

DESCRIPTION

METHOD AND SYSTEM FOR OBTAINING A HYDROGEN-CONTAINING PRODUCT USING AMMONIA

5

[0001] The invention relates to a method and a system for producing a hydrogen-containing product using ammonia.

BACKGROUND OF THE INVENTION

10

[0002] Ammonia (NH_3) can be catalytically broken down (cracked, reformed) according to $2 \text{NH}_3 \rightarrow \text{N}_2 + 3 \text{H}_2$ to form nitrogen (N_2) and hydrogen (H_2). The reaction is endothermic and is favored by low pressure and high temperature. However, to avoid a hydrogen compressor, higher pressures are desirable.

15

[0003] The main reaction products, hydrogen and nitrogen, can be provided in a mixture as a product, or the hydrogen can be purified. A hydrogen-nitrogen mixture is also referred to here as forming gas. The hydrogen or hydrogen-nitrogen mixture can also be used for other purposes - for example, in a gas turbine coupled to a generator. In all cases, which may correspond to embodiments of the invention, hydrogen is obtained from ammonia. In the sense understood here, "producing a hydrogen-containing product" does not exclude producing a hydrogen-containing gas mixture, other products such as nitrogen, and/or subsequent use.

25

[0004] Different method concepts and reactors for the breakdown of ammonia into hydrogen and nitrogen are described in the patent and non-patent literature. For further details, reference is made to relevant literature - for example, to D. Sima et al., Int. J. Hydrogen Energy 45 (2020) 9342-9352.

30

[0005] Corresponding method concepts can include a reaction unit (also called an ammonia cracker) similar to a reforming reactor, to which a pressure swing

adsorption is assigned for hydrogen purification. For example, reference is made in this connection to EP 4 112 539 A1 and EP 4 112 540 A1. These concepts use a catalyst for the cracking reaction.

- 5 [0006] Typical catalysts are either nickel-based catalysts, which must be operated at minimum temperatures of more than 700°C to be sufficiently active to achieve economically viable conversion rates, or noble-metal-based catalysts (such as ruthenium, platinum or palladium), whose minimum temperatures are below 650°C. Catalysts based on iron, cobalt or nickel as
10 solid material are currently still under development.

- [0007] Operating an ammonia cracker at temperatures below 650°C is energy-efficient, but requires a noble-metal-based catalyst, which is significantly more expensive than a nickel-based catalyst. If these less expensive, nickel-based
15 coated catalysts are to be used, the operating temperature must be increased to over 700°C to achieve sufficient activity. The first part of the catalyst bed (from the inlet) is less active because the temperatures are still low here. A sufficiently high temperature is usually only reached further along the catalyst bed.

- 20 [0008] Both options therefore have at least one disadvantage that leads to increased operating costs: high catalyst costs (noble metal) or higher temperatures (nickel).

- [0009] Operation at temperatures above 600°C and high ammonia partial
25 pressure further increases the risk that the material stability of the reactor material will be reduced due to nitridation effects.

- [0010] The present invention has the object of improving corresponding processes and plants for producing a hydrogen product using ammonia and,
30 in particular, to make them more efficient.

DISCLOSURE OF THE INVENTION

[0011] Against this background, a process and a plant for producing a hydrogen-containing product with the features of the independent claims are proposed. Embodiments are the subject matter of the dependent claims and
5 of the following description.

[0012] An ammonia cracker is proposed that has a reactor with at least two catalyst regions, wherein in a first region, which is at the inlet side of the reactor, a catalyst containing a noble metal is used. In a second catalyst region,
10 which is downstream of the first catalyst region, i.e., closer to the reactor outlet, catalysts with a non-noble metal, for example cobalt or nickel, are used. The temperature of the catalyst in the ammonia cracker increases from an inlet to an outlet.

15 [0013] This advantageously makes it possible to achieve a high ammonia conversion and increase the efficiency of the ammonia cracker.

[0014] Furthermore, the amount of expensive catalysts containing a noble metal is reduced, since only a portion of the entire catalyst bed in the reactor
20 needs to be equipped therewith. Nevertheless, high catalyst activity is also present in a part of the catalyst bed with temperatures below 800°C.

[0015] Additionally, the costs of the ammonia cracker can be optimized, since, for example, a smaller reactor wall thickness is necessary because a high
25 temperature does not have to be maintained over the entire reactor region. This also allows for a more compact reactor design, meaning it can be installed in large plants with limited space.

[0016] Furthermore, the risk of nitridation can advantageously be reduced at
30 medium temperatures by the high activity of catalysts containing a noble metal. When used, ammonia is split into nitrogen and hydrogen at temperatures of around 600°C. Nitridation takes place at temperatures above 600°C. Since the

partial pressure of ammonia is reduced by cracking in the first catalyst region, the nitridation potential decreases in the subsequent catalyst regions, which are operated at higher temperatures. Nitriding, which is a type of corrosion effect, negatively impacts the stability of the reactor material above 600°C.

