

Process and Plant

Field of the Invention

The present invention relates to processes and systems for producing hydrogen. More
5 specifically, the present invention relates to processes for operating an ammonia cracking
plant to produce hydrogen, and ammonia cracking plants for producing hydrogen.

Background of the Invention

There is renewed interest in using hydrogen as a green, carbon free, fuel in a variety of
10 industrial settings. Hydrogen may be combusted to produce heat energy or electrical energy.
Alternatively, hydrogen may be used as a fuel to produce electrochemical energy in, for
example, a fuel cell.

Ammonia has received interest as a possible compound to enable the storage and transport
15 of hydrogen. Liquid ammonia has a higher hydrogen density than liquid hydrogen, and may
be transported using existing infrastructure which is already in use for this purpose, such as
that used for the transportation of ammonia in the agrochemical fertiliser industry.

Once the liquid ammonia has been transported it may be converted to hydrogen by the
20 process of cracking in an ammonia cracking plant.

The catalytic cracking of ammonia into hydrogen and nitrogen has been known for many
years. The reaction may be depicted as follows:



The ammonia cracking reaction is endothermic and may usefully be achieved by passing
ammonia over a suitable catalyst in externally heated catalyst-containing reaction tubes
disposed in a furnace. Such furnaces are known, for example, for the steam reforming of
30 natural gas or naphtha feedstocks.

Combusting hydrogen streams in gas turbines to produce electrical energy is known.
US2022162999 and US2022162989 disclose processes comprising a gas turbine, driven by
the combustion of a stream comprising hydrogen with a compressed air stream. The stream
35 comprising hydrogen is produced in an ammonia cracker fed with an ammonia stream. The
gas turbine is used to generate electrical and mechanical energy. Heat produced by the

combustion of the stream comprising hydrogen is either supplied directly to the cracker or used to pre-heat the ammonia stream upstream of the cracker through a heat exchanger.

WO2024/018169A1 discloses a process comprising an ammonia cracking reactor and a gas turbine driven by combustion of a hydrogen containing stream.

Alternatively, hydrogen may be fed to a so-called "hydrogen grid", where it may be drawn down and directly combusted to produce heat energy.

However, demand for energy varies with time and therefore so too does the demand for hydrogen. This is true regardless of whether the hydrogen is being used to generate electricity or to produce heat energy. For instance, demand for electricity being supplied to domestic consumers or to an industrial plant will vary depending upon the time of day, week, or year. As such, where ammonia is being cracked to produce a hydrogen fuel, the ammonia cracking plant must be able to quickly respond to rises and falls in demand for energy. In other words, the ammonia cracking plant must be designed and operated in such a way as to produce more hydrogen when energy demand increases, and less hydrogen when energy demand falls.

Typically, an ammonia cracking plant must be able to return to normal operation (e.g. producing greater than 40 % of maximum molar hydrogen output for energy production purposes) from a "turndown state" within two hours.

To overcome the problem of variable demands for energy, and hence hydrogen, several possible solutions have been proposed.

A first option is to shut down the ammonia cracking plant and restart it when demand for hydrogen resumes. However, the start-up and shutdown procedures can be lengthy, and would not meet the required two hour notice period to return to normal operation. Additionally, thermal cycling of the catalyst containing reaction tubes within the ammonia cracker reactor can reduce the lifetime of the tubes themselves and result in a high degree of breakage to the catalyst.

A second option is to run the ammonia cracking plant at lower rates of hydrogen production, for example producing less than 40 % (e.g. less than 30 %, or less than 20 %) of the maximum molar hydrogen output of the plant. In this case, the hydrogen output of the plant can be increased to normal operation in <1 hour, meeting the required notice period of two

hours. However, this option requires any hydrogen produced, but not utilised in producing energy, to be sent to flare. This wastes significant quantities of the ammonia feedstock and the fuel required to heat the ammonia cracking reactor (which may also be ammonia).

Alternatively, the hydrogen which is produced can be stored. However, this requires the
5 construction of large and expensive storage facilities.

There is therefore a need for ammonia cracking processes and plants which can accommodate variable demands for hydrogen and hence energy production.

10 Summary of the Invention

Accordingly, in a first aspect of the present invention there is provided a process for controlling an ammonia cracking plant comprising a fired ammonia cracking reactor, the process comprising the steps of:

- 15 i) decreasing a flowrate of an ammonia feedstock stream to an inlet of one or more catalyst containing reaction tubes disposed within a radiant section of the ammonia cracking reactor;
- ii) decreasing the heat output of a fuel combustion zone of the ammonia cracking reactor;
- 20 iii) obtaining a cracked gas stream from an outlet of the one or more catalyst containing reaction tubes;
- iv) cooling the cracked gas stream;
- v) increasing the pressure of the cracked gas stream;
- vi) heating the cracked gas stream;
- vii) recirculating the cracked gas stream to the inlet of the one or more catalyst
25 containing reaction tubes; and
- viii) passing the cracked gas stream through the one or more catalyst containing reaction tubes.

In a second aspect of the invention there is provided an ammonia cracking plant in a
30 turndown state. The ammonia cracking plant in the turndown state is the ammonia cracking plant which has operated the process of the first aspect of the invention. The ammonia cracking plant in the turndown state may be the ammonia cracking plant which has operated steps i) to viii) of the process of the first aspect of the invention and is repeating, or continuing to operate, steps iii) through viii) of the process of the first aspect of the invention.

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In a third aspect of the invention there is provided a process for returning the ammonia cracking plant from the turndown state of the second aspect of the invention to a state of normal operation.

- 5 The process of the third aspect of the invention for returning the ammonia cracking plant from the turndown state of the second aspect of the invention to the state of normal operation comprises the steps of:
- 10 i) increasing the flowrate of an ammonia feedstock stream to the inlet of the one or more catalyst containing reaction tubes disposed within the radiant section of the ammonia cracking reactor; and
 - ii) increasing the heat output of the fuel combustion zone of the ammonia cracking reactor;
 - 15 iii) cracking the ammonia in the ammonia feedstock stream to produce a cracked gas stream comprising hydrogen (H_2), nitrogen (N_2), and residual ammonia (NH_3); and
 - iv) obtaining the cracked gas stream from the outlets of the one or more catalyst containing reaction tubes.

20 Chemical plants which operate an exothermic reaction (e.g. the synthesis of ammonia or methanol) can be returned to normal operation from a turndown state with relative ease. In most cases the plant may be maintained at or below a minimum "light-off" temperature and the flow of reagents reduced or terminated. Once reagents are reintroduced to the process the exothermic reaction generates the heat required to sustain the reaction (i.e. the process is autothermal).

25 In comparison, chemical plants which operate endothermic reactions, such as those for the cracking of ammonia, do not benefit from the generation of heat from the reaction. In an ammonia cracking plant, when the flowrate of an ammonia feedstock stream to the catalyst containing reaction tubes is decreased or stopped, the catalyst containing reaction tubes
30 increase in temperature due to the continued combustion of fuel in the ammonia cracking reactor. However, if the combustion of fuel is ceased, the addition of an ammonia feedstock to the catalyst containing reaction tubes drastically cools the temperature of the catalyst containing reaction tubes and the catalyst therein, inhibiting the reaction.

35 The present inventors have found that an ammonia cracking plant may be placed into a certain turndown state using the process of the first aspect of the invention which recirculates heated cracked gas to the one or more catalyst containing reaction tubes. It has

surprisingly been found that the process of the first aspect of the invention is able to place an ammonia cracking plant into a certain turndown state which allows it to rapidly return to normal operation (e.g. within a period of two hours) without wasting ammonia feedstock and/or wasting hydrogen. The process of the first aspect of the invention and turndown state of the second aspect of the invention maintains the ammonia cracking plant at a temperature significantly higher than the minimum temperature required for the endothermic reaction to occur. The process of the third aspect of the invention is surprisingly able to take the ammonia cracking plant from the turndown state of the second aspect of the invention to a state of normal operation within a period of two hours.

