METHOD AND APPARATUS FOR PRODUCING AMMONIA VIA A SUPERSONIC QUENCHING PROCESS

FILED OF THE INVENTION

[0001] The present invention generally relates to a method and apparatus for producing ammonia, and more particularly relates to a method and apparatus for producing ammonia through a supersonic quenching process using a convergent-divergent nozzle.

BACKGROUND OF THE INVENTION

[0002] Ammonia (NH_3) is a colorless, pungent gas that consists of nitrogen and hydrogen. It has been primarily used as nitrogen fertilizer in agriculture, enhancing crop growth by being directly injected into the soil. In addition to its agriculture use, ammonia is a key industrial chemical, involved in producing fertilizer, plastics, explosives, and textiles, as well as serving as refrigerant in large-scale cooling systems. Despite its applicability in various industries, it requires careful handling due to its hazardous nature.

[0003] Conventionally, the industrial production of ammonia primarily relies on Haber-Bosch process, which involves synthesizing ammonia from nitrogen and hydrogen under high pressure (generally 150-250 atmospheres) and temperature (generally 400-500ºC) in the presence of an iron-based catalyst. This Haber-Bosch process is generally powered by fossil fuels. The hydrogen necessary in this process is generally derived from fossil fuel and is often produced through steam reforming of methane. Specifically, in the steam reforming method, methane reacts with steam and carbon to produce hydrogen and carbon dioxide. This conventional ammonia production method, while effective, presents several significant drawbacks. It requires high temperatures and pressures, leading to substantial energy consumption and associated high operation costs. Additionally, the production of hydrogen via steam reforming results in significant CO_2 emissions. This not only contributes to increased greenhouse gas emissions but also impacts the overall economic feasibility of ammonia production. Furthermore, this conventional ammonia production method achieves a relatively low conversion rate per pass. To improve the overall yield, it necessitates extensive

recycling of unreacted gases, which would further escalate operational costs as well as its negative impacts to the environment.

[0004] The use of water electrolysis coupled with renewable technologies, such as wind and solar energy, has been adopted as an alternative to address the drawbacks resulting from the hydrogen production in the Haber-Bosch process. This hydrogen production method, while sustainable and greener as compared to conventional hydrogen production methods adopted in the Haber-Bosh process, requires a continuous stream of pretreated water with high purity levels for its operation. For every tonne of hydrogen produced, approximately 9 tonnes of water may be needed. This high-water consumption can contribute to water scarcity issues. Moreover, achieving high-quality water (low-dissolved-solid concentration/deionized water) necessary for efficient electrolysis often involves energy-intensive processes, such as desalination, which can be detrimental to the marine biodiversity and hence exacerbate environmental concerns.

[0005] Another alternative method, for example, a carbothermic reduction process for ammonia production has been introduced. This carbothermic reduction process generally involves reacting metal oxides and carbon as reducing agent to produce ammonia, under a relatively milder condition. The carbothermic reduction process uses renewable carbon sources and operates at a lower temperature and pressure. It therefore offers a more sustainable and cost-effective pathway for ammonia production, as compared to the Haber-Bosch process, which is energy-intensive and heavily reliant on fossil fuels. However, these conventional carbothermic reduction processes currently face challenges related to their low ammonia yield.

[0006] Therefore, there arises a need to provide an efficient method and apparatus for producing ammonia that address the drawbacks associated with the conventional ammonia production methods, and that are energy efficient, economically viable, and have a high production yield.

[0007] Furthermore, other desirable features and characteristics will become apparent from the subsequent detailed description and the appended claims, taken in conjunction with the accompanying drawings and this background of the disclosure.

SUMMARY OF THE INVENTION

[0008] The present invention has been made in consideration of the above-mentioned problem. Certain embodiments commensurate in scope with the originally claimed subject matter are summarized below. These embodiments are not intended to limit the scope of the claimed subject matter, but rather these embodiments are intended only to provide a summary of possible forms of the subject matter. Indeed, the subject matter may encompass a variety of forms that may be similar to or different from the embodiments set forth below.

[0009] Accordingly, it is an object of the present invention to provide a method for producing ammonia. The method comprises carbothermic reduction of a composite material comprising a metal oxide, using a carbonaceous reducing agent in a nitrogen atmosphere to form a functional material in a gaseous state. The gaseous functional material is subjected to supersonic quenching process whereby the gaseous functional material is supersonically cooled to directly form a solid functional material The gaseous functional material may be supersonically cooled at a fluid flow speed of at least 700 m/s. The solid functional material may be used as a catalytic material or a precursor, for subsequent ammonia production.

