Combined Methane Decomposition and Ammonia Formation Cell DIV

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John Bradenburg
University of Central Florida

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An ammonia synthesis process and apparatus are provided which are energy efficient and minimize greenhouse-gas emission during the processing of natural gas and air. In the process a stream of natural gas is divided into two streams, one of which is mixed with air and ignited to provide heat for the thermal decomposition of natural gas into hydrogen and carbon and also to provide deoxygenated nitrogen for an ammonia synthesis process. The process essentially prepares hydrogen and nitrogen on a low average temperature side of a chemical reactor and then feeds both gases to the high average temperature side of the chemical reactor where they react to form ammonia. The formation of ammonia is exothermic, whereas the thermal decomposition of methane is endothermic and the combustion of methane to remove oxygen is also exothermic; the sum of the heats absorbed and released in these reactions is positive. Catalysts, high temperatures and pressure are used to promote the rapid formation of ammonia, as is standard practice in the chemical industry. Catalysts, and high temperatures are used to promote the thermal decomposition of natural gas and combustion of oxygen that provides hydrogen and nitrogen for ammonia synthesis.
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COMBINED METHANE DECOMPOSITION AND AMMONIA FORMATION CELL

This invention claims the benefit of priority to U.S. Provisional Application No. 60/409,943 filed Sep. 11, 2002.

FIELD OF THE INVENTION

This invention relates to the production of ammonia from natural gas and more particularly to an apparatus and its application to a novel method of the production of ammonia from natural gas in concurrent exothermic and endothermic processes that releases no greenhouse gases to the environment.

BACKGROUND AND PRIOR ART

It is conventional to synthesize ammonia by the Haber-Bosch process developed in the mid-twentieth century. The Haber-Bosch ammonia synthesis is accomplished by the reaction of nitrogen and hydrogen at 700° C. and requires 700 atmospheres to achieve good yields. This exothermic reaction releases heat, which must be removed from the reaction facility. Due to low conversion efficiency per pass, hydrogen and nitrogen must be recycled and ammonia removed by condensation at high pressures. Nitrogen is prepared by combustion of the oxygen from air to leave CO₂ and water vapor; the heat of combustion is used for thermal decomposition of methane.

Numerous patents discuss ammonia synthesis from nitrogen including:

U.S. Pat. No. 4,142,993 which deals only with an improved Haber process, using an improved doped carbon catalyst, for ammonia synthesis;

U.S. Pat. No. 4,180,552 to Graham, et al. again discloses an improved Haber process, which involves hydrogen recovery from ammonia synthesis in which purging streams are recycled to the reaction zone to improve ammonia yields.

U.S. Pat. No. 4,180,553 to Null, et al. again discloses an improved Haber process, which involves hydrogen recovery from ammonia synthesis in which purging streams are recycled to the reaction zone;

U.S. Pat. No. 4,390,509 to Weston, et al. in which synthesis gas is used to produce ammonia and digestion of phosphate rock and eventually ammonium phosphate;

U.S. Pat. No. 4,891,262 to Lichtin, et al. produces ammonia by catalyzed reduction of nitrogen absent photo energy;

U.S. Pat. No. 4,938,855 to Lichtin, et al. produces ammonia by photo promoted catalyzed reduction of nitrogen; and,

U.S. Pat. No. 4,981,669 to Pinto produces ammonia synthesis gas from natural gas by several reforming steps involving the water reforming shift process by adjusting the temperature of the reforming tubes and the air fed to the secondary reformer stage.

Hydrogen can be prepared from natural gas by water reforming or thermal decomposition. Water reforming is most often used because it is exothermic, and thus requires no energy input. Thermal decomposition is not often used because it requires energy input. In thermal decomposition, refractories are heated and natural gas is flowed over them; in the process of the endothermic decomposition the refractories cool and must be reheated. For this reason this process is not often used, as discussed in the McGraw-Hill Encyclopedia of Science and Technology 8th Ed., 1997, "Carbon Black" p. 234–235. To be cost effective the thermal decomposition process must be combined with some process or processes that release heat. With catalysts the thermal decomposition process can be made to operate at 700° C. This process is sometimes called the Bosch process.

