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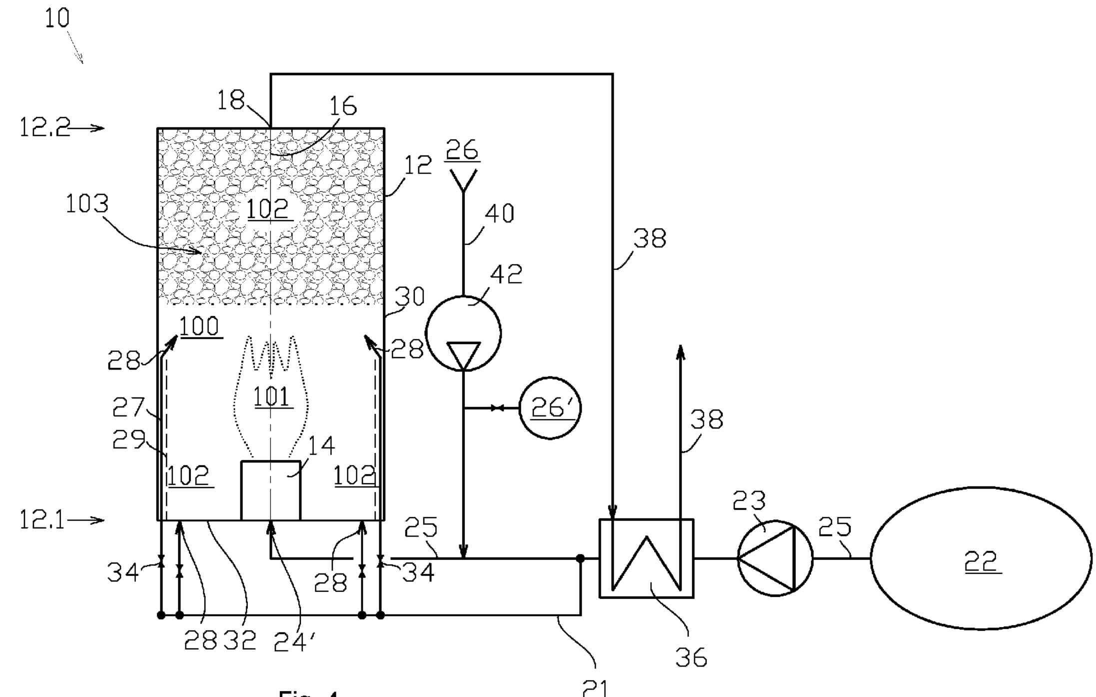

Fig. 4

(57) Abstract: Invention relates method of cracking ammonia comprising - feeding a first portion of ammonia into a burner (14) in arranged to a cracking vessel (12); - feeding gas containing oxygen to the burner (14); - combusting the first portion of ammonia forming a combustion zone (101) in the cracking vessel (12) producing heat; - feeding a second portion of ammonia into a cracking zone (102) of the cracking vessel (12) outside the combustion zone (101), and - cracking the second portion of ammonia by utilizing the heat produced by the combustion of the first portion of ammonia and producing product gas comprising hydrogen and nitrogen from the second portion of ammonia. Invention relates also to racking arrangement (10) for cracking ammonia.

WO 2024/008270 A1

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METHOD OF CRACKING AMMONIA AND A CRACKING ARRANGEMENT FOR CRACKING AMMONDIA

Technical field

[001] The present invention relates to a method of cracking ammonia and a cracking arrangement of cracking ammonia.

Background art

[002] Despite of being toxic, ammonia is considered to be a promising candidate for carbon free fuel and/or a hydrogen carrier. Excess energy in one location can be used to produce NH_3, that can be transported to locations where energy is needed. The energy in the NH_3 can be utilised by direct combustion or cracked into H_2. At high temperature, and in the presence of a suitable catalyst, ammonia is cracked into its constituent elements. Cracking of ammonia is a slightly endothermic process requiring 23 kJ/mol (5.5 kcal/mol) of ammonia and yields hydrogen and nitrogen gas.

[003] As an example of using NH_3 as hydrogen carrier and the hydrogen contained in the NH_3 it is referred to US 6936363. The document discloses a process for producing a hydrogen and nitrogen mixture from gaseous ammonia and utilizing the mixture in an alkaline fuel cell. Ammonia is fed into an ammonia cracker. Off gas from the fuel cell is fed to a heating unit of the ammonia cracker. The heating unit is either a lean gas combustor or a catalytic burner.

[004] Conventional plants for decomposing molecular compounds requires high temperature heat due to the endothermic nature of the process. The source of this energy is for small scale normally electricity, for large scale combustion of NH_3 or of fossil fuel is used, and the heat is transferred to the feed NH_3. This heat transfer is at elevated/high temperatures and sets strict requirements to the heat exchanger.

[005] An object of the invention is to provide method of and cracking arrangement for cracking ammonia in which the improvement is its simple construction and effective operation.

Disclosure of the Invention

[006] Objects of the invention can be met substantially as is disclosed in the independent claims and in the other claims describing more details of different embodiments of the invention.

[007] According to the invention a method of cracking ammonia comprises

- feeding a first portion of ammonia into a burner arranged to a cracking vessel;
- feeding gas containing oxygen into the burner;
- combusting the first portion of ammonia forming a combustion zone in the cracking vessel producing heat;
- feeding a second portion of ammonia into a cracking zone of the cracking vessel outside the combustion zone, and
- cracking the second portion of ammonia by utilizing the heat produced by the combustion of the first portion of ammonia and producing product gas comprising hydrogen and nitrogen from the second portion of ammonia.

[008] According to an aspect of the invention in the combustion zone the first portion of the ammonia is consuming the fed oxygen forming a non-oxidizing zone outside the combustion zone in the cracking vessel.

[009] According to an aspect of the invention second portion of ammonia is cracked in a presence of an ammonia cracking catalyst.

[0010] According to an aspect of the invention in the combustion zone the first portion of the ammonia is consuming the fed oxygen forming annon-oxidizing zone outside the combustion zone in the cracking vessel and the second portion of ammonia is cracked in a presence of an ammonia cracking catalyst.

[0011] According to an aspect of the invention second portion of ammonia is cracked using non-catalytic reactions.

[0012] According to an aspect of the invention the combustion zone the first portion of the ammonia is consuming the fed oxygen forming and non-oxidizing zone is formed outside the combustion zone in the cracking vessel and that second portion of ammonia is cracked using non-catalytic reactions.

[0013] According to an aspect of the invention the first portion of ammonia and the gas containing oxygen are fed as a gas mixture into the burner.

[0014] According to an aspect of the invention ammonia is preheated by transferring heat from the product gas to the gas mixture before feeding to the burner.

[0015] According to an aspect of the invention ammonia is evaporated by transferring heat from the product gas to the gas mixture before feeding to the burner.

[0016] According to an aspect of the invention the vessel has a cylindrical inner reaction space, having a diameter and a length, the length being greater than the diameter, wherein the first portion of ammonia and the gas containing oxygen are fed to a first end of the reaction space of the vessel in its longitudinal direction and the product gas is removed from a second end of reaction space of the cracking vessel.

[0017] According to an aspect of the invention the second portion of the ammonia is heated to a predetermined temperature by the heat provided by combustion of the first portion of the ammonia, and the heated second portion of the ammonia is fed in non-oxidizing conditions to the cracking catalyst.

[0018] According to an aspect of the invention the combustion zone is formed to a centre axis of the cracking vessel and at least part of the second portion of the ammonia is fed around the combustion zone from the first end of the space in the vessel.