- 5 Cost savings are possible due to lower stability requirements for the material used in the reactor. This not only saves production costs for the reactor, but also further reduces maintenance and repair costs.

[0017] In other words, the proposed method for producing a hydrogen-containing product comprises reacting ammonia in an ammonia cracker to which heat is supplied. The ammonia cracker has a catalyst bed with at least two catalyst segments, wherein in a first catalyst segment the ammonia is reacted at a first minimum temperature using a first catalyst and in a second catalyst segment, which is downstream of the first catalyst segment, the ammonia is reacted at a second minimum temperature using a second catalyst.

[0018] The first minimum temperature is, in particular, lower than the second minimum temperature, and the temperature in the catalyst bed and/or the ammonia gas increases in the direction from the inlet to the outlet of the reactor, i.e., in the direction of flow. At the inlet of the catalyst bed, the first minimum temperature is, in particular, at least 450°C, at least 525°C or at least 600°C, and at most 650°C or at most 625°C, whereas the second, and, in the case of more than two catalyst regions, the further (third, fourth, ...), minimum temperature(s), is/are, in particular, at least 700°C, at least 800°C or at least 850°C, and at most 950°C or at most 925°C.

[0019] In one embodiment, the catalyst arranged in the first catalyst segment contains or consists of a noble metal, in particular ruthenium. The ammonia cracking reaction with a noble metal catalyst can be carried out at lower temperatures, which saves on operating costs as well as on design costs for the ammonia cracker. Furthermore, nitridation is still low at these temperatures

and the partial pressure of ammonia in the later catalyst segments is reduced, thus reducing investment costs.

5 [0020] In one embodiment, the catalyst arranged in the second catalyst segment contains or consists of iron, cobalt or nickel. In contrast to catalysts based on noble metals, the costs for catalysts based on iron, cobalt or nickel are lower, so production costs for the ammonia cracker can advantageously be reduced.

10 [0021] In one embodiment, the ammonia cracker has a heatable inert packed bed upstream of the first catalyst segment, i.e., upstream of the first catalyst segment. By means of the inert packed bed, ammonia can be introduced into the ammonia cracker at low temperatures and is brought to the high temperature required for the reaction only within the ammonia cracker by the
15 heated inert packed bed.

[0022] As a result, when designing the method and the system for carrying out the method, the high temperature of the ammonia only has to be taken into account in the design of the ammonia cracker itself and not in upstream
20 components, thereby allowing investment costs to be reduced.

[0023] In one embodiment, the catalyst bed has at least three catalyst segments, wherein in a third catalyst segment, which is downstream of the second catalyst segment, ammonia is reacted at a third minimum temperature
25 using a third catalyst.

[0024] By using further catalyst segments, the cracking reaction can be adapted to the composition of the ammonia gas predominant in each catalyst segment, thereby optimizing the design costs for the ammonia cracker and the
30 efficiency of the ammonia cracking reaction.

[0025] In one embodiment, the catalyst in the first catalyst segment contains or consists of a noble metal, in particular ruthenium, and the catalyst in the second catalyst segment contains nickel, wherein the proportion of nickel is at least 10 wt.% or at least 25 wt.% or at least 40% or 60 wt.%, and the catalyst
5 in the third catalyst segment contains nickel, wherein the proportion of nickel is at most 5 wt.% or at most 10 wt.% or at most 15 wt.%. The remaining proportion by weight is attributable to the support material on which the catalyst material is applied.

10 [0026] In an alternative embodiment, the catalyst in the first catalyst segment contains or consists of a noble metal, in particular ruthenium, the catalyst in the second catalyst segment contains or consists of cobalt, and the catalyst in the third catalyst segment contains nickel. In this way, the design of the catalyst bed can be further optimized.

15

[0027] The invention further relates to a system for producing a hydrogen-containing product, wherein the system is configured to react ammonia in the ammonia cracker to produce unreacted ammonia as well as ammonia gas containing hydrogen and nitrogen.

20

[0028] The ammonia cracker has a reactor with at least two segments, wherein in a first segment a fraction of the ammonia is reacted at a first temperature using a first catalyst, and in a second segment, which is downstream of the first segment, a further portion of the ammonia is reacted at a second
25 temperature using a second catalyst. The system is, in particular, configured to carry out the method according to any of the preceding embodiments.

[0029] For further features and advantages of a corresponding system and embodiments thereof, reference is expressly made to the above explanations
30 relating to the method proposed according to the invention and its embodiments, since they apply in the same way here.