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Brief Description of the Drawings

Figure 1 shows a schematic of the Compact Reformer available from Johnson Matthey Davy Technologies Limited.

15 **Figure 2** shows a block flow diagram of a process according to the first aspect of the invention, and an ammonia cracking plant in a turndown state according to the second aspect of the invention.

Detailed Description

20 Preferred and/or optional features of the invention will now be set out. Any aspect of the invention may be combined with any other aspect of the invention unless the context demands otherwise. Any of the preferred and/or optional features of any aspect may be combined, either singly or in combination, with any aspect of the invention unless the context demands otherwise. Lower and/or upper limits of any ranges disclosed herein are envisaged to be combinable with one another to provide new ranges, whether explicitly stated or not.

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The present invention relates to a process for controlling an ammonia cracking plant comprising a fired ammonia cracking reactor.

30 The ammonia cracking plant of the invention comprises the fired ammonia cracking reactor. Suitable fired ammonia cracking reactors are known and comprise a fuel combustion zone having a radiant section comprising one or more burners to which one or more fuel streams and an oxygen containing feed, such as air, oxygen enriched air, or oxygen, are fed. The radiant section comprises one or more catalyst containing reaction tubes each having an inlet and an outlet, and through which the ammonia feedstock stream is passed. Combustion of the one or more fuel streams in the one or more burners of the fuel combustion zone creates heat energy (e.g. radiant heat) for heating the one or more catalyst containing

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reaction tubes. There may be tens, hundreds, or thousands of catalyst containing reaction tubes in the radiant section. If desired, downstream of the radiant section, a flue gas from the combustion of the one or more fuel streams may be used to pre-heat one or more feed streams in a convection section, such as a flue duct, through which the flue gas may be
5 passed. Typically, the convection section is the flue duct of the ammonia cracking reactor.

Reactors comprising a radiant section containing catalyst containing reaction tubes and a convection section for preheating feeds are known in steam methane reforming and may be applied to the present invention.

10 Alternatively, fired ammonia cracking reactors may be used where the combustion of the one or more fuel streams in a fuel combustion zone is separate to the reactor comprising the catalyst containing reaction tubes. Such a reactor is the compact reformer available from Johnson Matthey Davy Technologies Limited, a schematic of which is shown in Figure 1.

15 The catalyst in the catalyst containing reaction tubes may be any ammonia cracking catalyst. For instance, nickel catalysts and/or ruthenium catalysts may be used. Preferred catalysts are nickel catalysts. The catalyst may comprise 3 to 30% by weight nickel, preferably 8 to 20% by weight nickel, expressed as NiO, on a suitable refractory support, such as alumina
20 or a metal aluminate. The catalyst may be in the form of pelleted shaped units, which may comprise one or more through holes, or may be provided as a wash coat on a structured metal or ceramic catalyst. A particularly preferred catalyst is KATALCO^{RTM} 27-2 available from Johnson Matthey PLC, which comprises 12% nickel, expressed as NiO, on a cylindrical pellet formed from a high surface area calcium aluminate support.

25 The one or more catalyst containing reaction tubes may suitably be formed of an iron-based alloy, a nickel based alloy, or a cobalt based alloy. The iron-based alloy may be an iron-chromium based alloy such as a stainless steel, preferably 316 stainless steel, or a high nickel steel such as those described by WO03/051771A1. Preferably, the one or more
30 catalyst containing reaction tubes are formed of a nickel-based alloy or a cobalt based alloy. More preferably, the one or more catalyst containing reaction tubes are formed of a cobalt based alloy.

The process of the first aspect of the invention may be a process for controlling an ammonia cracking plant comprising a fired ammonia cracking reactor to place the ammonia cracking
35 plant into a turndown state. The process for controlling an ammonia cracking plant may be a

process for taking an ammonia cracking plant from a state of normal operation to a turndown state.

By "normal operation" of the ammonia cracking plant it is meant that the ammonia cracking
5 plant is producing greater than 40% of its maximum molar hydrogen output. The normal
operation of the ammonia cracking plant will be understood to include the state of the
ammonia cracking plant when it is producing hydrogen gas for energy production purposes
(e.g. for feeding hydrogen into a hydrogen grid, or for combustion in a gas turbine to produce
electricity). Normal operation of the ammonia cracking plant may further be understood to
10 include the situation where most (e.g. 70% or more, 80 % or more, 90 % or more, or 95 % or
more, such as up to 100 %) of the cracked gas is being removed from the ammonia cracking
plant (e.g. to generate energy) and where most (e.g. 70% or more, 80 % or more, 90 % or
more, or 95 % or more, such as up to 100 %) of the cracked gas is not recirculated to the
inlets of the one or more catalyst containing reaction tubes.

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The skilled person is aware of processes and plants suitable for operating an ammonia
cracking plant in a state of normal operation. The description of suitable normal operating
conditions provided herein are not to be considered limiting on the processes or plant of the
invention in any way. Alternative normal operating conditions may be known to the skilled
20 person and may be suitable for combination with the processes or plant of the present
invention.

The normal operation of an ammonia cracking plant may comprise the steps of:

- 25 a) providing an ammonia feedstock stream to an inlet of one or more catalyst containing
reaction tubes disposed within a radiant section of a fired ammonia cracking reactor;
- b) cracking the ammonia in the ammonia feedstock stream to produce a cracked gas
stream comprising hydrogen (H_2), nitrogen (N_2), and residual ammonia (NH_3); and
- c) obtaining the cracked gas stream from the outlets of the one or more catalyst
30 containing reaction tubes.

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During normal operation of the ammonia cracking plant, the heat output of the fuel
combustion zone of the fired ammonia cracking reactor may be operated such that the one
or more catalyst containing reaction tubes are maintained at a temperature of 600 °C or
more, 620 °C or more, 650 °C or more, 680 °C or more, 700 °C or more, or 720 °C or more
35 as measured at the outlet of the one or more reaction tubes. During normal operation of the
ammonia cracking plant, the heat output of the fuel combustion zone of the fired ammonia
cracking reactor may be operated such that the one or more catalyst containing reaction

- tubes are maintained at a temperature of 850 °C or less, 830 °C or less, 810 °C or less, 790 °C or less, 780 °C or less, or 770 °C or less as measured at the outlet of the one or more reaction tubes. For example, during normal operation of the ammonia cracking plant, the heat output of the fuel combustion zone of the fired ammonia cracking reactor may be
- 5 operated such that the one or more catalyst containing reaction tubes are maintained at a temperature of from 600 °C to 850 °C, from 620 °C to 830 °C, from 650 °C to 810 °C, or from 680 °C to 790 °C, from 700 °C to 780 °C, or from 720 °C to 770 °C as measured at the outlet of the one or more reaction tubes, such as 730 °C, 740 °C, 750 °C, or 760 °C.
- 10 During the normal operation of the ammonia cracking plant, the one or more fuel streams used to provide the heat for the ammonia cracking reaction is not particularly limited and may comprise one or more different fuels which may be combusted with an oxygen containing feed to produce heat energy. Typically, the one or more fuel streams used to provide the heat for the ammonia cracking reaction may be a carbon-free fuel stream and/or
- 15 a carbon-containing fuel stream. As used herein the term "carbon-free fuel stream" will be understood to include combustible compounds which do not contain carbon, for instance ammonia, and/or hydrogen. As used herein the term "carbon-containing fuel stream" will be understood to include combustible compounds such as a hydrocarbon, for instance methane, ethane, propane, and/or butane. It may be preferred that the one or more fuel
- 20 streams comprises ammonia and/or hydrogen.
- The ammonia feedstock stream may be derived from any source. The ammonia feedstock stream may be produced by the catalytic combination of hydrogen and nitrogen, for example the ammonia feedstock stream may be produced from a Haber-Bosch ammonia synthesis
- 25 process. The ammonia feedstock stream may be produced in an ammonia production facility located upstream of the ammonia cracking reactor. Alternatively, the ammonia feedstock stream may be provided from an ammonia gas storage facility, an ammonia storage unit, an ammonia storage tank, or an ammonia gas pipeline.
- 30 The ammonia feedstock stream may comprise 90 mol% ammonia or more, 95 mol% ammonia or more, 97 mol% ammonia or more, or 99 mol% ammonia or more. The ammonia feedstock stream may be substantially 100 mol% ammonia. By "substantially 100 mol% ammonia" it is meant that any other component that may be present as an incidental impurity and may be present at an amount of less than 1 mol%, less than 0.5 mol%, or less than 0.1 mol% of the
- 35 ammonia feedstock stream.