[0019] According to an aspect of the invention at least part of the second portion of the ammonia is fed into the vessel near its side wall between a first end and a second end of space in the vessel.

[0020] According to an aspect of the invention at least part of the second portion of the ammonia is fed near wall of the vessel into the cracking zone.

[0021] According to an aspect of the invention gas containing oxygen is a mixture of NH3 and gas containing oxygen.

[0022] According to an aspect of the invention gas containing oxygen is air.

[0023] According to an aspect of the invention gas containing oxygen is pure O2.

[0024] According to an aspect of the invention the ammonia cracking catalyst is for example Nickel based catalyst, Ruthenium based catalyst, Lithium amide or Sodium amide-based catalyst.

[0025] According to an aspect of the invention the combustion zone temperature is maintained at about 800 - 1800°C.

[0026] According to an aspect of the invention temperature in the cracking zone is maintained at 350 - 800°C by combusting the first portion of ammonia in a combustion zone of the vessel.

[0027] According to an aspect of the invention amount of oxygen present in the combustion zone is controlled such that all of the oxygen is reacted with the ammonia.

[0028] According to an aspect of the invention gas containing oxygen is a mixture of NH_3 and air and air-fuel ratio in the combustion zone is rich.

[0029] According to an aspect of the invention product gas is fed from the reaction space to an oxidizer part where the product gas is oxidized by feeding oxygen containing gas into a stream of the product gas.

[0030] A cracking arrangement for cracking ammonia according to the invention comprises

a cracking vessel and a burner arranged to the cracking vessel, the burner comprising a first inlet for feeding ammonia into the burner, and a second inlet for feeding gas containing oxygen into the burner, and

an outlet for product gas in the cracking vessel, characterized in that

the cracking vessel is a cylindrical vessel where the burner is arranged at the first end of the vessel arranged to a centre axis of the vessel, and the outlet is arranged to the second end of the space of the vessel, the cracking vessel further comprising a third inlet for feeding ammonia into cracking vessel arranged near to a side wall and/or near to the first end of the space in the vessel.

[0031] According to an aspect of the invention the cracking vessel comprises an open space inside, that space comprising a combustion zone adjacent to the burner at the first end of the vessel and a cracking zone at the second end of the space in the vessel and around the burner.

[0032] According to an aspect of the invention the vessel is provided with an ammonia cracking catalytic converter in the cracking zone at the second end of the space in the vessel.

[0033] According to an aspect of the invention catalytic converter comprises at least one of a catalyst bed of loose material, a catalyst support coated with catalyst material or catalyst coat on inner surface of the vessel.

[0034] According to an aspect of the invention the third inlet comprises several inlets into the inner reaction space of the vessel arranged to an end wall at the first end of the space in the vessel around the burner.

[0035] According to an aspect of the invention the third inlet comprises several inlets arranged near a side wall of the vessel at a distance from the end wall at the first end of the space in the vessel.

[0036] According to an aspect of the invention the vessel comprises an oxidizer part, arranged downstream of the cracking zone, and the oxidizer part is provided with at least one inlet for oxygen containing gas.

[0037] The invention provides several advantageous effects. Since the basic concept is to mix both NH_3 to be cracked and combustion gases in a single vessel heat is directly mixed into the NH_3 to be cracked. The NH_3 to be cracked is heated by an internal combustion inside the vessel. Effective heat transfer between combustion gases and NH_3 is accomplished because heat is transferred by mixing, convective heat transfer and radiation.

[0038] The exemplary embodiments of the invention presented in this patent application are not to be interpreted to pose limitations to the applicability of the appended claims. The verb “to comprise” is used in this patent application as an open limitation that does not exclude the existence of also unrecited features. The features recited in dependent claims are mutually freely combinable unless otherwise explicitly stated. The novel features which are considered as characteristic of the invention are set forth in particular in the appended claims.

Brief Description of Drawings

[0039] In the following, the invention will be described with reference to the accompanying exemplary, schematic drawings, in which

Figure 1 illustrates a cracking arrangement according to an embodiment of the invention,

Figure 2 illustrates a cracking arrangement according to another embodiment of the invention,

Figure 3 illustrates a cracking arrangement according to still another embodiment of the invention,

Figure 4 illustrates a cracking arrangement according to still another embodiment of the invention and

Figure 5 illustrates a cracking arrangement according to still another embodiment of the invention.

Detailed Description of Drawings

[0040] Figure 1 depicts schematically a cracking arrangement 10 for cracking ammonia according to an embodiment of the invention. The arrangement comprises a cracking vessel 12. The cracking vessel 12 is advantageously rotationally symmetrical, such as cylindrical, vessel having a longitudinal centre axis 16. When the vessel is cylindrical the length of inner reaction space 100 of the vessel is greater than diameter of the vessel. There is a burner 14 arranged at the first end 12.1 of the rection space 100 of the vessel 12 for combustion of fuel. The cracking vessel 12 is provided with an outlet 18 for product gas in the second end 12.2 of the reaction space 100 of the vessel 12, opposite to the burner 14. The outlet 18 is not necessarily arranged to the centre axis 16 even if that is shown in the figure.

[0041] The burner 14 is, however, arranged to the centre axis 16 of the vessel such that its flame is directed coaxially to the centre axis 16 inside the vessel 12. The burner 14 comprises a first inlet 20 which is connected to a source of ammonia 22 for feeding ammonia as fuel into the burner 14, and a second inlet 24, which is connected to a source of gas containing oxygen 26 for feeding gas containing oxygen into the burner 14. The first inlet 20 and the second inlet 24 function as introduction of gases needed for production of heat for cracking ammonia in the vessel 12.

[0042] The cracking vessel 12 further comprising a number of third inlets 28 for feeding ammonia into cracking vessel 12 arranged to a side wall 30 and/or to an end wall 32 at the first end 12.1 of the space 100 in the vessel. The third inlets 28 function as introduction of ammonia into the cracking vessel 12 for cracking the ammonia by means of the heat produced by combustion of gases with the burner 14.

[0043] The reaction space 100 inside the cracking vessel 12 is an open space 100, in which a combustion zone 101 adjacent to the burner 14 is formed when the burner 14 is in operation and a cracking zone 102 in the portion of the space 100 at the second end 12.2 of the space 100 of the vessel 12. The combustion zone 101 can be considered to be a flame area where oxidation of fuel takes place in a presence of oxygen. The diameter of the space of the vessel at its first end 12.1 is greater than effective diameter of the flame, that is the combustion zone 101, and therefore an annular portion around the combustion zone 101 is part of the cracking zone 102. Since the vessel is intended to operate at considerably high temperatures, its walls are preferably provided with a heat insulation and/or with a cooling system, like a fluid jacket.

[0044] Advantageously the vessel 12 comprises several third inlets 28 arranged to an end wall 32 at the first end of the space 100 of the vessel evenly around the burner 14. These inlets 28 at the end wall 32 are arranged to feed ammonia into the annular cracking zone 102 around the burner. Advantageously there are several third inlets 28 arranged at a side wall 30 of the vessel at a distance from the end wall 32 at the first end 12.1 of the space 100 of the vessel 12. The third inlets 28 are positioned such that ammonia which is introduced via the third inlets 28 is heated by the combustion in the burner in the space 100. The cracking zone 102 outside the combustion zone 101 is practically non-oxidizing zone. There may be control valves 34 arranged in connection with each one of the inlets and/inlet channels suitable balancing the gas flows.

