.8791	73.8791	31.8188	100.0000	0.0000
Nitrogen	mol%	0.0000	0.0000	76.6909	24.6264	24.6264	64.2803	0.0000	75.6694
Ammonia	mol%	99.8100	99.8100	0.0000	1.3981	1.3981	3.6492	0.0000	0.0000
Water	mol%	0.1900	0.1900	1.8500	0.0964	0.0964	0.2517	0.0000	22.7084
Oxygen	mol%	0.0000	0.0000	20.6000	0.0000	0.0000	0.0000	0.0000	1.0762
Argon	mol%	0.0000	0.0000	0.9200	0.0000	0.0000	0.0000	0.0000	0.5287
Carbon Dioxide	mol%	0.0000	0.0000	0.0300	0.0000	0.0000	0.0000	0.0000	0.0172
Methane	mol%	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Ethane	mol%	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Flowrate (total)	kmol/hr	17.0021	0.8500	16.1778	33.5035	33.5035	12.8355	20.6680	28.1505
Pressure	bar (abs)	1.0000	1.0000	1.0133	11.0000	11.0000	1.4000	10.5000	1.0500
Temperature	°C	-33.6938	-33.6938	20.0000	500.0000	50.0000	40.0000	49.9922	117.4344

Table 1

- 10 [0088] In this Reference Example, hydrogen recovery from the ammonia is 77.18% with the PSA recovery at 83.5%. The total power of the ammonia feed pump (P201), the ammonia fuel pump (P202) and the air fan (K201) is about 1.36 kW. In addition, the percentage of ammonia in the PSA offgas is 3.6492%.

REFERENCE EXAMPLE 2

- 15 [0089] The process depicted in Fig. 3 has been simulated by computer (Aspen Plus, ver. 10) and the results are depicted in Table 2. This example assumes an equilibrium for the cracking reaction at 11 bar and 500°C.

Fluid Description		Feed Ammonia	Air	Cracked Ammonia	Cooled Crude Hydrogen to PSA	PSA Offgas	Hydrogen Product	Cooled Flue Gas
Stream number		2	22	12	28	18	30	48
Composition								
Hydrogen	mol%	0.0000	0.0000	73.8791	73.8791	36.8306	100.0000	0.0000
Nitrogen	mol%	0.0000	76.6000	24.6264	24.6264	59.5552	0.0000	75.6244
Ammonia	mol%	99.8100	0.0000	1.3981	1.3881	3.3810	0.0000	0.0000
Water	mol%	0.1900	1.8500	0.0964	0.0964	0.2332	0.0000	22.7504
Oxygen	mol%	0.0000	20.6000	0.0000	0.0000	0.0000	0.0000	1.0783
Argon	mol%	0.0000	0.9200	0.0000	0.0000	0.0000	0.0000	0.5297
Carbon Dioxide	mol%	0.0000	0.0300	0.0000	0.0000	0.0000	0.0000	0.0173
Methane	mol%	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Ethane	mol%	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Flowrate (total)	kmol/hr	17.8832	16.3022	35.2398	35.2398	14.5719	20.6680	28.3138
Pressure	bar (abs)	1.0000	1.0133	11.0000	11.0000	1.4000	10.5000	1.0500
Temperature	°C	-33.6938	20.0000	500.0000	50.0000	40.0000	40.9822	119.1601

Table 2

[0090] In this Reference Example, hydrogen recovery from the ammonia is 77.05% with the PSA recovery at 79.4%. The total power of the ammonia feed pump (P201) and the air fan (K201) is about 1.37 kW. In addition, the percentage of ammonia in the PSA offgas is 3.3810%.

REFERENCE EXAMPLE 3

[0091] The process depicted in Fig. 4 has been simulated by computer (Aspen Plus, ver. 10) and the results are depicted in Table 3. For the purposes of the simulations, an equilibrium for the cracking reaction at 11 bar and 500 °C was assumed.