[0010] The solid functional material may be hydrolysed with a solvent to regenerate a composite material comprising metal oxide and to form hydrous ammonia. The regenerated composite material may be recycled back to the carbothermic reduction process. The hydrous ammonia may be subjected to a heat treatment to generate anhydrous ammonia.

[0011] The supersonic quenching process may be performed by using a convergent-divergent nozzle. The convergent-divergent nozzle comprises a ratio of an exit diameter of a throat diameter in a range of 1:5.1 to 2.7:1. Preferably, the ratio of an exit diameter to a throat diameter may be about 2.28: 1. The convergent-divergent nozzle comprises a ratio of an inlet diameter to a throat diameter in a range of 3:1 to 6:1. Preferably, the ratio of an inlet diameter to a throat diameter may be about 4.28: 1.

[0012] The carbothermic reduction condition may include a temperature in a range of 1200ºC to 1600ºC and a pressure in a range of 100kPa to 1000kPa.

[0013] The metal oxide includes metal oxide nanoparticles. The metal oxide nanoparticles comprise a particle size of equal to or less than 100nm. Preferably, the metal oxide nanoparticles comprise a particle size in a range of 20nm to 30nm. The carbonaceous

reducing agent may be carbon-rich substances, such as graphite, methane, biomass and other hydrocarbon. The metal oxide may be a binary or a ternary metal oxide. In one embodiment, the binary metal oxide comprises a metal compound selected from the group consisting of magnesium (Mg), aluminum (Al), manganese (Mn), calcium (Ca), lithium (Li), sodium (Na), nickel(Ni) and iron (Fe). In one embodiment, the binary metal oxide may be iron oxide, aluminum oxide, zinc oxide, copper oxide or titanium oxide. The ternary metal oxide comprises a metal compound selected from Group 2, Group 7, Group 8 or Group 13 of the periodic table. In one embodiment, the ternary metal oxide comprises a metal compound selected from the group consisting of magnesium (Mg), aluminum (Al), manganese (Mn), calcium (Ca), lithium (Li), sodium (Na), nickel(Ni) and iron (Fe).

[0014] It is another aspect of the present invention to provide an apparatus for producing ammonia. The apparatus comprises a reaction chamber and a supersonic quenching unit operatively coupled with the reaction chamber. The reaction chamber is configured to carry out carbothermic reduction of a composite material comprising metal oxide with a carbonaceous reducing agent in a nitrogen atmosphere to form a functional material in a gaseous state. The supersonic quenching unit is configured to supersonically cool the gaseous functional material to directly form a solid functional material.

[0015] The supersonic quenching unit may be configured to supersonically cool the gaseous functional material at a fluid flow speed of at least 700 m/s. The supersonic quenching unit may be a convergent-divergent nozzle. In a preferred embodiment, the convergent-divergent nozzle may be a de Laval nozzle. The convergent-divergent nozzle may comprise a ratio of an exit diameter to a throat diameter in a range of 2: 1 to 2.28:1. Preferably, the convergent-divergent nozzle may comprise a ratio of an exit diameter to a throat diameter of about 2.28: 1. The convergent-divergent nozzle may comprise a ratio of an inlet diameter to a throat diameter in a range of 3.75:1 to 4.28:1. Preferably, the convergent-divergent nozzle may comprise a ratio of an inlet diameter to a throat diameter of about 4.28:1. The supersonic quenching unit may further comprises a conduit operatively coupled therewith.

[0016] These and other aspects, objects, features and advantages of the example embodiments will become apparent to those having ordinary skill in the art with reference to the following description and appended claims. The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate embodiments of the invention and, together with the description, explain the principles of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] A full and enabling disclosure of the present invention, including the best mode thereof, directed to one of ordinary skill in the art, is set forth in the specification, which makes reference to the appended figures, in which:

FIG.1 illustrates an exemplary process of producing ammonia in accordance with one embodiment of the present invention;

FIG.2 illustrates an exemplary system using a supersonic quenching unit with accordance with one embodiment of the present invention to optimize the formation of solid metal nitride from a carbothermic reduction process;

FIG.3 illustrates an exemplary convergent-divergent nozzle, being the supersonic quenching unit as depicted in FIG.2, with accordance with one embodiment of the present invention;

FIG.4a and 4b are schematic illustrations of velocity and temperature contour of Nozzle 1, respectively, based on Computational Fluid Dynamic (CFD), in accordance with an embodiment of the present invention;

FIG.5a and 5b are schematic illustrations of velocity and temperature contour of Nozzle 2, respectively, based on Computational Fluid Dynamic (CFD), in accordance with an embodiment of the present invention.