[0045] In the embodiment shown in the Figure 1 the space 100 is empty. When the space 100 is empty the cracking reaction is non-catalytic thermal cracking, therefore the cracking zone 102 in the embodiment of figure 1 can be called non-catalytic cracking zone 102. Alternatively, an inner wall bordering the space 100 may be provided with a catalyst coat on its surface wherein the catalyst will promote cracking reactions in the vessel 12.

[0046] Method of cracking ammonia is practised in the cracking vessel according to figure 1 in a following manner. Ammonia is fed from the source of ammonia 22 into the burner 14 and additionally gas containing oxygen is fed also to the burner 14. The first portion of ammonia is combusted in the burner 14 wherein heat is produced into the vessel 12 and the combustion zone 101 is formed in the cracking vessel 12. The first portion of ammonia is fed via the first inlet 20 and the gas containing oxygen is fed via the second inlet 24 into the burner 14. The gas containing oxygen fed through the first inlet 20 may be air or other gas containing oxygen, or even pure O_2.

[0047] Combustion of ammonia follows generally the following reaction:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

Combustion of ammonia is exothermic reaction producing heat and consuming oxygen in the vessel. Therefore, combustion of the first portion ammonia forms outside the combustion zone in the vessel is substantially oxygen free, that is the non-oxidizing zone 102.

[0048] Second portion of ammonia is fed via the third inlets 28 into the cracking zone 102 of the cracking vessel 12 outside the combustion zone 101, wherein the second portion of ammonia is cracked thermally by utilizing the heat produced by the combustion of the first portion of ammonia. As is shown in the figure 5 the second portion of ammonia may originate from different source of ammonia than the first portion of ammonia. This is technically applicable also the embodiments shown in the figure 1 to 4.

[0049] Cracking of ammonia follows generally the following reaction:

$2NH_3 \rightarrow 3H_2 + N_2$

so the produced product gas produced from the second portion of ammonia comprises hydrogen and nitrogen. In this embodiment the space in vessel is empty and cracking is non-catalytic reaction.

[0050] Gases resulting from the cracking and combustion of ammonia are led out of the vessel 12 via the outlet 18 to desired use of the product gas.

[0051] More precisely the first portion of ammonia and the gas containing oxygen are fed to a first end 12.1 of the space 100 of the vessel in its longitudinal direction and the product gas is removed from a second end of the space of the cracking vessel 12.

[0052] The second portion of the ammonia is heated to a predetermined temperature at which the cracking of ammonia takes place without any catalyst. The heat is provided by combustion of the first portion of the ammonia, and the heated second portion of the ammonia is cracked in non-oxidizing conditions in the empty cracking zone 102. Effective heat transfer between combustion gases and ammonia in the cracking zone is provided because heat is transferred by mixing, convective heat transfer, and radiation.

[0053] By combustion of the first portion of ammonia combustion zone temperature is maintained at 800 – 1800°C and the cracking zone temperature is maintained at 350 – 800°C. In some practical cases temperature could also be higher, but spontaneous cracking will occur when NH_3 temperature approaches 800°C. Cracking reaction itself cools down the gas as being endothermic reaction. Catalyst is required to support cracking at the lower part of the temperature range.

[0054] Since the burner is arranged to the center axis 16 also the combustion zone 101 is formed to the center axis 16 of the cracking vessel 12 and advantageously at least part of the second portion of the ammonia is fed around the combustion zone 101, that means also around the burner 14, from the first end wall 32 of the vessel 12. At least part of the second portion of the ammonia is fed through side wall 30 of the vessel longitudinally between the combustion zone and the cracking zone 102.This way the space of the vessel and heat effect of the combustion zone is utilized effectively for cracking reaction.

[0055] Advantageously amount of oxygen present in the combustion zone is controlled such that all of the oxygen is reacted with the ammonia in the combustion zone so as to provide non-oxidizing cracking zone 102 in the vessel 12. Advantageously, the gas containing oxygen is air and the air-fuel ratio in the combustion zone is rich. This way it is ensured that all oxygen present in the combustion zone 101 is consumed. This also means that a part of the first portion of the ammonia fed into the burner may remain as ammonia. Even if the burner may generate ammonia slip the remaining ammonia will be cracked into hydrogen and nitrogen in the cracking zone 102.

[0056] Figure 2 discloses a cracking arrangement 10 for cracking ammonia according to another embodiment of the invention. Practically this is otherwise similar to that shown in the figure 1 except that the first and the second inlets are combined as one common gas inlet 24’ so that the gas containing oxygen that is fed to the burner 14 is a mixture of NH_3 and gas containing oxygen. In other words, in the embodiment according to figure 2 the source of gas containing oxygen 26 and the source of ammonia 22 are both connected with the common gas inlet 24’. This makes possible to control the operation of the burner more easily and preheat both of the gases as a mixture in more straight forward manner.

[0057] Figure 3 discloses a cracking arrangement 10 for cracking ammonia according to another embodiment of the invention. Practically this is otherwise similar to that shown in the figure 1 except that the first and the second inlets are combined as one common gas inlet 24’, as is shown in the figure 2 and that the cracking zone 102 comprises an ammonia catalytic converter 103 in the zone.

[0058] The common second outlet 24' results in that the gas containing oxygen that is fed to the burner 14 is a mixture of NH_3 and gas containing oxygen. In other words, in the embodiment according to figure 2 the source of gas containing oxygen 26 and the source of ammonia 22 are both connected with the common gas inlet 24'. This makes possible to control the operation of the burner more easily and preheat both of the gases as a mixture in more straight forward manner.

[0059] The catalytic converter 103 is arranged at the second end of the space in the vessel, at outlet side of the vessel 12 from the third inlets 28 arranged to a side wall 30 of the vessel 12. This way the second portion of ammonia is cracked in a presence of an ammonia cracking catalyst.

[0060] Here the catalytic converter 103 is shown as a support grid with catalyst material arranged on its surface. The catalytic converter may be arranged also in different manner, for example to comprise alternatively a bed of loose material with catalyst on its surface as is shown in the figure 4. As an example for making use of the invention, currently considered suitable catalyst materials are: Nickel based, Ruthenium based, Lithium amide or Sodium amide catalyst. Each of the catalyst are effective at temperature 350 – 800°C. However, conversion efficiency and expected lifetime are different.

[0061] The second portion of the ammonia is heated to a predetermined temperature at which the cracking of ammonia takes place without any catalyst. The heat is provided by combustion of the first portion of the ammonia, and the heated second portion of the ammonia is fed in non-oxidizing conditions to the cracking catalyst.

[0062] Figure 4 depicts schematically a cracking arrangement 10 for cracking ammonia according to still another embodiment of the invention. The arrangement comprises a cracking vessel 12 which is advantageously rotationally symmetrical vessel, such as cylindrical, having a longitudinal centre axis 16. When the vessel is cylindrical the length of inner reaction space 100 of the vessel is greater than diameter of the vessel.

[0063] Advantageously the vessel 12 is at upright position such that the centre axis 12 is arranged substantially in vertical position. This way the flame and heat distribution in the vessel are formed advantageously symmetrical in respect to the centre axis 16. The burner 14 is arranged at the lower end 12.1 of the vessel 12 for combustion of fuel. The cracking vessel 12 is provided with an outlet 18 for product gas in the upper end 12.2 of the vessel 12, opposite to the burner 14.