Fluid Description		Feed Ammonia	NG Fuel	Air	Cracked Ammonia	Cooled crude H2	Feed to PSA 1	PSA1 Offgas
Stream number		2	50	22	12	28	62	54
Composition								
Hydrogen	mol%	0.000	0.000	0.000	73.881	73.881	74.754	32.822
Nitrogen	mol%	0.000	1.003	76.600	24.627	24.627	24.918	66.307
Ammonia	mol%	99.810	0.000	0.000	1.398	1.398	0.024	0.063
Water	mol%	0.190	0.000	1.850	0.094	0.094	0.304	0.809
Oxygen	mol%	0.000	0.000	20.600	0.000	0.000	0.000	0.000
Argon	mol%	0.000	0.000	0.920	0.000	0.000	0.000	0.000
Carbon Dioxide	mol%	0.000	0.502	0.030	0.000	0.000	0.000	0.000
Methane	mol%	0.000	94.281	0.000	0.000	0.000	0.000	0.000
Ethane	mol%	0.000	4.214	0.000	0.000	0.000	0.000	0.000
Flowrate (total)	kmol/hr	14.283	1.300	16.019	28.930	28.930	28.591	10.745
Pressure	bar (abs)	1.000	10.113	1.013	11.000	11.000	11.000	1.400
Temperature	°C	-33.694	30.000	20.000	500.000	5.000	50.000	40.000
Fluid Description		PSA2 Offgas	stripper offgas	Wash Water	Purge Stream	Washed, compressed PSA offgas	H2 Product	Flue Gas
Stream number		18	76	61	86	56	68	48
Composition								
Hydrogen	mol%	8.950	0.144	0.000	0.000	32.952	100.000	0.000
Nitrogen	mol%	90.401	0.033	0.000	0.000	66.570	0.000	78.032
Ammonia	mol%	0.083	99.823	0.000	0.204	0.061	0.000	0.000
Water	mol%	0.567	0.000	100.000	99.796	0.417	0.000	14.758
Oxygen	mol%	0.000	0.000	0.000	0.000	0.000	0.000	1.206
Argon	mol%	0.000	0.000	0.000	0.000	0.000	0.000	0.592
Carbon Dioxide	mol%	0.000	0.000	0.000	0.000	0.000	0.000	5.412
Methane	mol%	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ethane	mol%	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Flowrate (total)	kmol/hr	7.881	0.398	0.076	0.017	10.702	20.668	24.876
Pressure	bar (abs)	1.358	11.000	12.000	11.000	11.000	10.500	1.050
Temperature	°C	40.000	27.997	30.000	183.438	30.000	47.259	210.625

Table 3

[0092] In this Invention Example, hydrogen recovery from the ammonia is 96.47%. In addition, the percentage of ammonia in the PSA offgas from the second PSA is 0.083%. One can see that the crude hydrogen has had a reduction in ammonia content from 1.398 to 0.024%. Not all of the ammonia has been recovered from the cracked gas. There is an optimization to be carried out as more ammonia recovery requires more reboiler duty in the stripping column and there is a

limit to the heat available for this duty within the process without impacting the efficiency of the process.

REFERENCE EXAMPLE 4

- 5 [0093] The process depicted in Fig. 4 has been simulated by computer (Aspen Plus, ver. 10) and the results are depicted in Table 4. For the purposes of the simulations, an equilibrium for the cracking reaction at 21 bar and 500 °C was assumed.