During normal operation of the ammonia cracking plant, the ammonia feedstock stream may be heated prior to being supplied to the inlet of the one or more catalyst containing reaction tubes. During normal operation of the ammonia cracking plant, the ammonia feedstock stream may be heated to a temperature of greater than 350 °C, greater than 400 °C, greater than 450 °C, greater than 500 °C, or greater than 550 °C. During normal operation of the ammonia cracking plant, the ammonia feedstock stream may be heated to a temperature of less than 1000 °C, less than 950 °C, less than 850 °C, less than 750 °C, or less than 700 °C. For example, the ammonia feedstock stream may be heated to a temperature of from 350 °C to 1000 °C, from 400 °C to 950 °C, from 450 °C to 850 °C, or from 500 °C to 750 °C, such as from 550 °C to 700 °C or from 550 °C to 650 °C.

During normal operation of the ammonia cracking plant, the cracked gas stream obtained at the outlets of the one or more catalyst containing reaction tubes may have a temperature of greater than 600 °C, greater than 650 °C, greater than 670 °C, greater than 690 °C, or greater than 700 °C. During normal operation of the ammonia cracking plant, the cracked gas stream obtained at the outlets of the one or more catalyst containing reaction tubes may have a temperature of less than 900 °C, less than 850 °C, less than 800 °C, less than 770 °C, or less than 750 °C. For example, during normal operation of the ammonia cracking plant, the cracked gas stream obtained at the outlets of the one or more catalyst containing reaction tubes may have a temperature of from 600 °C to 900 °C, from 650 °C to 850 °C, from 670 °C to 800 °C, or from 690 °C to 770 °C, such as from 700 °C to 750 °C.

During normal operation of the ammonia cracking plant, the pressure at the inlets to the one or more catalyst containing reaction tubes will be set by the flowsheet design and may be in the range 1 to 100 bar absolute, preferably 10 to 90 bar absolute, such as 31 to 51 bar absolute.

The normal operation of the ammonia cracking plant may comprise the step of cracking the ammonia in the ammonia feedstock stream to produce a cracked gas stream comprising hydrogen (H₂), nitrogen (N₂), and optionally residual ammonia (e.g. unreacted ammonia, NH₃).

The cracked gas stream may comprise 60 mol% or more H₂, 65 mol% or more H₂, 70 mol% or more H₂, 72 mol% or more H₂, or 73 mol% or more H₂. The cracked gas stream may comprise up to 75 mol% or less H₂. For example, the cracked gas stream may comprise from 60 mol% to 75 mol% H₂. Preferably, the cracked gas stream comprises from 70 mol% to 75 mol% H₂, such as 72 mol% to 75 mol% H₂.

The cracked gas stream may comprise 20 mol% or more N_2 , 21 mol% or more N_2 , 22 mol% or more N_2 , or 23 mol% N_2 or more. The cracked gas stream may comprise up to 25 mol% or less N_2 . For example, the cracked gas stream may comprise from 20 mol% to 25 mol% N_2 . Preferably the cracked gas stream comprises from 22 mol% to 25 mol% N_2 , such as
5 from 23 mol% to 25 mol% N_2 .

The cracked gas stream may comprise less than 20 mol% NH_3 , less than 15 mol% NH_3 , less than 10 mol% NH_3 , less than 5 mol% NH_3 , less than 1 mol% NH_3 , or less than 0.1 mol% NH_3 . Preferably, the cracked gas stream comprises less than 4 mol% NH_3 , less than 2 mol%
10 NH_3 , less than 1 mol% NH_3 , or less than 0.1 mol% NH_3 .

Preferably, the cracked gas stream comprises an equilibrium mixture of ammonia, hydrogen, and nitrogen. In other words, the cracked gas stream preferably comprises a mixture of ammonia, hydrogen, and nitrogen at partial pressures such that no further hydrogen and
15 nitrogen may be produced from further cracking reaction. An equilibrium mixture may comprise from 72 mol% to 75 mol% H_2 , from 23 mol% to 25 mol% N_2 , and less than 4 mol% NH_3 (e.g. less than 1 mol% or less than 0.1 mol% NH_3).

The normal operation of the ammonia cracking plant may comprise the step of obtaining the
20 cracked gas from the outlets of the one or more catalyst containing reaction tubes. Typically, the temperature of the cracked gas stream being obtained from the outlets of the one or more catalyst containing reaction tubes of the ammonia cracking reactor may be greater than about 600 °C, 700 °C, 800 °C, or 900 °C. For instance, the temperature of the cracked gas stream being obtained from the outlets of the one or more catalyst containing reaction
25 tubes may be in the range of from 600 °C to 900 °C, or 700 °C to 800 °C.

During normal operation of the ammonia cracking plant, the cracked gas stream may be fed to one or more purification units, such as a pressure swing absorption unit, to produce a hydrogen stream and a tail gas stream.
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The hydrogen stream may comprise 70 mol% or more H_2 , 75 mol% or more H_2 , 80 mol% or more H_2 , 85 mol% H_2 or more, or 90 mol% H_2 or more. The hydrogen stream may comprise up to 100 mol% or less H_2 . For example, the hydrogen stream may comprise from 70 mol% to 100 mol% H_2 , from 75 mol% to 100 mol% H_2 , from 80 mol% to 100 mol% H_2 , from 85
35 mol% to 100 mol% H_2 , or from 90 mol% to 100 mol% H_2 . Preferably, the hydrogen stream may comprise greater than 90 mol% H_2 , greater than 95 mol% H_2 , greater than 98 mol% H_2 , or greater than 99 mol% H_2 . More preferably, the hydrogen stream may comprise greater

than 99.9% mol% H₂, greater than 99.95 mol% H₂, or about 100 mol% H₂. Most preferably, the hydrogen containing stream may comprise greater than 99.95 mol% H₂ or about 100 mol% H₂.

- 5 The tail gas stream may comprise nitrogen (N₂), hydrogen (H₂), and residual ammonia (e.g. unreacted ammonia, NH₃). Typically, the tail gas stream may comprise from 20 mol% to 95 mol% N₂, from 45 mol% to 85 mol% N₂, or from 65 mol% to 80 mol% N₂. Typically, the tail gas stream may comprise from 10 mol% to 70 mol% H₂, such as from 20 mol% to 50 mol% H₂. It may be preferred that the tail gas stream comprises from 15 mol% to 40 mol% H₂, from
10 20 mol% H₂ to 35 mol% H₂, or from 22 mol% H₂ to 30 mol% H₂. Typically, the tail gas stream may comprise from 3 mol% to 10 mol% ammonia, from 3.2 mol% to 7 mol% ammonia, or from 3.3 mol% to 5 mol% ammonia.