[0064] The burner 14 is arranged to the centre axis 16 of the vessel such that its flame is directed upwards coaxially to the centre axis 16 inside the vessel 12. The burner 14 comprises a combined second inlet 24', which is connected to a surrounding air 26, a source of ammonia 22 and a source of pressurized oxygen 26', for feeding a mixture of oxygen enriched air and ammonia into the burner 14. The source of oxygen is not a necessary feature of the invention and when it is not present the gas mixture fed into the burner substantially consist of air and ammonia. The combined second inlet 24' functions as introduction of gases needed for production of heat for cracking ammonia in the vessel 12.

[0065] The cracking vessel 12 further comprising a number of third inlets 28 for feeding ammonia into cracking vessel 12 arranged to or near to a side wall 30 and/or to an end wall 32 at the first end 12.1 of the space 100 in the vessel. The third inlets 28 function as introduction of ammonia into the cracking vessel 12 for cracking the ammonia by means of the heat produced by combustion of gases with the burner 14.

[0066] The cracking vessel 12 comprises an open space 100 inside, in which a combustion zone 101 adjacent to the burner 14 is formed when the burner 14 is in operation and a cracking zone 102 in the portion of the space 100 at the second end 12.2 of the space in the vessel 12. The diameter of the space 100 in the vessel at its first end 12.1 is greater than effective diameter of the flame, that is the combustion zone 101 and therefore an annular portion of around the combustion zone 101 is part of the cracking zone 102.

[0067] Advantageously the vessel 12 comprises third inlets 28 arranged to an end wall 32 at the first end of the space 100 of the vessel evenly around the burner 14. Like in other embodiments of the invention, these inlets 28 at the end wall 32 are arranged to feed ammonia into the annular cracking zone 102 formed around the burner. Advantageously there are several third inlets 28 arranged to a side wall 30 of the vessel at a distance from the end wall 32 at the first end 12.1 of the space 100 in the vessel 12. The third inlets 28 are positioned such that ammonia which is introduced via the third inlets 28 is heated by the combustion in the burner and is in non-oxidizing zone in the space 100. The third inlets at side wall are connected to feed channels 27 which are arranged in direct heat transfer communication with the annular cracking zone 102, which preheats the ammonia due to heat transfer from the gas and/or flame in the space 100. The feed channels 27 running inside the vessel are an optional feature. The feed channels 27 may run also outside the vessel 12, as is depicted in figures 1-3, If the preheating is not required in terms of process design. The feed channels may be practically realized for example by providing an annular slot channel inside the vessel 12 between the wall of the vessel and a sleeve or a shield 29 inside the vessel 12 as is illustrated by dashed line. The cracking zone 102 outside the combustion zone 101 is practically non-oxidizing zone. There may be control valves 34 arranged in connection with each one of the inlets and/inlet channels suitable balancing the gas flows.

[0068] In the embodiments shown in the Figures 1 and 2 the space 100 is empty at the combustion zone 101 and at the upper part of the vessel 12, while in the embodiment shown in the figure 3 is provided with a catalytic converter 103 in the upper part of the space 100. In the figure 4 there is shown an embodiment where the upper part of the space 100 is provided with a catalytic converter 103. In practise, both options – using a catalyst of refrain from using a catalyst – may be used depending on the required design, but using catalyst is preferred because that way cracking of ammonia is practised at lower temperature, which result in decreased heat losses and consumption of ammonia as fuel, which reduces yield of H_2 from the available ammonia. Cracking reaction in the embodiment shown in the figure 4 is catalytic thermal cracking, therefore the cracking zone 102 in the embodiment of figure 1 can be called catalytic cracking zone 102.

[0069] There is a gas mixture feed line 25 provided in the arrangement 10, which feed line 25 is connected to the burner 14, more precisely to the combined second inlet 24' at the second end of the feed line 25. The first end of the feed line 25, it is connected to the source of ammonia 22. The source of ammonia is in this example configured to store the ammonia in liquid phase. The feed line 25 is provided with a pump 23 for raising the pressure of the ammonia to suitable pressure.

[0070] The cracking arrangement according to figure 4 comprises further a heat recovery device 36, such as a heat exchanger, which is connected to the feed line 25 and to an outlet line 38, evaporating the ammonia with heat contained in the product gas. The vessel outlet 18 is connected by the outlet line 38 to the heat recovery device 36 such that product gas is arranged to cool in the heat recovery device 36 and the ammonia is arranged to evaporate in the heat recovery device 36. Thus, the heat recovery device 36 functions as an after cooler of the process gas and evaporator of the ammonia. This way, the ammonia is evaporated and preheated by transferring heat from the product gas to the gas mixture before feeding to the burner. There is a branch feed line 21 which is connected to the feed line 25 at downstream position to the heat recovery device 36, such that evaporated ammonia is arranged to flow through the branch feed line 21 to the third inlets 28 of the vessel 12. The term downstream refers to the flow direction from the source of ammonia 22 to the vessel 12.

[0071] The arrangement further comprises an air feed line 40 which is configured to feed air in the ammonia into the gas mixture feed line 25. The air feed line is provided with a compressor 42 for suitable pressurizing of the air, alternatively the air feed line 40 may be connected to a source of pressurized air. The air feed line is connected to the gas mixture feed line 25 at location downstream to the heat recovery device 36 and also downstream to the branch feed line 21 delivering ammonia to the third inlets 28 of the vessel 12. Optionally, the air feed line 40 is connected with a source of oxygen 26', from which pure oxygen can be fed into the air so that the gas containing oxygen fed into the burner 14 is a mixture of ammonia, air and pure oxygen.

[0072] Method of cracking ammonia is practised in the cracking vessel according to figure 4 in a following manner. Ammonia is fed from the source of ammonia 22 into the gas mixture feed line 25 by suction of the pump 23. The pump 23 raises the pressure of the ammonia to a desired level and feeds the ammonia (in liquid phase) to the heat recovery device 36. Ammonia is evaporated in the heat recovery device 36 by transferring heat from the product gas. A portion of the evaporated ammonia is passed via the branch feed line 21 to the third inlets 28 of the vessel 12.

[0073] Air, optionally enriched by oxygen, is fed into the stream gaseous ammonia after the heat recovery device 36. Mixture of ammonia and air (optionally oxygen enriched air) is fed to the burner 14 via the gas mixture feed line 25. This way the first portion of ammonia is combusted in the burner 14 wherein heat is produced into the vessel 12 and the combustion zone 101 is formed in the cracking vessel 12.

[0074] Combustion of ammonia and cracking of ammonia in the cracking vessel 12 and other operational features of the cracking vessel 12 are described in connection with the description of figure 1, which applies also to the embodiment of the figure 4.

[0075] Figure 5 discloses a cracking arrangement 10 for cracking ammonia according to another embodiment of the invention. The invention relates to a practical application where the product gas is not intended to be produced for use but merely it is gas transformed into environmentally less harmful composition. Practically the cracking arrangement 10 differs from that shown in the figure 1 as follows. The first and the second inlets are combined as one common gas inlet 24’ so that the gas containing oxygen that is fed to the burner 14 is a mixture of NH_3 and gas containing oxygen. In other words, the source of gas containing oxygen 26 and the source of ammonia 22 are both connected with the common gas inlet 24’ of the burner 14. Also, the cracking vessel 12 is provided with an oxidizer part 104 after the cracking zone 120 in the flow direction of the gas when in use. Furthermore, the vessel 12 has at least part of its walls cooled. It is also distinctive to the embodiment of the figure 5 that the gas mixture feed line 25 is connected to the first source of ammonia 22, which corresponds to the source of ammonia in the embodiments of the figure 1 to 4 such that the first portion of ammonia is fed to the burner 14. The second portion of ammonia originates from a second source of ammonia 22’ which may be different from that from which the first portion of ammonia fed to the burner 14. This way in this embodiment the combustion gas used in the burner 14 may have different composition compared to the ammonia containing gas cracked in cracking zone 102 of the vessel. For example, the second source of ammonia 22’ may be ammonia fuel line in connection with a gas consumer, such as an internal combustion engine, during inerting procedure of the fuel line with nitrogen.