Fluid Description		Feed Ammonia	NG Fuel	Air	Cracked Ammonia	Cooled crude H2	Feed to PSA 1	PSA1 Offgas
Stream number		2	50	22	12	28	62	54
Composition								
Hydrogen	mol%	0.000	0.000	0.000	72.971	72.971	74.792	32.866
Nitrogen	mol%	0.000	1.003	76.600	24.323	24.323	24.931	66.396
Ammonia	mol%	99.810	0.000	0.000	2.614	2.614	0.029	0.078
Water	mol%	0.190	0.000	1.850	0.093	0.093	0.248	0.660
Oxygen	mol%	0.000	0.000	20.600	0.000	0.000	0.000	0.000
Argon	mol%	0.000	0.000	0.920	0.000	0.000	0.000	0.000
Carbon Dioxide	mol%	0.000	0.502	0.030	0.000	0.000	0.000	0.000
Methane	mol%	0.000	94.281	0.000	0.000	0.000	0.000	0.000
Ethane	mol%	0.000	4.214	0.000	0.000	0.000	0.000	0.000
Flowrate (total)	kmol/hr	14.286	1.304	16.070	29.293	29.293	28.577	10.730
Pressure	bar (abs)	1.000	10.113	1.013	21.000	21.000	21.000	1.400
Temperature	°C	-33.694	30.000	20.000	500.000	5.000	50.000	40.000
Fluid Description		PSA2 Offgas	stripper offgas	Wash Water	Purge Stream	Washed, compressed PSA offgas	H2 Product	Flue Gas
Stream number		18	76	61	86	56	68	48
Composition								
Hydrogen	mol%	8.970	0.222	0.000	0.000	33.008	100.000	0.000
Nitrogen	mol%	90.609	0.047	0.000	0.000	66.683	0.000	78.075
Ammonia	mol%	0.102	99.731	0.000	0.430	0.075	0.000	0.000
Water	mol%	0.319	0.000	100.000	99.570	0.235	0.000	14.703
Oxygen	mol%	0.000	0.000	0.000	0.000	0.000	0.000	1.208
Argon	mol%	0.000	0.000	0.000	0.000	0.000	0.000	0.593
Carbon Dioxide	mol%	0.000	0.000	0.000	0.000	0.000	0.000	5.421
Methane	mol%	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ethane	mol%	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Flowrate (total)	kmol/hr	7.863	0.757	0.504	0.463	10.684	20.668	24.913
Pressure	bar (abs)	1.358	21.000	22.000	21.000	21.000	20.500	1.050
Temperature	°C	40.000	51.243	30.000	213.691	30.000	47.260	160.735

Table 4

[0094] In this Invention Example, hydrogen recovery from the ammonia is 96.45%. In addition, one can see that the crude hydrogen has had a reduction in ammonia content from 2.614% to 0.029%.

INVENTION EXAMPLE 1

[0095] The process depicted in Fig. 5 has been simulated by computer (Aspen Plus, ver. 10) and the results are depicted in Table 5. For the purposes of the simulations, an equilibrium for the cracking reaction at 11 bar and 500 °C was assumed.

Fluid Description		Feed Ammonia	NG Fuel	Air	Cracked Ammonia	Cooled crude H2	Feed to PSA 1	PSA1 Offgas
Stream number		2	50	22	12	28	62	54
Composition								
Hydrogen	mol%	0.000	0.000	0.000	73.950	73.950	74.707	32.766
Nitrogen	mol%	0.000	1.003	76.600	24.650	24.650	24.902	66.194
Ammonia	mol%	99.810	0.000	0.000	1.401	1.401	0.087	0.232
Water	mol%	0.190	0.000	1.850	0.000	0.000	0.304	0.807
Oxygen	mol%	0.000	0.000	20.600	0.000	0.000	0.000	0.000
Argon	mol%	0.000	0.000	0.920	0.000	0.000	0.000	0.000
Carbon Dioxide	mol%	0.000	0.502	0.030	0.000	0.000	0.000	0.000
Methane	mol%	0.000	94.281	0.000	0.000	0.000	0.000	0.000
Ethane	mol%	0.000	4.214	0.000	0.000	0.000	0.000	0.000
Flowrate (total)	kmol/hr	14.274	1.293	16.015	28.824	28.824	28.531	10.733
Pressure	bar (abs)	1.000	10.113	1.013	11.000	11.000	11.000	1.400
Temperature	°C	-33.694	30.000	20.000	500.000	5.000	50.000	40.000
Fluid Description		PSA2 Offgas	stripper offgas	Wash Water	Purge Stream	Washed, compressed PSA offgas	H2 Product	Flue Gas
Stream number		18	76	61	86	56	68	48
Composition								
Hydrogen	mol%	8.930	0.005	0.000	0.000	32.899	100.000	0.000
Nitrogen	mol%	90.205	0.001	0.000	0.000	66.463	0.000	78.008
Ammonia	mol%	0.306	99.994	0.000	0.000	0.226	0.000	0.000
Water	mol%	0.559	0.000	100.000	0.000	0.412	0.000	14.804
Oxygen	mol%	0.000	0.000	0.000	0.000	0.000	0.000	1.210
Argon	mol%	0.000	0.000	0.000	0.000	0.000	0.000	0.593
Carbon Dioxide	mol%	0.000	0.000	0.000	0.000	0.000	0.000	5.386
Methane	mol%	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ethane	mol%	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Flowrate (total)	kmol/hr	7.876	14.614	0.060	0.000	10.690	20.611	24.866
Pressure	bar (abs)	1.358	11.000	12.000	MISSING	11.000	10.500	1.050
Temperature	°C	40.000	28.015	30.000	MISSING	30.000	47.259	120.256