- The normal operation of the ammonia cracking plant may comprise the step of combining
15 the cracked gas stream with an oxygen containing feed and combusting the cracked gas stream with the oxygen containing feed to produce a combusted gas stream.

- The oxygen containing feed is not particularly limited and may suitably be air, oxygen, oxygen-enriched air, a mixture of nitrogen and oxygen, or a tail gas from a gas turbine (such
20 as that disclosed by WO2024018169A1).

- The normal operation of the ammonia cracking plant may comprise the step of using the combusted gas stream to drive a gas turbine to produce an oxygen containing off-gas stream. The oxygen containing off-gas stream is therefore the exhaust gas from the gas turbine.

- 25 As the gas turbine is driven, the gas turbine may be used to produce energy, for instance electrical energy and/or mechanical energy. The gas turbine may produce energy directly or indirectly. For instance, the gas turbine may be coupled to any suitable generator for the creation of electrical energy (i.e. electricity), and/or the gas turbine may be coupled to a
30 compressor for the creation of mechanical energy. Alternatively, the gas turbine may produce electrical energy or mechanical energy directly.

- The gas turbine which may find use in the normal operation of the ammonia cracking plant may be any suitable type of gas turbine. The combustion of the cracked gas stream with the
35 oxygen containing feed to produce the combusted gas stream may take place in a gas turbine combustion zone. The gas turbine combustion zone may be incorporated within the gas

turbine or may be external to the gas turbine. Typically, the gas turbine combustion zone may be incorporated within the gas turbine.

5 The process of the first aspect of the invention will now be described in further detail. Typically, the process of the first aspect of the invention may be applied to an ammonia cracking plant at normal operation, such as a plant at normal operation as described hereinabove.

10 The process of the first aspect of the invention comprises the step of decreasing a flowrate of an ammonia feedstock stream to the inlet of the one or more catalyst containing reaction tubes disposed within the radiant section of the ammonia cracking reactor.

15 The flowrate of the ammonia feedstock stream may be decreased to 40 % or less, to 35 % or less, to 30 % or less, or to 25 % or less relative to the flowrate of the ammonia feedstock stream where the ammonia cracking plant is producing 100 % of maximum molar hydrogen output. The lower limit to which the flowrate of the ammonia feedstock stream may be decreased is not particularly limit and may be 0 % or more (e.g. 1 % or more, 2 % or more, 3 % or more, or 5 % or more) relative to the flowrate of the ammonia feedstock stream where the ammonia cracking plant is producing 100 % of maximum molar hydrogen output. In certain processes of the invention the flowrate of the ammonia feedstock stream may be terminated. For example, the flowrate of the ammonia feedstock stream may be decreased to from 0 % to 40 %, from 1 % to 35 %, from 2 % to 30 %, or from 5 % to 25 % of the flowrate of the ammonia feedstock stream where the ammonia cracking plant is producing 100 % of maximum molar hydrogen output.

25 As will be understood, the step of decreasing the flowrate of the ammonia feedstock stream may occur in response to a reduction or cessation of the demand for energy and consequently hydrogen gas (e.g. hydrogen gas contained in the cracked gas stream). Such a reduction or cessation may occur at times of low energy demand. For example, where the energy is electrical energy, produced by (e.g.) a gas turbine, which is being fed to a domestic power grid, the demand for electrical energy may reduce at night.

The process of the first aspect of the invention comprises the step of decreasing the heat output of the fuel combustion zone of the ammonia cracking reactor.

35 The heat output of the fuel combustion zone of the ammonia cracking reactor may be decreased to 5 % or more, 8 % or more, 10 % or more, or 12 % or more of the maximum heat output of the fuel combustion zone. The heat output of the fuel combustion zone of the

ammonia cracking reactor may be decreased to 40 % or less, 35 % or less, 30 % or less, or 25 % or less of the maximum heat output of the fuel combustion zone. For example, the heat output of the fuel combustion zone of the ammonia cracking reactor may be decreased to from 5 % to 40 %, from 8 % to 35%, from 10 % to 30 %, or from 12 % to 25 % of the maximum heat output of the fuel combustion zone, such as 18 %, 20 %, or 22 % of the maximum heat output of the fuel combustion zone.

The heat output of the fuel combustion zone of the ammonia cracking reactor may be decreased such that the cracked gas stream at the outlets of the one or more catalyst containing reaction tubes may have a temperature of greater than 600 °C, greater than 650 °C, greater than 670 °C, greater than 690 °C, or greater than 700 °C. The heat output of the fuel combustion zone of the ammonia cracking reactor may be decreased such that the cracked gas stream at the outlets of the one or more catalyst containing reaction tubes may have a temperature of less than 900 °C, less than 850 °C, less than 800 °C, less than 770 °C, or less than 750 °C. For example, the heat output of the fuel combustion zone of the ammonia cracking reactor may be decreased such that the cracked gas stream at the outlets of the one or more catalyst containing reaction tubes may have a temperature of from 600 °C to 900 °C, from 650 °C to 850 °C, from 670 °C to 800 °C, or from 690 °C to 770 °C, such as from 700 °C to 750 °C. The temperature of the cracked gas being recirculated may be the temperature of the cracked gas being obtained from the outlets of the one or more catalyst containing reaction tubes.

As will be understood by the skilled person, in the process of the first aspect of the invention the one or more fuel streams being fed to the fuel combustion zone of the ammonia cracking reactor may be the same or different to those used when the ammonia cracking plant is in a state of normal operation. For instance, it may be advantageous for the one or more fuel streams supplied to the fuel combustion zone to comprise methane in the process of the first aspect of the invention, in particular where (for example) the one or more fuel streams comprise ammonia and/or hydrogen when the ammonia cracking plant is in a state of normal operation. Accordingly, the process of the first aspect of the invention may comprise the step of supplementing or changing the one or more fuel streams being fed to the fuel combustion zone.

The process of the first aspect of the invention comprises the step of obtaining the cracked gas stream from the outlets of the one or more catalyst containing reaction tubes.

The cracked gas stream may be a cracked gas stream having a composition as defined hereinabove in relation to the normal operation of the ammonia cracking plant.

5 The cracked gas stream obtained from the outlets of the one or more catalyst containing reaction tubes may have a temperature of 600 °C, greater than 650 °C, greater than 670 °C, greater than 690 °C, or greater than 700 °C. The cracked gas stream obtained from the outlets of the one or more catalyst containing reaction tubes may have a temperature 900 °C, less than 850 °C, less than 800 °C, less than 770 °C, or less than 750 °C. For example, the cracked gas stream obtained from the outlets of the one or more catalyst containing
10 reaction tubes may have a temperature of from 600 °C to 900 °C, from 650 °C to 850 °C, from 670 °C to 800 °C, or from 690 °C to 770 °C, such as from 700 °C to 750 °C.

The process of the first aspect of the invention comprises the step of cooling the cracked gas stream.

15 The cracked gas stream may be cooled to a temperature of 130 °C or less, 120 °C or less, 115 °C or less, or 110 °C or less. The cracked gas stream may be cooled to a temperature of 20 °C or more, 25 °C or more, 30 °C or more, or 35 °C or more. For example, the cracked gas stream may be cooled to a temperature of 20 °C to 130 °C, 25 °C to 120 °C, 30 °C to
20 115 °C, or 35 °C to 110 °C, such as 45 °C, 55 °C, 65 °C, or 75 °C.