Numerous patents discuss hydrogen synthesis in which hydrogen, if desired, can be reacted with nitrogen to produce ammonia including:

U.S. Pat. No. 4,836,898 to Noyes discusses high temperature conversion of methane to hydrogen and carbon;

U.S. Pat. No. 5,266,175 to Murphy and U.S. Pat. No. 5,411,649 to Roussey, et al. are concerned with conversion of a methane feed to hydrogen by microwave radiation in an electromagnetic field;

U.S. Pat. No. 6,002,059 to Hellring, et al. is concerned with the upgrading of natural gas into higher order hydrocarbons;

U.S. Pat. No. 6,245,309 B1 to Etiévant, et al. discloses a hydrogen generator from fuel gas having a chamber provided with means for maintaining a predetermined temperature and electrical discharges at a reduced current level; and,

U.S. Pat. No. 6,293,979 B1 to Choudhury, et al. catalytically converts natural gas to synthesis gas.

It is also known to use the exothermic energy from a reaction in one area of a plant to provide energy to facilitate the reaction of endothermic reaction in another area of the plant. Numerous patents discuss such utilization including:

U.S. Pat. No. 6,002,059 to Hellring, et al. are concerned with the upgrading of natural gas into higher order hydrocarbons discloses the concept of balancing the heat requirements of the several steps by transferring energy from the exothermic reactions to the endothermic (see col. 7 lines 1–30).

U.S. Pat. No. 6,228,341 B1 to Hebert, et al. also involves the transfer of energy from the exothermic reaction area to the reaction streams by indirect heat exchange through heat exchange channels.

U.S. Pat. No. 6,245,309 B1 to Etiévant, et al. discloses a hydrogen generator from fuel gas having a chamber provided with means for maintaining a predetermined temperature and electrical discharges at a reduced current level.

U.S. Pat. No. 6,293,979 B1 to Choudhury, et al. catalytically converts natural gas to synthesis gas by a technique where the exothermic oxidative conversion of the oxygen with the natural gas is carried out in the same environment as the endothermic steam reforming of the natural gas resulting in an enhanced energy efficient environment (see col. 7, lines 15–63).

U.S. Pat. No. 6,333,014 B1 to Filippi in a process arrangement for the co-production of ammonia and methanol, transfers energy from a hot stream by indirect heat exchange with another input stream; and,

U.S. Pat. No. 6,340,451 B1 to Paganì, et al. in a plant for the synthesis of ammonia and urea increases its output capacity by using a means for adjusting the various feed streams.

The methods disclosed above and their respective apparatuses are deficient in that none suggest carrying out the processing of methane or natural gas into ammonia in a limited environment that prevents the emission of greenhouse gases or utilizing the exothermic energy of one intermediate process enclosed in a reaction vessel to energize the endothermic energy consumption of a second intermediate process in said vessel and adjacent thereto for improved efficiency of production of ammonia. The importance of ammonia as a safe compound and carrier of hydrogen for fuel cells has been recognized in the new hydrogen fuel economy. Thus, the present invention fills the need for an energy efficient means to produce a safe hydro-
It is a primary objective of the invention to develop a novel method and apparatus for the production of ammonia with reduced amounts of carbon dioxide.

A second object of the invention is to develop a method and apparatus for the production of ammonia with improved efficiency.

A third object of the invention is to develop a method and apparatus for the production of ammonia with improved yield.

A fourth object of the invention is to develop a method and apparatus for converting a fossil fuel, such as natural gas, to ammonia without the release of greenhouse gases.