Table 5

[0096] In this Invention Example, hydrogen recovery from the ammonia is 96.41%. In addition, one can see that the crude hydrogen has had a reduction in ammonia content from 1.401% to 0.087%.

5

INVENTION EXAMPLE 2

[0097] The process depicted in Fig. 5 has been simulated by computer (Aspen Plus, ver. 10) and the results are depicted in Table 6. For the purposes of the simulations, an equilibrium for the cracking reaction at 21 bar and 500°C was assumed.

Fluid Description		Feed Ammonia	NG Fuel	Air	Cracked Ammonia	Cooled crude H2	Feed to PSA 1	PSA1 Offgas
Stream number		2	50	22	12	28	62	54
Composition								
Hydrogen	mol%	0.000	0.000	0.000	73.036	73.036	74.763	32.832
Nitrogen	mol%	0.000	1.003	76.600	24.345	24.345	24.921	66.326
Ammonia	mol%	99.810	0.000	0.000	2.619	2.619	0.053	0.142
Water	mol%	0.190	0.000	1.850	0.000	0.000	0.263	0.700
Oxygen	mol%	0.000	0.000	20.600	0.000	0.000	0.000	0.000
Argon	mol%	0.000	0.000	0.920	0.000	0.000	0.000	0.000
Carbon Dioxide	mol%	0.000	0.502	0.030	0.000	0.000	0.000	0.000
Methane	mol%	0.000	94.281	0.000	0.000	0.000	0.000	0.000
Ethane	mol%	0.000	4.214	0.000	0.000	0.000	0.000	0.000
Flowrate (total)	kmol/hr	14.290	1.301	16.046	29.263	29.263	28.586	10.741
Pressure	bar (abs)	1.000	10.113	1.013	21.000	21.000	21.000	1.400
Temperature	°C	-33.694	30.000	20.000	500.000	5.000	50.000	40.000
Fluid Description		PSA2 Offgas	stripper offgas	Wash Water	Purge Stream	Washed, compressed PSA offgas	H2 Product	Flue Gas
Stream number		18	76	61	86	56	68	48
Composition								
Hydrogen	mol%	8.963	0.006	0.000	0.000	32.988	100.000	0.000
Nitrogen	mol%	90.537	0.001	0.000	0.000	66.643	0.000	78.072
Ammonia	mol%	0.184	99.992	0.000	0.000	0.136	0.000	0.000
Water	mol%	0.316	0.000	100.000	0.000	0.232	0.000	14.729
Oxygen	mol%	0.000	0.000	0.000	0.000	0.000	0.000	1.191
Argon	mol%	0.000	0.000	0.000	0.000	0.000	0.000	0.593
Carbon Dioxide	mol%	0.000	0.000	0.000	0.000	0.000	0.000	5.414
Methane	mol%	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Ethane	mol%	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Flowrate (total)	kmol/hr	7.868	15.015	0.048	0.000	10.690	20.666	24.895
Pressure	bar (abs)	1.358	21.000	22.000		21.000	20.500	1.050
Temperature	°C	40.000	51.374	30.000		30.000	47.260	210.043

Table 6

[0098] In this Invention Example, hydrogen recovery from the ammonia is 96.41%. In addition, one can see that the crude hydrogen has had a reduction in ammonia content from 2.619% to 0.053%.