BRIEF DESCRIPTION OF THE DRAWING

[0030] Embodiments of the invention will be described below purely by way of example with reference to the accompanying drawing and explanation of the technical background.

[0031] Fig. 1 illustrates a method or a system according to an embodiment of the present invention, and
Fig. 2 shows a catalyst bed with three catalyst segments and an associated temperature profile in the catalyst bed.

EMBODIMENTS OF THE INVENTION

[0032] The embodiments described below are described solely for the purpose of assisting the reader in understanding the features claimed and previously discussed. They are merely representative examples and are not intended to be considered to be exhaustive and/or limiting with respect to the features of the invention. It goes without saying that the advantages, embodiments, examples, functions, features, structures and/or other aspects described above and below are not to be considered to limit the scope of the invention as defined in the claims, or to limit equivalents to the claims, and that other embodiments may be used and changes made without departing from the scope of the claimed invention.

[0033] Different embodiments of the invention may comprise, have, consist of, or substantially consist of further expedient combinations of the described elements, components, features, parts, steps, means, etc., even if such combinations are not specifically described herein. Furthermore, the disclosure may comprise other inventions that are presently not claimed, but which may be claimed in the future, in particular when included in the scope of the independent claims.

[0034] Explanations relating to devices, apparatuses, arrangements, systems, etc. according to embodiments of the present invention may also apply to procedures, processes, methods, etc. according to the embodiments of the present invention, and vice versa. Elements, method steps, etc. that are
5 identical, have the same effect, correspond in terms of their function, are structurally identical or have a similar structure can be indicated by identical reference signs.

[0035] Fig. 1 illustrates a system 100 according to an embodiment of the
10 present invention. Fig. 2 shows a catalyst bed with three catalyst segments 20a, 20b, 20c and an associated temperature profile in the catalyst bed.

[0036] In the embodiment illustrated here, an ammonia feedstock 1, e.g., from a tank, is pressurized if necessary by means of a pump and is evaporated and
15 superheated in a pretreatment unit 10. The vaporized and superheated ammonia 2 is supplied to an ammonia cracker 20. A raw gas or cracked gas 3 taken from the ammonia cracker 20 typically contains a certain amount of unconverted ammonia, since the thermodynamic equilibrium favors conversion at high temperature and low pressure, but under technically
20 relevant conditions the conversion is carried out at increased pressure and limited temperature.

[0037] Heat is supplied to the ammonia cracker 20, and thus to the catalyst bed and ammonia 2 in the reactor, from the outside, e.g., by combustion of a
25 fuel, to drive the endothermic reaction, wherein the coldest portion is in the inlet region and the hottest portion is at the outlet of the ammonia cracker 20. The temperature in the reactor increases from the inlet region to the outlet region of the ammonia cracker 20.

[0038] The ammonia cracker 20 has a catalyst bed with three catalyst segments 20a, 20b, 20c. Upstream of the catalyst segments, an inert packed bed (not shown), through which the ammonia 2 is brought to the temperature

necessary for the reaction, can also be provided in the ammonia cracker 20. In a first catalyst segment 20a, a fraction of the ammonia 2, which has been heated by the pretreatment unit 10 in particular to a first minimum temperature T_1 of at least 450°C or at least 525°C or at least 600°C and at most 650°C or
 5 at most 625°C, is cracked into nitrogen and hydrogen with a first catalyst made of noble metal, in particular ruthenium. The temperatures in the reactor are set so that the first catalyst is operated with high activity and/or conversion rate.

[0039] In a second catalyst segment 20b, a further fraction of the ammonia 2,
 10 which has a lower partial pressure due to the cracking in the first catalyst segment 20a, is cracked into nitrogen and hydrogen with a second catalyst. The second catalyst can, in particular, contain or consist of cobalt or nickel, wherein in the case of a nickel-based catalyst the second catalyst has a nickel content of at least 10 wt.% or at least 25 wt.% or at least 40 wt.% or 60 wt.%.
 15 Furthermore, the ammonia cracking reaction takes place in the second catalyst segment 20b at a second minimum temperature T_2 that is higher than the first minimum temperature T_1 of the first catalyst segment. The second minimum temperature T_2 is, in particular, at least 700°C or at least 800°C or at least 850°C and at most 950°C or at most 925°C. The second minimum temperature
 20 T_2 is in turn selected such that the second catalyst is operated with high activity and/or conversion rate.

[0040] In a third catalyst segment 20c, ammonia 2, which has an even lower partial pressure due to the cracking in the first catalyst segment 20a and in the
 25 second catalyst segment 20b, is cracked into nitrogen and hydrogen with a third catalyst. The third catalyst contains, in particular, nickel, wherein the nickel content is at most 5 wt.% or at most 10 wt.% or at most 15 wt.%. The third minimum temperature in the third catalyst segment 20c is particularly higher than the second minimum temperature T_2 .