A preferred embodiment of the invention is the preparation of ammonia by an apparatus comprising: a reaction chamber with upper and lower reaction cavities; the lower cavity containing a third inner cavity functioning as an oxidation structure for burning of natural gas in air, said upper and lower cavities separated by a hydrogen permeable structure; means for supplying air into said lower inner reaction cavity; an oxidation structure within said lower cavity for burning said air; means for transferring nitrogen oxides and water using technology known to those skilled in the art. Carbon oxides and water and other by products are removed from a scrubber port as limestone or calcium salts. The removal of carbon oxides, water and other by-products by the scrubber leaves a substantially pure nitrogen gas that can be sent by pipe to a scrubber to remove carbon oxides and water using technology known to those skilled in the art. Carbon oxides and water and other by products are removed from a scrubber port as limestone or calcium salts.

The upper reaction cavity 2 contains an upper chamber 13 with permeable walls that creates a reservoir for the substantially pure nitrogen gas from the scrubber. The upper chamber 13 is conveniently located directly above the hot cylinder 6 of the lower chamber to maximize the heat transfer efficiencies between exothermic and endothermic reactions. Meanwhile, in the lower reaction cavity 3, hydrogen is released by the thermal decomposition of natural gas having methane content in the range of approximately 90 to 98 volume percent. Thus, the terms methane and natural gas are used interchangeably herein. The thermal decomposition of methane occurs in the lower reaction cavity 3 on the hot cylinder and elsewhere within the lower reaction cavity. The decomposition reaction is represented as follows:

\[ \text{CH}_4 \rightarrow \text{C} + \text{H}_2 \]

The hydrogen gas rises and crosses through the membrane to react with nitrogen in the upper cavity 2 to form ammonia. Carbon 14 formed in the lower cavity falls near the hot cylinder 6 and is removed by a suitable screw type device that allows the solid carbon residue to exit the chamber.

Ammonia is catalytically formed in and about the permeable walls of the upper chamber and is removed from the upper reaction cavity 2 by a pipe. The reaction products in the upper reaction cavity 2 include ammonia (NH₃) and unreacted nitrogen (N₂) and hydrogen (H₂), which are separated in a condenser. The unreacted nitrogen-hydrogen mixture is a separated fraction that is returned to the steam of nitrogen gas by pipe.

As ammonia forms in the upper reaction cavity 2, via known catalytic reaction processes, heat is released as discussed in more detail below. The heat in the upper

The sole FIGURE shows a Combined Process Chemical (CPC) reactor.
chamber moves via thermal conduction to the lower reaction cavity 3 because the entire reactor is made of a conductive metal, such as steel.

The process of the invention involves first the combustion of natural gas, primarily composed of methane, in air. The combustion of natural gas and air in the inner chamber 7 of the lower cavity 3 of the reaction vessel decomposes the natural gas/methane to release hydrogen and decomposes the air to release nitrogen. The combustion of methane and air is an exothermic reaction, which removes oxygen with the production of heat. Thermodynamically, it is known that the combustion of methane with oxygen produces 212.79 Kcal, which even when allowing for heat losses due to hot exhaust gases, the production of heat. Thermodynamically, it is known that the combustion of methane with oxygen produces 212.79 Kcal, which even when allowing for heat losses due to hot exhaust gases.

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To burn methane (CH₄) in air to get rid of oxygen 0.105 mole is required per mole of air, 1.28x0.105x212.79 Kcal is released to prepare one mole of purified nitrogen (N₂) of which carbon dioxide (CO₂) and water (H₂O) can be removed by a scrubber means that enough energy from the exothermic reactions should be available to drive the endothermic reaction. As demonstrated in the present invention, the production of ammonia from natural gas can be an exothermic process; because, the thermal decomposition of methane is endothermic, the combustion of methane to remove oxygen is exothermic, and the formation of ammonia is exothermic; thus the sum of the heats absorbed and released within a single reaction chamber is positive.