[0076] The vessel 12 comprises a fluid jacket 44 which is arranged for cooling the vessel by circulating a cooling fluid, such as water therein. For that purpose, the fluid jacket 44 is provided with a fluid inlet 46 and a fluid outlet 48. In the cracking vessel 12 the cracking zone 102 is provided with an outlet 18' which forms a constriction to the cross-sectional area of the cracking zone 102. As it is shown, the constriction is preferable conical at both sides of the constriction smoothly separating the cracking zone and the oxidizer part 104. The oxidizer part 104 is provided with one or more oxidizer inlets 50 connected to the source of gas containing oxygen 26 via flow channels 52. The flow channels open into an annular slot 54 which is arranged radially outside to the sleeve 29. The annular slot 54 is formed between an inner wall of the vessel 12 and a second sleeve 56. The second sleeve 56 extends from the end wall 32 to the outlet 18' such that the slot 54 has substantially constant radial width. The slot and the second sleeve 56, which extend axially farther than the sleeve 29 from the end wall 32 which is arranged in direct heat transfer communication with the cracking zone 102 pre-heating the gas, due to heat transfer from the gas and/or flame in the space 100. The flow channels 52 are preferably arranged not to be in direct heat transfer connection with the fluid jacket 44, or cooled wall of the vessel 12. The source of gas containing oxygen 26 is connected to the flow channel 52. As is shown in the figure the source of gas containing oxygen 26 which is connected to the flow channel 52 may be different from the source of gas containing oxygen connected to the burner 14 for improving controllability of the burner 14. The oxidizer inlet 50 opens into a space in the oxidizer part 104 at proximity to the outlet 18' of the cracking zone.

[0077] The burner 14 combusts the ammonia and provides heat for cracking, and ammonia is cracked in the cracking zone 102 as is described in the other embodiments. The product gas from the cracking zone 102 is fed into the oxidizer part 104 is auto ignited in the presence of oxygen due to the gas temperature being higher than its autoignition temperature.

[0078] Ammonia 22 and combustion air 26 is premixed and swirled in the burner inlet 14, ignited and making a rich i.e. excess fuel flame 101. This flame will provide heat for ammonia cracking 102. Vent gas from inerting procedure of the fuel line with nitrogen (a second source of ammonia 22'), preferably a mixture of ammonia and nitrogen (vent composition will vary), is injected in the annular space between the side wall 30 and the inner shield 29 and heated as it flows towards the cracking zone 102. There, the heat from combustion will decompose ammonia into nitrogen and hydrogen. As the combustion is rich, there is no air available to burn the hydrogen. The exhaust, consisting of N_2, NO, NO_2 and H_2, will leave the cracking zone 102 stage through the outlet 18', where air is supplied through the inlets 50, mixing with the hydrogen and being ignited by the hot surface. The outlet area is made of high temperature resistant material, being not cooled by cooling fluid and the mixture will burn in the oxidizer part 104. The downstream exhaust will consist of N_2, H_2O and small traces of NO and NO_2 (in the 10-15 ppm range).

[0079] While the invention has been described herein by way of examples in connection with what are, at present, considered to be the most preferred embodiments, it is obvious to the skilled person that, along with the technical progress, the basic idea of the invention can be implemented in many ways. The invention and its embodiments are thus not limited to the examples and samples described above but they may vary within the contents of patent claims and their legal equivalents. The details mentioned in connection with any embodiment above may be used in connection with another embodiment when such combination is technically feasible.

Part list

a cracking arrangement 10
a cracking vessel 12
a first end 12.1 of the space in the vessel
a second end 12.2 of the space in the vessel
a burner 14
a centre axis of the cracking vessel 16
an outlet 18

a first inlet 20
a branch feed line 21
a source of ammonia 22
a pump 23
a second inlet 24
common gas inlet 24'
a gas mixture feed line 25
a source of gas containing oxygen 26
a source of pressurized oxygen 26'
feed channels 27
a third inlet 28
a sleeve 29
a side wall 30
an end wall 32
valve 34
a heat recovery device 36
an outlet line 38
an air feed line 40
a compressor 42
a fluid jacket 44
a fluid inlet 46
a fluid outlet 48
oxidizer inlet 50
oxidizer flow channel 52
inner space of the vessel 100
a combustion zone 101
a cracking zone 102
an ammonia cracking catalytic converter 103
an oxidizer part 104

Claims

1. A method of cracking ammonia comprising

- feeding a first portion of ammonia into a burner (14) arranged to a cracking vessel (12);
- feeding gas containing oxygen into the burner (14);
- combusting the first portion of ammonia with the burner (14) forming a combustion zone (101) in the cracking vessel (12) and producing heat;
- feeding a second portion of ammonia into a cracking zone (102) of the cracking vessel (12) outside the combustion zone (101), and
- cracking the second portion of ammonia by utilizing the heat produced by the combustion of the first portion of ammonia and producing product gas comprising hydrogen and nitrogen from the second portion of ammonia.

2. A method of cracking ammonia according to claim 1, **characterized** in that in the combustion zone (101) the first portion of the ammonia is consuming the fed oxygen forming a non-oxidizing zone outside the combustion zone (101) in the cracking vessel (12).

3. A method of cracking ammonia according to claim 1 or 2, **characterized** in that second portion of ammonia is cracked in a presence of an ammonia cracking catalyst (103).

4. A method of cracking ammonia according to claim 1 or 2, **characterized** in that second portion of ammonia is cracked using non-catalytic reactions.

5. A method of cracking ammonia according to claim 1, **characterized** in that the first portion of ammonia and the gas containing oxygen are fed as a gas mixture into the burner (14).

6. A method according to claim 1, **characterized** in the that ammonia is preheated by transferring heat from the product gas to the gas mixture before feeding to the burner (14).

7. A method of cracking ammonia according to anyone of the preceding claims, wherein the vessel (12) has a cylindrical inner reaction space (100), having a diameter and a length, the length being greater than the diameter, **characterized** in that the first portion of ammonia and the gas containing oxygen are fed to a first end (12.1) of the reaction space (100) of the vessel (12) in its longitudinal direction and the product gas is removed from a second end (12.2) of the reaction space (100) of the cracking vessel (12).

8. A method of cracking ammonia according to claims 3 or 7, **characterized** in that the second portion of the ammonia is heated to a predetermined temperature by the heat provided by combustion of the first portion of the ammonia, and the heated second portion of the ammonia is fed in non-oxidizing conditions to the cracking catalyst.

9. A method of cracking ammonia according to anyone of the preceding claims, **characterized** in that the combustion zone (101) is formed to a center axis (16) of the cracking vessel (12) and at least part of the second portion of the ammonia is fed around the combustion zone (101) from the first end (12.1) of the space (100) in the vessel (12).

10. A method of cracking ammonia according to anyone of the preceding claims, **characterized** in that at least part of the second portion of the ammonia is fed into the vessel (12) near its side wall between a first end (12.1) and a second end (12.2) of the space (100) in the vessel (12).