- [0099] The present invention is not to be limited in scope by the specific aspects or embodiments disclosed in the examples which are intended as illustrations of a few aspects of the invention and any embodiments that are functionally equivalent are within the scope of this invention. Various modifications of the invention in addition to those shown and described herein will
- 5 become apparent to those skilled in the art and are intended to fall within the scope of the appended claims.

CLAIMS

1. A method for producing hydrogen from ammonia, comprising:
 - pressurizing liquid ammonia feed comprising water as a trace impurity to produce pressurized liquid ammonia feed;
- 5 combusting a primary fuel in a furnace to heat catalyst-containing reactor tubes and to form a flue gas;
 - supplying heated ammonia to the catalyst-containing reactor tubes to cause cracking of the ammonia into a cracked gas containing hydrogen gas, nitrogen gas and residual ammonia;
 - cooling the cracked gas by heat exchange to produce cooled cracked gas;
- 10 scrubbing ammonia from the cooled cracked gas using water in a scrubbing column to produce ammonia-depleted cracked gas and an aqueous ammonia solution;
 - stripping ammonia from the aqueous ammonia solution in a distillation column system to produce water-depleted ammonia feed vapour and an aqueous ammonia-depleted bottoms liquid;
- 15 heating the water-depleted ammonia feed vapour by heat exchange with one or more hot fluids to produce the heated ammonia;
 - purifying the ammonia-depleted cracked gas in a first PSA device to produce a hydrogen product gas and a first PSA tail gas;
- 20 characterised in that the pressurized liquid ammonia feed is heated and vaporised by heat exchange against the one or more hot fluids to produce ammonia feed vapour which is fed to the distillation column system to remove water from the ammonia feed vapour,
 - wherein the one or more hot fluids comprises the cracked gas and/or the flue gas.
2. A method according to Claim 1 comprising reboiling the bottoms liquid in or from the distillation column system by heat exchange against the one or more hot fluids.
- 25 3. A method according to Claim 1 or Claim 2 comprising reboiling the bottoms liquid in or from the distillation column system using an electrically powered heater.
4. A method according to Claim 3, wherein the heater is powered at least in part by electricity generated from at least one renewable source.

5. A method according to any of the preceding claims comprising partially condensing overhead vapour in or from the distillation column system by heat exchange to produce a condensed liquid and the water-depleted ammonia feed vapour, said condensed liquid being recycled as reflux to the distillation column system.
- 5 6. A method according to any of the preceding claims comprising feeding the aqueous bottoms liquid from the distillation column system to the scrubbing column.
7. A method according to Claim 6, wherein the aqueous ammonia solution being fed to the distillation column system is warmed by heat exchange against the aqueous bottoms liquid being fed to the scrubbing column.
- 10 8. A method according to Claim 6 or Claim 7, wherein the aqueous bottoms liquid is further cooled by heat exchange prior to being fed to the scrubbing column.
9. A method according to any of the preceding claims comprising pumping the aqueous ammonia solution from the scrubbing column to the distillation column system.
10. A method according to any of the preceding claims comprising:
- 15 compressing the first PSA tail gas to produce compressed first PSA tail gas; and
recycling the compressed PSA tail gas to the first PSA device to recover further hydrogen gas.
11. A method according to any of Claims 1 to 9 comprising:
- compressing the first PSA tail gas to produce compressed first PSA tail gas; and
- 20 purifying the compressed first PSA tail gas in a second PSA device to produce further hydrogen product gas and a second PSA tail gas.
12. A method according to Claim 11 comprising combusting the second PSA tail gas as a secondary fuel in the furnace.
13. Apparatus for producing hydrogen from ammonia, comprising:
- 25 a pump for pressurizing liquid ammonia feed comprising water as a trace impurity to produce pressurised liquid ammonia feed;

at least one first heat exchanger in fluid communication with the pump for vaporizing pressurised liquid ammonia by heat exchange with one or more hot fluids to produce ammonia feed vapour;