The step of cooling the cracked gas stream may be accomplished in any number of ways. For example, the cracked gas stream may be cooled by heat exchange with water to produce steam (e.g. intermediate pressure steam), and/or the cracked gas stream may be
25 cooled by heat exchange with one or more process fluids (e.g. cooling water, the oxygen containing stream and/or the one or more fuel streams being fed to the fuel combustion zone of the ammonia cracking reactor, and/or the cracked gas stream of step vi) of the process of the first aspect of the invention).

30 The cracked gas stream is cooled to allow the pressure of the cracked gas stream to be increased in a following step. Compressors used to increase the pressure of hydrogen containing gas streams, such as the cracked gas stream of the invention, must not exceed a temperature of 135 °C, as required by API standard 618.

35 The process of the first aspect of the invention comprises the step of increasing the pressure of the cracked gas stream.

The pressure of the cracked gas stream may be increased to a pressure of 10 bar absolute or more, 20 bar absolute or more, 25 bar absolute or more, or 31 bar absolute or more. The pressure of the cracked gas stream may be increased to a pressure of 100 bar absolute or less, 90 bar absolute or less, 70 bar absolute or less, or 51 bar absolute or less. For

5 example, the pressure of the cracked gas stream may be increased to a pressure of from 10 to 100 bar absolute, from 20 to 90 bar absolute, from 25 to 70 bar absolute, or from 31 to 51 bar absolute, such as 40 bar absolute or 45 bar absolute.

10 The pressure of the cracked gas stream may be increased using any suitable method known in the art. For example, the pressure of the cracked gas may be increased using a pump or a compressor, such as a reciprocating compressor or a centrifugal compressor.

15 The process of the first aspect of the invention comprises the step of heating the cracked gas stream.

The cracked gas stream may be heated to a temperature of 650 °C or more, 675 °C or more, 690 °C or more, or 700 °C or more. The cracked gas stream may be heated to a temperature of 900 °C or less, 850 °C or less, 800 °C or less, or 775 °C or less. For example, the cracked gas stream may be heated to a temperature of from 650 °C to 900 °C, 20 from 675 °C to 850 °C, from 690 °C to 800 °C, or from 700 °C to 775 °C, such as 720 °C or 750 °C.

25 The cracked gas stream may be heated to a temperature in step vi) as described above in one or more stages. The cracked gas stream may be heated by one or more of the methods described hereinbelow.

The cracked gas stream may be heated using steam recovered from the step of cooling the cracked gas stream. Typically, where the cracked gas stream may be heated using steam recovered from the step of cooling the cracked gas stream, the cracked gas stream may be 30 heated to a temperature of from 100 °C to 450 °C, or from 200 °C to 300 °C, such as 250 °C.

35 The cracked gas stream may be heated by heat exchange with the flue gas from the ammonia cracking reactor. Preferably, the cracked gas stream may be heated by heat exchange with the flue gas from the ammonia cracking reactor in the flue duct of the ammonia cracking reactor. Typically, the cracked gas stream may be heated by heat exchange with the flue gas from the ammonia cracking reactor to a temperature of from 350 °C to 650 °C, from 400 °C to 600 °C, or from 450 °C to 550 °C, such as 500 °C.

As will be understood, the cracked gas stream may be heated by heat output from the fuel combustion zone, as described hereinabove. That is, the cracked gas stream may be heated as it passes through the one or more catalyst containing reaction tubes by heat output from
5 the fuel combustion zone (e.g. as described in step viii) of the process).

In preferred processes of the first aspect of the invention, the cracked gas stream may be heated using an auxiliary heater.

10 The auxiliary heater may generate heat for heating the cracked gas stream by combustion of an auxiliary fuel stream with an oxygen containing feed. The auxiliary fuel stream may be any combustible fuel. For example, the auxiliary fuel stream may be ammonia, hydrogen, and/or a hydrocarbon fuel (e.g. methane, ethane, propane, butane etc.). Preferably, the auxiliary fuel stream may be the same as the one or more fuel streams used in the fuel
15 combustion zone of the ammonia cracking reactor. More preferably, the one or more fuel streams of the ammonia cracking reactor and the auxiliary fuel stream may comprise ammonia.

The oxygen containing feed used for combustion of the auxiliary fuel stream may suitably be
20 air, oxygen, or oxygen-enriched air.

The combustion of the auxiliary fuel stream with the oxygen containing feed generates an auxiliary flue gas.

25 Typically, where the auxiliary heater generates heat by combustion of the auxiliary fuel stream, the cracked gas stream may be heated by heat exchange (e.g. convection heating) with the auxiliary flue gas. Alternatively or additionally, the cracked gas stream may be heated by direct (e.g. radiant heating) heating from combustion of the auxiliary fuel stream.

30 The auxiliary heater may be any suitable fired heater known to the skilled person. Auxiliary heaters may be smaller and simpler in design than the fuel combustion zone of the ammonia cracking reactor and may be operated at high turndowns with high efficiencies.

Where the auxiliary heater generates heat by combustion of the auxiliary fuel stream, the
35 auxiliary heater may be arranged to generate heat in the flue duct of the ammonia cracking reactor. The auxiliary heater may combust the auxiliary fuel stream in the flue duct of the ammonia cracking reactor.

Alternatively, the auxiliary heater may be arranged outside of the flue duct and combust the auxiliary fuel stream outside of the flue duct of the ammonia cracking reactor. Here, the auxiliary heater may provide heat to the cracked gas stream by direct or indirect heat exchange with the auxiliary flue gas. For example, the auxiliary heater may provide heat to the cracked gas stream by direct heat exchange with the auxiliary flue gas *via* a heat exchanger. For example, the auxiliary heater may heat the cracked gas stream indirectly using an intermediate fluid (e.g. air or water vapour), wherein the intermediate fluid may be heated by heat exchange with the auxiliary flue gas and/or by direct heating from combustion of the auxiliary fuel stream.

In preferred processes of the invention the auxiliary heater may generate heat for heating the cracked gas stream by combustion of an ammonia containing auxiliary fuel stream with the oxygen containing feed, and the auxiliary heater may be arranged to generate heat in the flue duct of the ammonia cracking reactor.

It is an advantage that the auxiliary heater combusts an ammonia containing auxiliary fuel stream. In particular, it is an advantage that the auxiliary heater combusts an ammonia containing auxiliary fuel stream where the one or more fuel streams, combusted in the fuel combustion zone of the ammonia cracking reactor, comprise an ammonia containing fuel stream. This is because any gas treatment systems used to treat the flue gas from the ammonia cracking reactor may also be used to treat the auxiliary flue gas from the auxiliary heater, for example catalytic N_2O and NO_x abatement systems, and/or afterburners.

Alternatively or additionally, the auxiliary heater may be an auxiliary electrical heater configured to generate heat for heating the cracked gas stream. For example, the auxiliary electrical heater may be an induction heater, a microwave heater, or comprise one or more heating elements configured to generate heat for heating the cracked gas stream. Where the auxiliary heater is an auxiliary electrical heater, the auxiliary heater may be arranged to heat the cracked gas stream upstream of the inlet of the one or more catalyst containing reaction tubes (e.g. on a process line feeding the cracked gas stream to the inlet of the one or more catalyst containing reaction tubes, outside of the ammonia cracking reactor).

The process of the first aspect of the invention comprises the step of recirculating the cracked gas stream to the inlet of the one or more catalyst containing reaction tubes.

The cracked gas stream may be recirculated at a volumetric flowrate of 70% or less, 60 % or less, 50 % or less or 45 % or less relative to the volumetric flowrate of the ammonia feedstock stream where the ammonia cracking plant is producing 100 % of maximum molar hydrogen output. The cracked gas stream may be recirculated at a volumetric flowrate of 5 % or more, 10 % or more, 20 % or more, or 30 % or more relative to the volumetric flowrate of the ammonia feedstock stream where the ammonia cracking plant is producing 100 % of maximum molar hydrogen output. For example, the cracked gas stream may be recirculated at a volumetric flowrate of from 5 % to 70 %, from 10 % to 60 %, from 15 % to 50 %, or from 20 % to 45 % relative to the volumetric flowrate of the ammonia feedstock stream where the ammonia cracking plant is producing 100 % of maximum molar hydrogen output, such as 30 %, 35 %, or 40 %.