FIG.6a and 6b are schematic illustrations of velocity and temperature contour of Nozzle 3 respectively, based on Computational Fluid Dynamic (CFD), in accordance with an embodiment of the present invention;

FIG.7a and 7b are schematic illustrations of velocity and temperature contour of Nozzle 4 respectively, in accordance with an embodiment of the present invention;

FIG.8a and 8b are schematic illustrations of velocity and temperature contour of Nozzle 5, respectively, based on Computation Fluid Dynamic (CFD), in accordance with an embodiment of the present invention;

FIG.9a and 9b are schematic illustrations of velocity and temperature contour of Nozzle 6, respectively, based on Computation Fluid Dynamic (CFD), in accordance with an embodiment of the present invention; and

FIG.10a and 10b are schematic illustrations of velocity and temperature contour of Nozzle 7,respectively, based on Computation Fluid Dynamic (CFD), in accordance with an embodiment of the present invention.

[0018] It will be appreciated that elements in the figures are illustrated for simplicity and clarity and have not necessarily been drawn to scale. For example, the dimensions of some of the elements in the figures may be exaggerated relative to other elements to help to improve the understanding of illustrated embodiments of the present disclosure.

DETAILED DESCRIPTION OF THE INVENTION

[0019] The description of exemplary embodiments of the present disclosure provided below is merely exemplary and is intended for purposes of illustration only; the following description is not intended to limit the scope of the invention disclosed herein. Moreover, recitation of multiple embodiments having stated features is not intended to exclude other embodiments having additional features or other embodiments incorporating different combinations of the stated features.

[0020] All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., "such as") provided herein, is intended merely to better illuminate the embodiments and does not pose a limitation on the scope of the claims unless otherwise stated. No language in the specification should be construed as indicating any non-claimed element as essential.

[0021] The use of the terms "a" and "an" and "the" and similar referents in the context of describing the elements (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range,

unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein.

[0022] The terms “comprising,” “including,” and “having” are intended to be inclusive and mean that there may be additional elements other than the listed elements.

[0023] Additionally, it should be understood that references to “one embodiment” or “an embodiment” of the present disclosure are not intended to be interpreted as excluding the existence of additional embodiments that also incorporate the recited features.

[0024] The term “ammonia” or “anhydrous ammonia” whenever used in this specification and claims refers to a compound composed of nitrogen and hydrogen. “Ammonia refers to the compound NH_3, in all its forms, including both aqueous solutions and the pure compound”. “Anhydrous ammonia” refers specifically to the undiluted form of ammonia NH_3 without any water content. Anhydrous ammonia can be in liquid or gas state.

[0025] The term “composite material” includes but not limited to a combination of two or more than two materials with different properties.

[0026] As used herein, "about" will be understood by a person of ordinary skill in the art and will vary to some extent depending upon the context in which it is used. If there are uses of the term which are not clear to a person of ordinary skill in the art, given the context in which it is used, "about" will mean within a range of plus or minus 10% of the specified value.

[0027] Ratios, reaction parameters, pressure, temperature, particle size, physical dimensions of apparatus or devices, and other numerical data may be presented herein in a range format. It is to be understood that such range format is used merely for convenience and brevity and should be interpreted flexibly to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, 150 to 200 mm should be interpreted to include not only the explicitly recited limits of 150 to 200 mm, but also to include sub-ranges, such as 160 to 190 mm, 155 mm to 180 mm, and so forth, as well as individual amounts, including fractional amounts, within the specified ranges, such as 160.5 mm, 170.5 mm, and 185.5 mm for example.

[0028] Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the invention, the typical methods and materials are herein described.