11. A method according to anyone of the preceding claims, **characterized** in the that gas containing oxygen is a mixture of NH_3 and gas containing oxygen.

12. A method according to anyone of the preceding claims 1-9, **characterized** in the that gas containing oxygen is air.

13. A method according to anyone of the preceding claims 1-9, **characterized** in the that gas containing oxygen is pure O_2.

14. A method according to claim 3, **characterized** in the that the ammonia cracking catalyst is selected from a group of: Nickel based catalyst, Ruthenium based catalyst, Lithium amide or Sodium amide-based catalyst.

15. A method according to anyone of the preceding claims, **characterized** in the that the combustion zone (101) temperature is maintained at 800 – 1800°C.

16. A method according to anyone of the preceding claims, **characterized** in the that the temperature in the cracking zone (102) is maintained at 350 – 800°C by combusting the first portion of ammonia in a combustion zone (101) of the vessel (12).

17. A method according to anyone of the preceding claims, **characterized** in the that amount of oxygen present in the combustion zone (101) is controlled such that all of the oxygen is reacted with the ammonia.

18. A method according to claim 12, **characterized** in the that air-fuel ratio in the combustion zone (101) is rich.

19. A method according to anyone of the preceding claims, **characterized** in the that product gas is fed from the reaction space (100) to an oxidizer part (104) where the product gas is oxidized by feeding oxygen containing gas into a stream of the product gas.

20. A cracking arrangement (10) for cracking ammonia, comprising
a cracking vessel (12) and a burner (14) arranged to an open space (100) inside the cracking vessel (12), the burner (14) comprising a first inlet (20) for feeding ammonia into the burner (14), and a second inlet (24) for feeding gas containing oxygen into the burner (14), and
an outlet (18) for product gas in the cracking vessel (12), **characterized** in that the cracking vessel (12) is a cylindrical vessel (12) where the burner (14) is arranged at the first end (12.1) of the space (100) in the vessel (12) arranged to a centre axis (16) of the vessel (12), and the outlet (18) is arranged to the second end (12.2) of the space (100) in the vessel (12),
the cracking vessel (12) further comprising a third inlet (28) for feeding ammonia into cracking vessel (12) arranged near to a side wall and/or to the first end (12.1) of the space (100) in the vessel (12).

21. A cracking arrangement (10) according to claim 19, **characterized** in that the open space (100) comprising a combustion zone (101) adjacent to the burner

(14) at the first end (12.1) of the space (100) in the vessel (12) and a cracking zone (102) at the second end (12.2) of the space (100) in the vessel (12) and around the burner (14).

22. A cracking vessel (12) according to claim 19 or 20, **characterized** in that the vessel (12) is provided with an ammonia cracking catalytic converter (103) in the cracking zone (102) at the second end (12.2) of the space (100) in the vessel (12).

23. A cracking vessel (12) according to claim 20, **characterized** in that catalytic converter (103) comprises at least one of a catalyst bed of loose material, a catalyst support coated with catalyst material or catalyst coat on inner surface of the vessel (12).

24. A cracking device according to claim 19, **characterized** in that the third inlet (28) comprises several inlets into the space (100) inside the vessel (12) arranged to an end wall at the first end (12.1) of the space (100) in the vessel (12) around the burner (14).

25. A cracking device according to claim 18 or 23, **characterized** in that the third inlet (28) comprises several inlets arranged near a side wall of the vessel (12) at a distance from the end wall at the first end (12.1) of the space (100) in the vessel (12).

26. A cracking device according to claim 23, **characterized** in that the first inlet (20) and the second inlet (24) are formed as a single common gas inlet (24’).

27. A cracking device according to claim 23 and 24.

28. A cracking device according to anyone of the claims 20 to 27, **characterized** in that the vessel comprises an oxidizer part (104), arranged downstream of the cracking zone (102), and that the oxidizer part (104) is provided with at least one inlet (50) for oxygen containing gas.

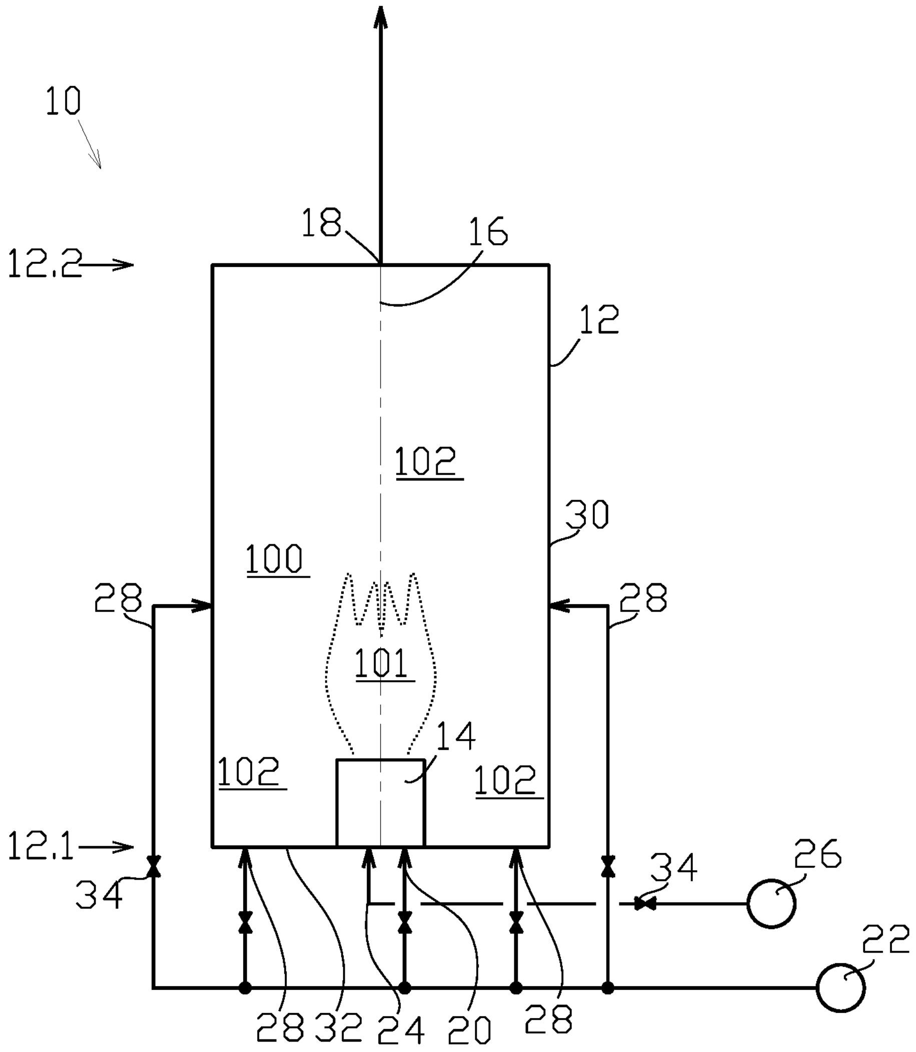
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Fig. 1