The process of the first aspect of the invention comprises the step of passing the cracked gas stream through the one or more catalyst containing reaction tubes.

The step of passing the cracked gas stream through the one or more catalyst containing reaction tubes functions to heat the catalyst in the catalyst containing reaction tubes. In other words, the cracked gas stream functions as a heat transfer fluid to provide heat to, and maintain heat in, the catalyst of the catalyst containing reaction tubes.

The process of the first aspect of the invention may comprise repeating, or continuing to operate, steps iii) through viii) of the process of the first aspect of the invention. The process of the first aspect of the invention may comprise repeating, or continuing to operate, steps iii) through viii) of the process of the first aspect of the invention inclusive of any intervening steps. The process of the first aspect of the invention may comprise repeating, or continuing to operate, steps iii) through viii), and optionally any intervening steps, until such time as hydrogen demand resumes and the ammonia cracking plant may be returned to normal operation. Accordingly, the process of the first aspect of the invention may comprise operating steps i) to viii) and repeating, or continuing to operate, steps iii) through viii) of the process of the first aspect of the invention. For the avoidance of doubt, "intervening steps" include any optional and/or preferred steps described herein which may be carried out between obtaining the cracked gas stream from the outlets of the one or more and recirculating the cracked gas stream to the inlet of the one or more catalyst containing reaction tubes.

The process of the first aspect of the invention may comprise the step of removing ammonia from the cracked gas stream.

Ammonia may be removed from the cracked gas stream by any means known in the art. For example, ammonia may be removed from the cracked gas stream by scrubbing with water in a scrubber, or ammonia may be removed from the cracked gas stream by adsorption.

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The step of removing ammonia from the cracked gas stream may suitably be carried out after the step of cooling the cracked gas stream, and before the step of increasing the pressure of the cracked gas stream.

- 10 Advantageously, the step of removing ammonia from the cracked gas stream prevents the condensation of ammonia, for example in pumping equipment, which may cause damage due to corrosive nature of ammonia. Moreover, removing ammonia from the cracked gas stream prevents further endothermic decomposition of ammonia in the one or more catalyst containing reaction tubes, thereby preventing cooling of the one or more catalyst containing
- 15 reaction tubes and the catalyst therein.

- In the process of the first aspect of the invention, it may be advantageous for the ammonia cracking plant to generate some cracked gas which may be used to, for example, provide power to the ammonia cracking plant itself and its associated facilities. As such, further
- 20 ammonia feedstock stream may be supplied to, and cracked in, the ammonia cracking reactor to replenish cracked gas which may be removed from the ammonia cracking plant. As will be understood, the amount of the ammonia feedstock stream supplied to the ammonia cracking reactor may be decreased to a flowrate as described hereinabove.

- 25 Accordingly, the process of the first aspect of the invention may comprise the step of combining the ammonia feedstock stream with the cracked gas stream. The process of the first aspect of the invention may comprise the step of cracking ammonia in the cracked gas stream in the one or more catalyst containing reaction tubes. The process of the first aspect of the invention may comprise the step of combining the ammonia feedstock stream with the
- 30 cracked gas stream and cracking the ammonia in the cracked gas stream in the one or more catalyst containing reaction tubes. The step of combining the ammonia feedstock stream with the cracked gas stream may occur before the step of recirculating the cracked gas stream to the inlet of the one or more catalyst containing reaction tubes.

- 35 The process of the first aspect of the invention may comprise the step of removing a portion of the cracked gas stream. The portion of the cracked gas stream may be removed to a further processing step, for example to a purification step (e.g. a pressure swing adsorption

unit), a combustion step to produce heat energy, or a combustion step to produce electrical energy (e.g. in a gas turbine).

The process of the first aspect of the invention may comprise the step of placing the ammonia cracking plant into a turndown state. The ammonia cracking plant in a turndown state is an ammonia cracking plant which has operated the process of the first aspect of the invention. Preferably, the ammonia cracking plant in a turndown state may be an ammonia cracking plant which has operated steps i) to viii) of the process of the first aspect of the invention and is repeating, or continuing to operate, steps iii) through viii) of the process of the first aspect of the invention. Accordingly, the process of the first aspect of the invention may be a process for controlling an ammonia cracking plant to place the ammonia cracking plant into a turndown state. The ammonia cracking plant in a turndown state may be an ammonia cracking plant where most (e.g. 70% or more, 80 % or more, 90 % or more, or 95 % or more, such as up to 100 %) of the cracked gas obtained from the outlet of the one or more catalysts containing reaction tubes is recirculated to the inlets of the one or more catalyst containing reaction tubes.

In a second aspect of the invention there is provided an ammonia cracking plant in a turndown state.

The ammonia cracking plant in a turndown state is an ammonia cracking plant which has operated the process of the first aspect of the invention. The ammonia cracking plant in the turndown state may be an ammonia cracking plant which has operated steps i) to viii) of the process of the first aspect of the invention and is repeating, or continuing to operate, steps iii) through viii) of the process of the first aspect of the invention. Accordingly, features which have been described in relation to the process of the first aspect of the invention may be incorporated into the system of the second aspect of the invention.

The ammonia cracking plant in the turndown state may be configured to:

- i) decrease a flowrate of an ammonia feedstock stream to an inlet of one or more catalyst containing reaction tubes disposed within a radiant section of the ammonia cracking reactor;
- ii) decrease the heat output of a fuel combustion zone of the ammonia cracking reactor;
- iii) obtain a cracked gas stream from an outlet of the one or more catalyst containing reaction tubes;
- iv) cool the cracked gas stream;

- v) increase the pressure of the cracked gas stream;
- vi) heat the cracked gas stream;
- vii) recirculate the cracked gas stream to the inlet of the one or more catalyst containing reaction tubes; and
- 5 viii) pass the cracked gas stream through the one or more catalyst containing reaction tubes.

The ammonia cracking plant in the turndown state of the second aspect of the invention may be configured to carry out steps i) and ii) and to repeat, or continue to operate, steps iii) through viii), above. For example, the ammonia cracking plant in the turndown state may be configured to carry out steps i) and ii) and to repeat, or continue to operate, steps iii) through viii) to maintain the ammonia cracking plant in the turndown state. The ammonia cracking plant in the turndown state may optionally be configured to carry out any of the intervening steps of the process of the first aspect of the invention. The ammonia cracking plant in a
 15 turndown state may be an ammonia cracking plant where most (e.g. 70% or more, 80 % or more, 90 % or more, or 95 % or more, such as up to 100 %) of the cracked gas obtained from the outlet of the one or more catalysts containing reaction tubes is recirculated to the inlets of the one or more catalyst containing reaction tubes.

20 In a third aspect of the invention there is provided a process for returning an ammonia cracking plant from the turndown state of the second aspect of the invention to a state of normal operation.

The process of the third aspect of the invention may proceed by increasing (e.g. gradually increasing) the ammonia feedstock stream to the one or more catalyst containing reaction tubes.
 25 tubes.

As will be understood, increasing the ammonia feedstock stream will result in the endothermic cracking of ammonia in the one or more catalyst containing reaction tubes recommencing to produce cracked gas. Accordingly:
 30

- heat energy will be absorbed from the catalyst of the one or more catalyst containing reaction tubes; and
- the amount of gas in the process (e.g. moles of gas, or pressure of gas) will increase.