The advantages of the present invention are several. The present invention allows the capture of hydrogen from natural gas, which is difficult to liquefy (-164°C) and store (0.4 g/cc) into ammonia, which has a much higher density (0.8 g/cc) and is much easier to liquefy (-33°C) in order to facilitate conversion into a hydrogen economy using ammonia as a hydrogen carrier. In addition, ammonia is readily broken down into hydrogen, which is used in fuel cells to produce water, and nitrogen, both of which can be freely vented into the air without harmful effects on the environment. Since the process utilizes exothermic processes to balance heat requirements of endothermic processes, it utilizes energy efficiently thus reduces net energy consumption and in particular, since the only carbon dioxide produced must be scrubbed from the nitrogen feedstock for the Haber process and captured, no carbon dioxide, a known deleterious greenhouse gas, is released into the atmosphere. In summary, the present invention produces ammonia, a valuable hydrogen carrier, in an energy efficient manner and without release of greenhouse gases. The use of catalysts, temperatures and pressures will allow optimization of the process for maximizing synergism between the exothermic processes of combustion and ammonia formation and the endothermic process of thermal decomposition of natural gas so as to achieve maximum ammonia production, optimal heat flows and energy efficiency.

While the invention has been described, disclosed, illustrated and shown in various terms of certain embodiments or modifications which it has presumed in practice, the scope of the invention is not intended to be, nor should it be deemed to be, limited thereby and such other modifications or embodiments as may be suggested by the teachings herein are particularly reserved especially as they fall within the breadth and scope of the claims here appended.

I claim:

1. A method for the production of ammonia comprising the steps of:
   a) selecting a single reaction chamber having a hydrogen permeable structure separating an upper reaction cavity from a lower reaction cavity containing a third inner cavity functioning as an oxidation structure;
   b) supplying air and natural gas to the oxidation structure in the lower reaction cavity;
   c) exothermically burning natural gas and air supplied to the oxidation structure thereby decomposing air to release nitrogen;
   d) supplying a gaseous hydrocarbon to the lower reaction cavity containing the oxidation structure;
   e) thermally decomposing the gaseous hydrocarbon in the lower reaction chamber to produce hydrogen;
   f) transferring the nitrogen from the oxidation structure in the lower reaction cavity to the upper reaction cavity;
   g) allowing the hydrogen from step e) to move from the lower reaction cavity through the hydrogen permeable member into the upper reaction cavity;
   h) reacting the hydrogen from step e) and the nitrogen from step c) in a catalytic reaction to produce ammonia and exothermic energy;
   i) producing ammonia that is removed from the upper reaction cavity; and
   j) allowing the exothermic energy produced in the upper reaction cavity to move via thermal conduction to the lower reaction cavity, thereby reducing the need for additional reaction energy to be supplied from external sources.

2. The method for the production of ammonia according to claim 1, wherein the gaseous hydrocarbon is natural gas.

3. The method for the production of ammonia according to claim 1, wherein the gaseous hydrocarbon is methane.

4. The method for the production of ammonia according to claim 1, wherein the hydrogen permeable membrane is formed of palladium (Pd) metal.

5. The method for the production of ammonia according to claim 1, wherein the step of exothermically burning natural gas and air further includes, thermally decomposing air to release oxygen-free nitrogen.

6. The method for the production of ammonia according to claim 1, wherein no greenhouse gases are released to the environment.

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3CH₄(-53.667 Kcal)+2N₂(+57.244 Kcal)=4NH₃

Thus the process requires 53.667 Kcal to decompose enough methane to produce 4 moles of ammonia but the production of the purified nitrogen and ammonia itself releases 101.36 Kcal, which even when allowing for heat losses due to hot nitrogen plus carbon oxides and water vapor being cooled as it runs through a scrubber means that enough energy from the exothermic reactions should be available to drive the endothermic reaction. As demonstrated in the present invention, the production of ammonia from natural gas can be an exothermic process; because, the thermal decomposition of methane is endothermic, the combustion of methane to remove oxygen is exothermic, and the formation of ammonia is exothermic; thus the sum of the heats absorbed and released within a single reaction chamber is positive.

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6. The method for the production of ammonia according to claim 1, wherein the step of exothermically burning natural gas and air further includes, thermally decomposing air to release oxygen-free nitrogen.

7. The method for the production of ammonia according to claim 1, wherein no greenhouse gases are released to the environment.