30

[0041] It is also conceivable that the catalyst bed has only two catalyst segments: a first catalyst segment with a catalyst made of a noble metal and

a second catalyst segment with a catalyst made of a non-noble metal such as cobalt or nickel. Catalyst beds with more than three segments are also conceivable.

5 [0042] After a heat integration 30, the raw gas 3 is present as cooled raw gas 4. Unconverted ammonia is recovered by means of pressure swing adsorption 40 in a material stream 5, wherein the material stream 5 is a residual gas of the pressure swing adsorption 40. In the pressure swing adsorption 40, a product fraction 6 is also obtained that, in the present specific embodiment,
10 can mainly contain hydrogen and traces of nitrogen, ammonia. Water can optionally be separated with the ammonia and be part of material stream 5. Water can be present in "anhydrous" ammonia of technical grade.

[0043] In this embodiment, the residual gas from the pressure swing
15 adsorption 40, i.e., from the material stream 5, is used as an energy source in one or more burners of the ammonia cracker 20. Alternatively, it can also be used in an externally fired heater (not shown). The difference in heat demand for the endothermic reaction of the ammonia cracker 20 can be covered by the combustion of part of the raw gas 7.

Claims

1. A method (100) for producing a hydrogen-containing product, wherein ammonia (2) is reacted in an ammonia cracker (20) to which heat is supplied,
5 wherein the ammonia cracker (20) has a catalyst bed with at least two catalyst segments (20a, 20b, 20c), wherein in a first catalyst segment (20a) a fraction of the ammonia (2) is reacted at a first minimum temperature (T_1) using a first catalyst and in a second catalyst segment (20b), which is downstream of the first catalyst segment (20a), a further fraction of the ammonia (2) is converted
10 at a second minimum temperature (T_2) using a second catalyst, **characterized in that** the first minimum temperature (T_1) is lower than the second minimum temperature (T_2).
2. The method according to any of the preceding claims, wherein the
15 temperature of the catalyst bed increases in the direction from an inlet of the catalyst bed to an outlet of the catalyst bed.
3. The method according to any of the preceding claims, wherein the first
minimum temperature (T_1) is at least 450°C or at least 525°C or at least 600°C
20 and at most 650°C or at most 625°C.
4. The method according to any of the preceding claims, wherein the
second minimum temperature (T_2) is at least 700°C or at least 800°C or at
least 850°C or at most 950°C or at most 900°C.
25
5. The method according to any of the preceding claims, wherein the catalyst arranged in the first catalyst segment contains a noble metal, in particular ruthenium, platinum or palladium.
- 30 6. The method according to any of the preceding claims, wherein the catalyst arranged in the second catalyst segment contains cobalt or nickel.

7. The method according to any of the preceding claims, wherein the ammonia cracker (20) has, upstream of the first catalyst segment (20a), a heated inert packed bed.

5 8. The method according to any of the preceding claims, wherein the catalyst bed has at least three catalyst segments (20a, 20b, 20c), wherein in a third catalyst segment (20c), which is downstream of the second catalyst segment (20b), a further fraction of the ammonia (2) is reacted at a third minimum temperature using a third catalyst.

10

9. The method according to claim 8, wherein the first catalyst contains a noble metal, in particular ruthenium, wherein the second catalyst contains nickel, wherein the proportion of nickel is at least 10 wt.% or at least 25 wt.% or at least 40 wt.% or 60 wt.%, wherein the third catalyst contains nickel,
15 wherein the proportion of nickel is at most 5 wt.% or at most 10 wt.% or at most 15 wt.%.

10. The method according to claim 8, wherein the first catalyst contains a noble metal, in particular ruthenium, wherein the second catalyst contains
20 cobalt and wherein the third catalyst contains nickel.

11. A system (100) for producing a hydrogen-containing product, comprising an ammonia cracker (20), wherein the system is configured to react ammonia (2) in the ammonia cracker (20), wherein the ammonia cracker (20)
25 has a catalyst bed with at least two catalyst segments (20a, 20b, 20c), wherein the system (100) is configured to react a fraction of the ammonia (2) in a first catalyst segment (20a) at a first minimum temperature (T_1) using a first catalyst and in a second catalyst segment (20b), which is downstream of the first catalyst segment (20a), a further portion of the ammonia (2) is reacted at a
30 second minimum temperature (T_2) using a second catalyst, **characterized in that** the catalyst in the first catalyst segment (20a) has a first minimum

temperature (T_1) that is lower than the second minimum temperature (T_2) of the catalyst in the second catalyst segment (20b).

12. The system (100) according to claim 11, wherein the system (100) is
5 configured to carry out a method according to any of claims 1 to 11.