To compensate for the absorption of heat, the fuel combustion zone must increase its heat output to maintain the temperature of the one or more catalyst containing reaction tubes and
 35 to support the cracking reaction. To compensate for the increase in the amount of gas in the process, cracked gas may be removed from the process.

The process of the third aspect of the invention may therefore be regarded as returning the ammonia cracking plant from the turndown state to a state of normal operation by balancing
i) the rate at which the ammonia feedstock stream is reintroduced, ii) the rate at which the
5 cracked gas stream is removed, and iii) the amount of heat which is introduced into the
process.

Accordingly, the process of the third aspect of the invention for returning the ammonia
cracking plant from the turndown state of the second aspect of the invention to the state of
10 normal operation comprises the steps of:

- i) increasing the flow of the ammonia feedstock stream to the inlet of one or more
catalyst containing reaction tubes disposed within the radiant section of the
ammonia cracking reactor; and
- 15 ii) increasing the heat output of a fuel combustion zone of the ammonia cracking
reactor;
- iii) cracking the ammonia in the ammonia feedstock stream to produce a cracked
gas stream comprising hydrogen (H_2), nitrogen (N_2), and residual ammonia
(NH_3); and
- 20 iv) obtaining the cracked gas stream from the outlets of the one or more catalyst
containing reaction tubes.

The step of increasing the flow of the ammonia feedstock stream to the inlet of the one or
more catalyst containing reaction tubes may be carried out by increasing the flowrate of the
ammonia feedstock stream incrementally. For example, it may be preferred that the flow of
25 the ammonia feedstock stream is resumed at a rate of from 0% to 5% per minute relative to
the flow of the ammonia feedstock stream where the ammonia cracking plant is producing
100 % of maximum molar hydrogen output, such as from 1% to 4% per minute or 2% to 3%
per minute relative to the flow of the ammonia feedstock stream where the ammonia
cracking plant is producing 100 % of maximum molar hydrogen output.

30 The heat output of the fuel combustion zone of the ammonia cracking reactor may be
increased to maintain the cracking reaction. The heat output of the fuel combustion zone of
the ammonia cracking reactor may be increased to maintain the ammonia cracking plant in a
state of normal operation according to one or more of the conditions described hereinabove
35 for the normal operation of the ammonia cracking plant. For example, the heat output of the
fuel combustion zone of the ammonia cracking reactor may be increased to maintain the
temperature of the one or more catalyst containing reaction tubes at from 600 °C to 850 °C,

from 620 °C to 830 °C, from 650 °C to 810 °C, or from 680 °C to 790 °C, from 700 °C to 780 °C, or from 720 °C to 770 °C as measured at the outlet of the one or more reaction tubes, such as 730 °C, 740 °C, 750 °C, or 760 °C. For example, the heat output of the fuel combustion zone of the ammonia cracking reactor may be increased to maintain the

5 temperature of the cracked gas stream at the outlet to the one or more catalyst containing reaction at from 600 °C to 900 °C, from 650 °C to 850 °C, from 670 °C to 800 °C, or from 690 °C to 770 °C, such as from 700 °C to 750 °C.

In preferred processes of the third aspect of the invention the step of increasing the flow of

10 the ammonia feedstock stream and the step of increasing the heat output of the fuel combustion zone may be carried out simultaneously.

The process of the third aspect of the invention may comprise the step of recirculating a portion of the cracked gas stream to the inlet of the one or more catalyst containing reaction

15 tubes and passing the portion of the cracked gas stream through the one or more catalyst containing reaction tubes.

The process of the third aspect of the invention may comprise the step of removing a portion of the cracked gas stream. The portion of the cracked gas stream may be removed to a

20 further processing step, for example to a purification step (e.g. a pressure swing adsorption unit), a flare step, a combustion step to produce heat energy, or a combustion step to produce electrical energy (e.g. in a gas turbine).

The amount of the cracked gas stream which is removed in the step of removing the portion

25 of the cracked gas stream may be determined by, or determine, the flow (e.g. the flowrate) of the ammonia feedstock stream to the inlet of the one or more catalyst containing tubes, for example such that the pressure at the inlet to the one or more catalyst containing reaction tubes remains in the range 1 to 100 bar absolute, preferably 10 to 90 bar absolute, such as 31 to 51 bar absolute.

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The process of the third aspect of the invention may comprise the step of decreasing the flowrate of, or terminating, the recirculation of the cracked gas stream to the inlet of the one or more catalyst containing reaction tubes. The process of the third aspect of the invention may comprise the step of decreasing the flowrate of, or terminating, the recirculation of the

35 cracked gas stream to the inlet of the one or more catalyst containing reaction tubes to bring the ammonia cracking plant to the state of normal operation.

In preferred processes of the third aspect of the invention, the process may comprise the steps of:

- i) increasing a flow of an ammonia feedstock stream to an inlet of one or more catalyst containing reaction tubes disposed within a radiant section of the ammonia cracking reactor; and
- ii) increasing the heat output of a fuel combustion zone of the ammonia cracking reactor;
- iii) cracking the ammonia in the ammonia feedstock stream to produce a cracked gas stream comprising hydrogen (H_2), nitrogen (N_2), and residual ammonia (NH_3);
- iv) obtaining the cracked gas stream from the outlets of the one or more catalyst containing reaction tubes;
- v) recirculating a portion of the cracked gas stream to the inlet of the one or more catalyst containing reaction tubes and passing the portion of the cracked gas stream through the one or more catalyst containing reaction tubes;
- vi) removing a portion of the cracked gas stream; and
- vii) decreasing the flowrate of, or terminating, the recirculation of the cracked gas stream to the inlet of the one or more catalyst containing reaction tubes once the ammonia cracking plant has returned to the state of normal operation.

Examples

Figure 2 shows a process flow diagram of an ammonia cracking plant operating a process according to the first aspect of the invention, and an ammonia cracking plant in a turndown state according to the second aspect of the invention.

Here, an ammonia cracking reactor (1) having one or more catalyst containing reaction tubes disposed in a radiant section is provided. The one or more catalyst containing reaction tubes having an inlet and an outlet. The flowrate of an ammonia feedstock stream (11) to the inlet of the one or more catalyst containing reaction tubes of the ammonia cracking reactor (1) is decreased. The heat output of a fuel combustion zone of the ammonia cracking reactor (1) is decreased by decreasing the amount of the one or more fuel streams (21) supplied to the fuel combustion zone. A cracked gas stream (101) is obtained from the outlet of the one or more catalyst containing reaction tubes of the ammonia cracking reactor (1). The cracked gas stream (101) is cooled, for example by heat exchange with water to produce steam (2), and the cooled cracked gas stream (102) passed to a pump or compressor (3) where the pressure of the cracked gas stream is increased. The cracked gas stream having an increased pressure (103) is heated, for example using an auxiliary heater (4). Optionally, the

cracked gas stream (104) is combined with the ammonia feedstock stream (11). The heated cracked gas stream (104) is recirculated to the inlet of the one or more catalyst containing reaction tubes of the ammonia cracking reactor (1) and passed through the one or more catalyst containing reaction tubes. Optionally, any ammonia in the cracked gas stream being

5 fed to the ammonia cracking reactor (1) is cracked in the one or more catalyst containing reaction tubes. Optionally, a portion of the cracked gas stream may be removed (105) and passed to a further processing step, such as to produce electrical energy by combustion to drive a gas turbine. The ammonia cracking plant in the turndown state repeats, or continues to operate, the steps of obtaining the cracked gas stream (101), cooling (2) it, increasing its

10 pressure (3), heating it (4), recirculating it, and passing it through the one or more catalyst containing reaction tubes. In doing so, the ammonia cracking plant retains the necessary heat to return the ammonia cracking plant to normal operation with a 2 hour notice period whilst not consuming ammonia feedstock or wasting hydrogen product.