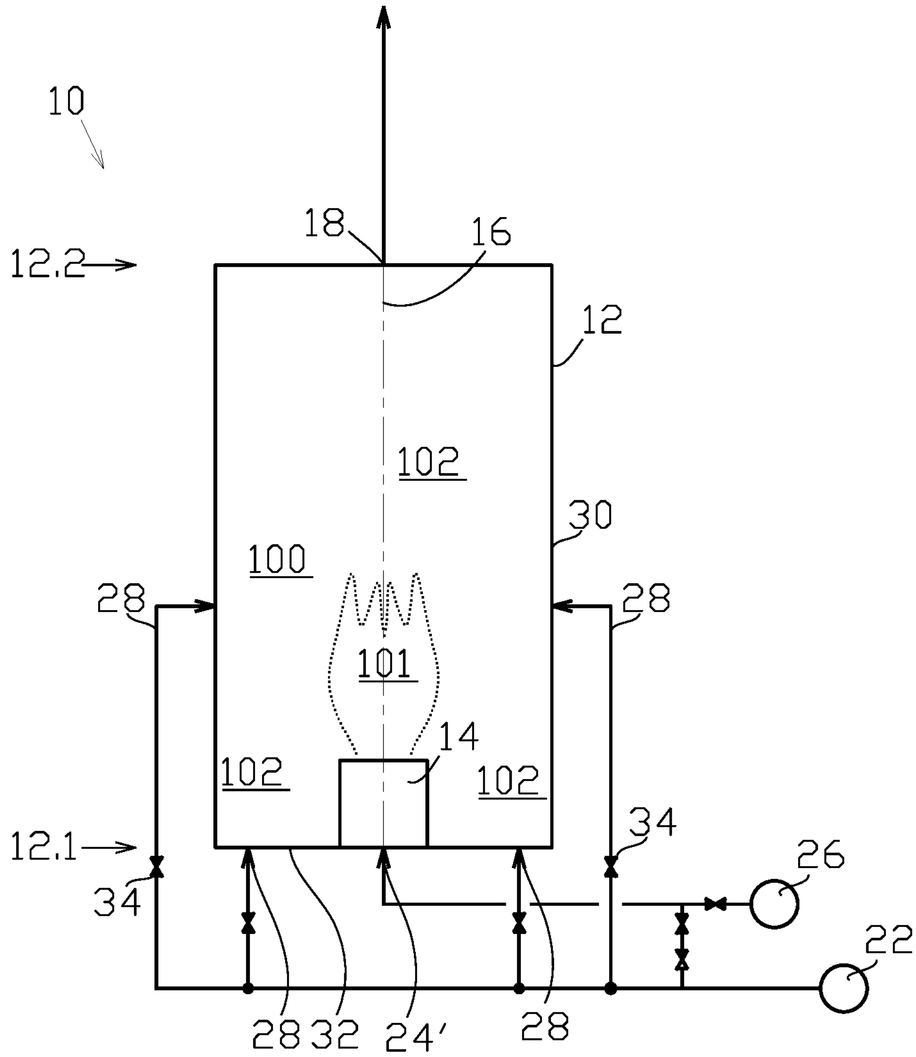
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Fig. 2

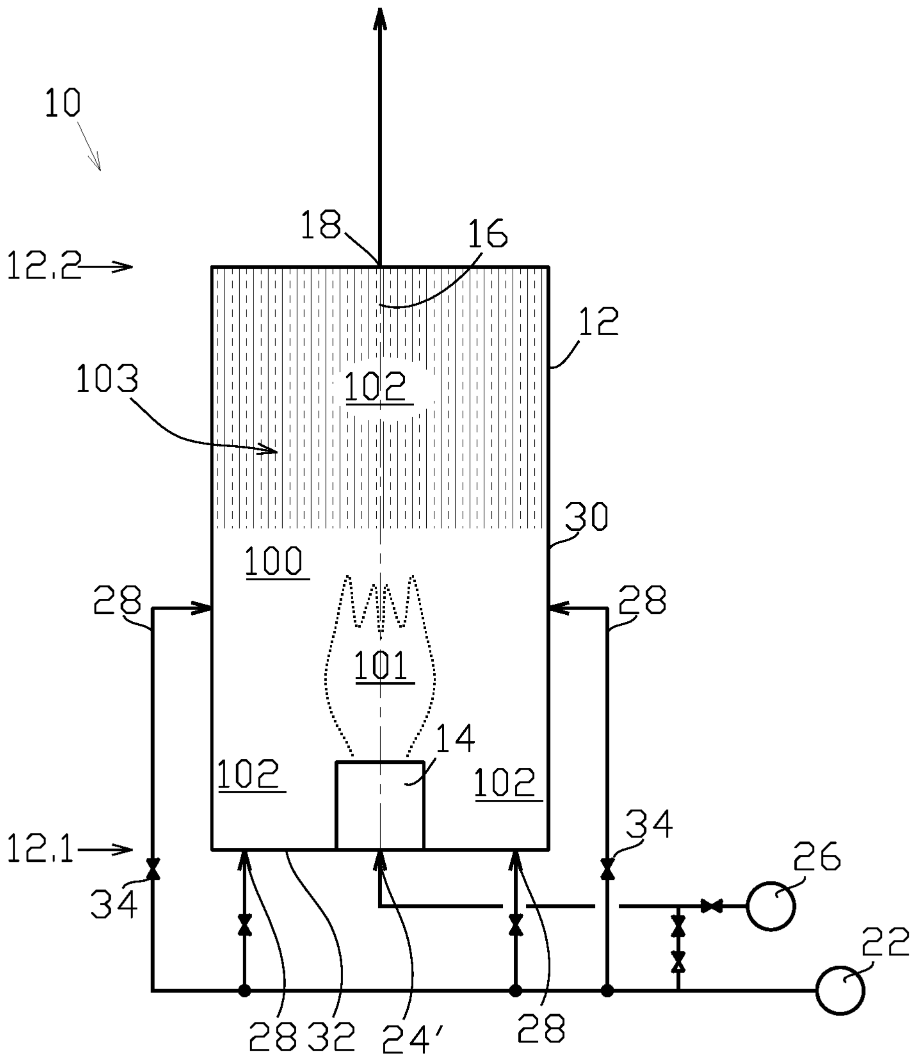
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Fig. 3