5 catalyst-containing reactor tubes in fluid communication with the first heat exchanger(s) for cracking heated ammonia from the first heat exchanger(s) to produce a cracked gas containing hydrogen gas, nitrogen gas and residual ammonia;

a furnace in thermal communication with the catalyst-containing reactor tubes for combustion of a fuel to heat the catalyst-containing reactor tubes and to form a flue gas;

10 a flue gas conduit for feeding flue gas from the furnace to the at least one first heat exchanger(s);

a cracked gas conduit for feeding cracked gas to the at least one first heat exchanger(s);

a scrubbing column in fluid communication with the at least one first heat exchanger(s) for scrubbing ammonia from cooled cracked gas using water to produce ammonia-depleted cracked gas and an aqueous ammonia solution;

15 a distillation column system in fluid communication with the scrubbing column for stripping ammonia from the aqueous ammonia solution to produce water-depleted ammonia feed vapour and an aqueous ammonia-depleted bottoms liquid;

an ammonia feed vapour conduit for feeding ammonia feed vapour from the first heat exchanger(s) to the distillation column system;

20 a water-depleted ammonia feed vapour conduit for feeding water-depleted ammonia feed from the distillation column system to the first heat exchanger(s) for further heating by heat exchange with one or more of the hot fluids to produce the heated ammonia;

a PSA device in fluid communication with the scrubbing column for purifying the ammonia-depleted cracked gas to produce a hydrogen product gas and a first PSA tail gas; and

25 a hydrogen product gas conduit for removing hydrogen product gas from the PSA device.

14. Apparatus according to Claim 13 wherein the distillation column system comprises a bottoms reboiler integrated thermally with the first heat exchanger(s).

15. Apparatus according to Claim 13 wherein the distillation column system comprises an electrically powered reboiler.

16. Apparatus according to any of Claims 13 to 15 wherein the distillation column system comprises an overhead condenser for partially condensing overhead vapor by heat exchange with a coolant.
17. Apparatus according to Claim 16 comprising a reflux conduit for feeding condensed liquid as reflux from the overhead condenser to the distillation column system.
18. Apparatus according to any one of Claims 13 to 17 comprising an aqueous bottoms liquid conduit for supplying aqueous bottoms liquid from the distillation column system to the scrubbing column.
19. Apparatus according to Claim 18 comprising a second heat exchanger for warming aqueous ammonia solution from the scrubbing column by heat exchange against aqueous bottoms liquid from the distillation column system.
20. Apparatus according to Claim 18 or Claim 19 comprising a third heat exchanger for cooling aqueous bottoms liquid from the distillation column system by heat exchange with a coolant.
21. Apparatus according to any of Claims 13 to 20 comprising a pump for pumping aqueous ammonia solution from the scrubbing column to the distillation column system.
22. Apparatus according to any of Claims 13 to 21 comprising:
- a compressor for compressing first PSA tail gas to produce compressed first PSA tail gas;
 - and
 - a recycle conduit for recycling compressed first PSA tail gas to the first PSA device.
23. Apparatus according to any of Claims 13 to 21 comprising:
- a compressor for compressing first PSA tail gas to produce compressed first PSA tail gas;
 - and
 - a second PSA device in fluid communication with the compressor for purifying the compressed first PSA tail gas to produce further hydrogen product gas and a second PSA tail gas.
24. Apparatus according to any of Claims 13 to 23 comprising a conduit for feeding second PSA tail gas to the first heat exchanger(s) for heating by heat exchange against the one or more hot fluids prior to combustion in the furnace.