Claims

1. A process for controlling an ammonia cracking plant comprising a fired ammonia cracking reactor, the process comprising the steps of:
 - 5 i) decreasing a flow of an ammonia feedstock stream to an inlet of one or more catalyst containing reaction tubes disposed within a radiant section of the ammonia cracking reactor;
 - ii) decreasing the heat output of a fuel combustion zone of the ammonia cracking reactor;
 - 10 iii) obtaining a cracked gas stream from an outlet of the one or more catalyst containing reaction tubes;
 - iv) cooling the cracked gas stream;
 - v) increasing the pressure of the cracked gas stream;
 - vi) heating the cracked gas stream;
 - 15 vii) recirculating the cracked gas stream to the inlet of the one or more catalyst containing reaction tubes; and
 - viii) passing the cracked gas stream through the one or more catalyst containing reaction tubes.
- 20 2. A process according to claim 1, wherein the flowrate of the ammonia feedstock stream is decreased to from 0 % to 40 %, from 1 % to 35 %, from 2 % to 30 %, or from 5 % to 25 % of the flowrate of the ammonia feedstock stream where the ammonia cracking plant is producing 100 % of maximum molar hydrogen output.
- 25 3. A process according to claim 1 or claim 2, wherein the heat output of the fuel combustion zone of the ammonia cracking reactor is decreased to from 5 % to 40 %, from 8 % to 35%, from 10 % to 30 %, or from 12 % to 25 % of the maximum heat output of the fuel combustion zone.
- 30 4. A process according any one of the preceding claims, wherein the heat output of the fuel combustion zone of the ammonia cracking reactor is decreased such that the cracked gas stream at the outlet of the one or more catalyst containing reaction tubes has a temperature of from 600 °C to 900 °C, from 650 °C to 850 °C, from 670 °C to 800 °C, or from 690 °C to 770 °C.
- 35 5. A process according to any one of the preceding claims, wherein the cracked gas stream comprises an equilibrium mixture of ammonia, hydrogen, and nitrogen.

6. A process according to any one of the preceding claims, wherein the cracked gas stream obtained from the outlets of the one or more catalyst containing reaction tubes has a temperature of from 600 °C to 900 °C, from 650 °C to 850 °C, from 670 °C to 800 °C, or from 690 °C to 770 °C.

7. A process according to any one of the preceding claims, wherein the cracked gas stream is cooled to a temperature of 20 °C to 130 °C, 25 °C to 120 °C, 30 °C to 115 °C, or 35 °C to 110 °C.

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8. A process according to any one of the preceding claims, wherein the pressure of the cracked gas stream is increased to a pressure of from 10 to 100 bar absolute, from 20 to 90 bar absolute, from 25 to 70 bar absolute, or from 31 to 51 bar absolute.

9. A process according to any one of the preceding claims, wherein the cracked gas stream is heated to a temperature of from 650 °C to 900 °C, from 675 °C to 850 °C, from 690 °C to 800 °C, or from 700 °C to 775 °C.

10. A process according to any one of the preceding claims, wherein the cracked gas stream is heated in step vi) in one or more stages.

11. A process according to any one of the preceding claims, wherein the cracked gas stream is heated using steam recovered from the step of cooling the cracked gas stream, with the flue gas from the ammonia cracking reactor, by heat output from the fuel combustion zone of the ammonia cracking reactor, and/or using an auxiliary heater.

12. A process according to claim 11, wherein the cracked gas stream is heated using an auxiliary heater and the auxiliary heater generates heat for heating the cracked gas stream by combustion of an ammonia containing auxiliary fuel stream with the oxygen containing feed.

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13. A process according to any one of the preceding claims, wherein the cracked gas stream is recirculated at a volumetric flowrate of from 5 % to 70 %, from 10 % to 60 %, from 15 % to 50 %, or from 20 % to 45 % relative to the volumetric flowrate of ammonia feedstock stream where the ammonia cracking plant is producing 100 % of maximum molar hydrogen output.

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14. A process according to any one of the preceding claims, wherein the process comprises repeating steps iii) through viii).
15. A process according to any one of the preceding claims, further comprising the step of removing ammonia from the cracked gas stream.
16. A process according to any one of the preceding claims, further comprising the step of combining the ammonia feedstock stream with the cracked gas stream.
17. A process according to any one of the preceding claims, further comprising the step of cracking ammonia in the cracked gas stream in the one or more catalyst containing reaction tubes.
18. A process according to any one of the preceding claims, further comprising the step of removing a portion of the cracked gas stream.
19. A process according to any one of the preceding claims, wherein the process comprises the step of placing the ammonia cracking plant into a turndown state.
20. An ammonia cracking plant in a turndown state, wherein the ammonia cracking plant has operated the process of any one of claims 1 to 19.
21. An ammonia cracking plant according to claim 20, wherein the ammonia cracking plant has operated steps i) to viii) and is repeating, or continuing to operate, steps iii) through viii) of any one of claims 1 to 19.
22. An ammonia cracking plant in a turndown state, wherein the ammonia cracking plant in the turndown state is configured to:
- i) decrease a flowrate of an ammonia feedstock stream to an inlet of one or more catalyst containing reaction tubes disposed within a radiant section of the ammonia cracking reactor;
 - ii) decrease the heat output of a fuel combustion zone of the ammonia cracking reactor;
 - iii) obtain a cracked gas stream from an outlet of the one or more catalyst containing reaction tubes;
 - iv) cool the cracked gas stream;
 - v) increase the pressure of the cracked gas stream;

- vi) heat the cracked gas stream;
- vii) recirculate the cracked gas stream to the inlet of the one or more catalyst containing reaction tubes; and
- viii) pass the cracked gas stream through the one or more catalyst containing reaction tubes.
- 5
23. A process for returning an ammonia cracking plant from the turndown state any one of claims 20 to 22 to a state of normal operation.
- 10 24. A process according to claim 23 comprising the steps of:
- i) increasing a flow of an ammonia feedstock stream to an inlet of one or more catalyst containing reaction tubes disposed within a radiant section of the ammonia cracking reactor; and
- 15 ii) increasing the heat output of a fuel combustion zone of the ammonia cracking reactor;
- iii) cracking the ammonia in the ammonia feedstock stream to produce a cracked gas stream comprising hydrogen (H₂), nitrogen (N₂), and residual ammonia (NH₃); and
- 20 iv) obtaining the cracked gas stream from the outlets of the one or more catalyst containing reaction tubes.
- 25 25. A process according to claim 24, wherein the process comprises the further steps of:
- v) recirculating a portion of the cracked gas stream to the inlet of the one or more catalyst containing reaction tubes and passing the portion of the cracked gas stream through the one or more catalyst containing reaction tubes;
- 25 vi) removing a portion of the cracked gas stream; and
- vii) decreasing the flowrate of, or terminating, the recirculation of the cracked gas stream to the inlet of the one or more catalyst containing reaction tubes to bring the ammonia cracking plant to the state of normal operation.
- 30 26. A process according to any one of claims 23 to 25, wherein the normal operation of the ammonia cracking plant comprises the steps of:
- a) providing an ammonia feedstock stream to an inlet of one or more catalyst containing reaction tubes disposed within a radiant section of a fired ammonia cracking reactor;
- 35 b) cracking the ammonia in the ammonia feedstock stream to produce a cracked gas stream comprising hydrogen (H₂), nitrogen (N₂), and residual ammonia (NH₃); and

- c) obtaining the cracked gas stream from the outlets of the one or more catalyst containing reaction tubes.