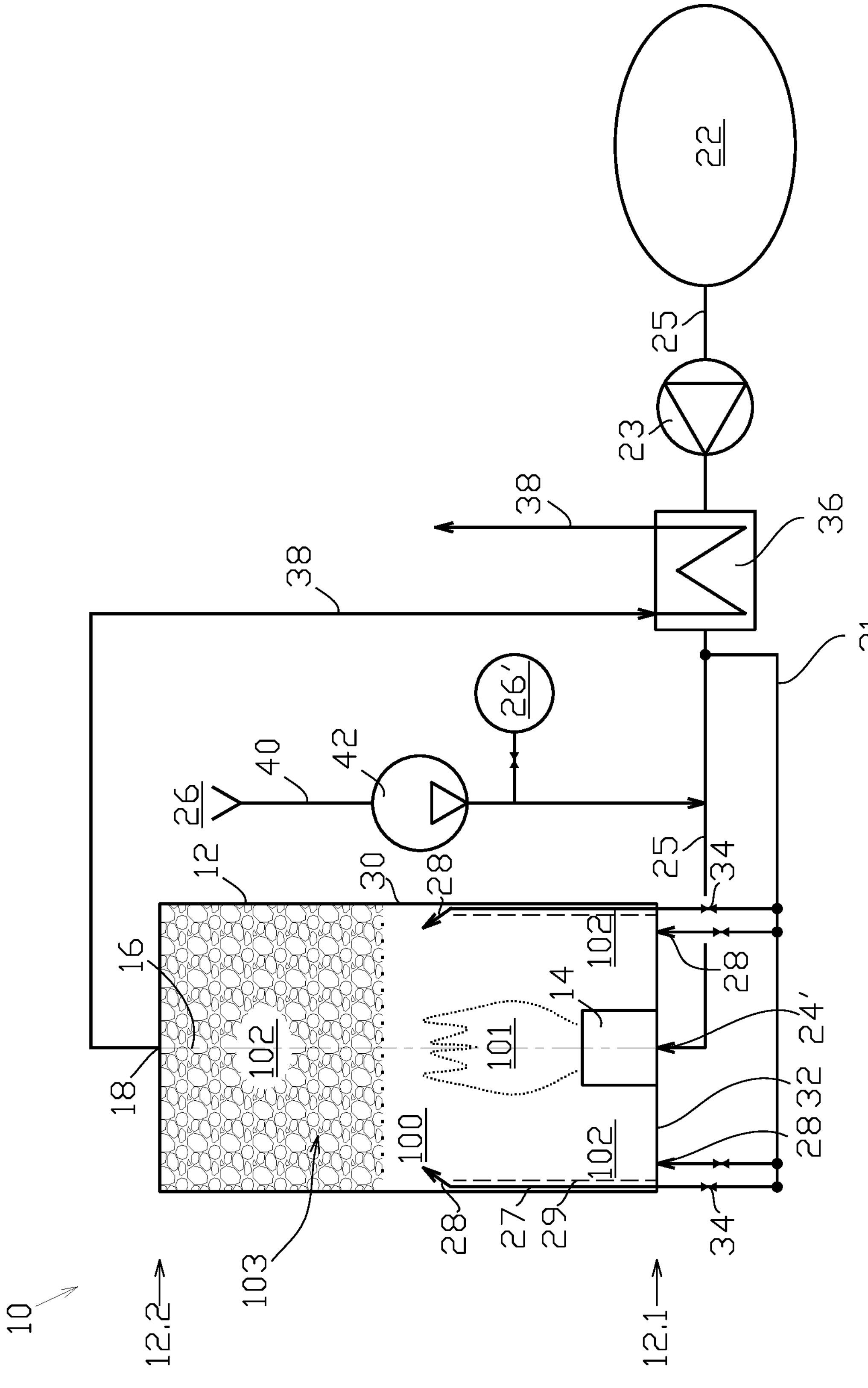
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Fig. 4

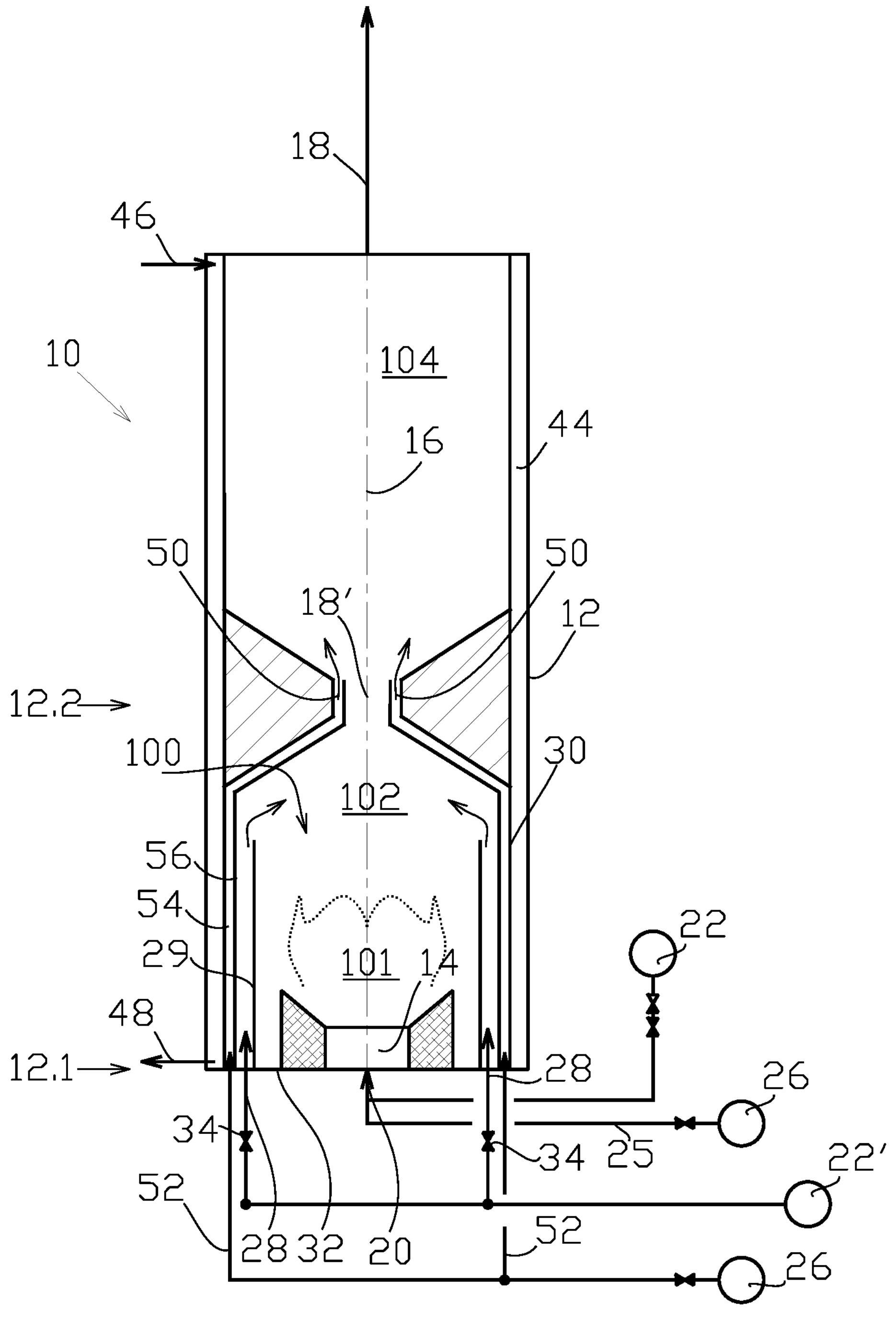
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Fig. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/068439

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B3/04 B01J19/26
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01B B01J

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 26 17 089 A1 (CALORIC GES APPARATEBAU) 3 November 1977 (1977-11-03)	1-4, 7-10,12, 14,15, 17,18, 20-23, 27,28
Y	page 4, line 17 - page 5, line 17; figure	5,6,11
A	1	19
X	CN 210 656 142 U (UNIV XIAMEN) 2 June 2020 (2020-06-02)	1,2,4,9, 10,13, 15,16, 20,21
Y	paragraph [0018] - paragraph [0032]; figure 1	5,6,11

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[x] Further documents are listed in the continuation of Box C.

[x] See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 February 2023	23/02/2023

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Cristescu, Ioana

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/068439

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 198 604 A (PFEFFERLE WILLIAM C) 3 August 1965 (1965-08-03) column 5, line 7 - column 6, line 12; figure 1 -----	5,6,11
X	US 2003/129555 A1 (MUKAI YUJI [JP] ET AL) 10 July 2003 (2003-07-10) paragraph [0056] - paragraph [0065]; figures 1,3 -----	20,21, 24-28

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2022/068439

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
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CN 210656142	U	02-06-2020	NONE		
US 3198604	A	03-08-1965	NONE		
US 2003129555	A1	10-07-2003	CN 1430302	A	16-07-2003
			EP 1327821	A1	16-07-2003
			KR 20030055147	A	02-07-2003
			US 2003129555	A1	10-07-2003