[0029] In more general terms, it is intent of the present embodiment to provide a method and a system for producing ammonia by optimizing the formation of solid metal nitride in a carbothermic reduction process via a supersonic quenching process or through a supersonic quenching unit. The supersonic quenching process or the supersonic quenching unit are configured to allow supersonically accelerating and expanding the gaseous functional material resulted from the carbothermic reduction process, at a speed of at least 700 m/s to achieve supersonic quenching of the gaseous functional material to directly form solid functional material without passing through a liquid phase. In a preffered embodiment, the supersonic quenching unit may cause the gaseous functional material to be supersonically accelerated and expanded at a speed of ranging from 700m/s to 900 m/s/., and more preferably 740-780 m/s. In the most preferred embodiment, the gaseous functional material has a flow velocity of 769 m/s when exiting from the supersonic quenching. The resultant solid functional material comprises solid metal nitride. The solid metal nitride may be used as a catalytic material or a precursor in subsequent ammonia production, for example, by ways of hydrolysis, thermal decomposition, catalytic decomposition, or chemical reduction of metal nitride.

[0030] FIG.1 illustrates an overview of a method of producing ammonia in one embodiment of the present invention. The production of ammonia may be performed via a 2-step process involving a carbothermic reduction of metal oxide nanoparticles in a nitrogen atmosphere followed by hydrolysis of the resultant metal nitride from the carbothermic reduction step to form ammonia and metal oxide. The metal oxide may be recycled back to the carbothermic reduction step. The reactions may be represented by the following general equations:

1st carbothermic reduction step : $M_xO_y + C + N_2 \rightarrow M_xN_y + CO$

2nd hydrolysis step : $M_xN_y + H_2O \rightarrow M_xO_y + NH_3$

where M denotes the metal, MxNy denotes metal nitride, and MxOy denotes metal oxide.

[0031] As illustrated in FIG.1, a composite material (10), a carbonaceous reducing agent (20) and nitrogen (30) may be first subjected to a ball milling process (100) where the composite material (10) comprising metal oxide, a carbonaceous reducing agent (20) and nitrogen (30) are blended and grinded to form a reaction mixture with a particle size of less than 100 nm. The nitrogen acts as a moisture-stabilizing agent during the grinding process under atmospheric conditions to maintain moisture levels throughout the grinding process and thereby ensuring the reaction mixture is formed with consistent particle size. In one embodiment, the reaction mixture comprises metal oxide nanoparticles with a particle size ranging from 20-30 nm. The reaction mixture is then subjected to a thermochemical heating process (200) in a carbothermic condition in the presence of nitrogen that sufficiently reduces the reaction mixture comprises metal oxide nanoparticles into a functional material comprises metal nitride (40) in a gaseous state. In one embodiment, the carbothermic condition includes a temperature in a range of 1200ºC to 1600ºC and a pressure in a range of 100kPa to 1000kPa. The resultant gaseous functional material is then subjected to a supersonic quenching process (300) where the gaseous functional material (40) is accelerated and expanded to a supersonic speed of at least 700 m/s, ranging from 700 m/s to 900m/s, preferably ranging from 740-780 m/s, and more preferably at 769m/s, so as to achieve a rapid cooling or supersonic quenching that will result the gaseous functional material to directly solidify into a solid functional material (50) without passing through a liquid phase. It is appreciated that, the acceleration and expansion of the gaseous functional material (40) at the supersonic fluid flow rate of at least 700m/s, allow the gaseous functional material to maintain in its gaseous form optimally and at the same time, to be rapidly cooled or supersonically quenched into the solid functional material (50) without passing through a liquid phase. The solid functional material (50) comprises solid metal nitride and is then subjected to a dispersion process (400) where the solid functional material (50) is dispersed with a suitable solvent to optimize the hydrolysis reaction of the solid functional material with the solvent. The resultant mixture of liquid and solid from the hydrolysis reaction may be then subjected to a filtration process (500) where the solid byproducts, for example, the composite material comprises metal oxide or impurities are separated from the liquid phase, which contains hydrous ammonia produced. During the hydrolysis reaction, the composite material (10) comprising metal oxide may be regenerated and can be recycled back to the ball milling process (100) through the supersonic quenching process (300) to form a solid

function material (50). It is understood that the carbothermic reduction step may be reversible.

[0032] Still referring to FIG.1, the hydrous ammonia (60) produced from the hydrolysis process may be further subject to a heat treatment process (600) for production of anhydrous ammonia (70). The heat treatment process (600) may be performed in atmospheric pressure and at a temperature ranging from 60 to 80°C. By this heat treatment process, pure anhydrous ammonia (70) may be obtained.

[0033] In one embodiment, the composite material 10 comprises binary metal oxides or ternary metal oxides. In one embodiment, the binary metal oxide comprises a metal compound selected from the group consisting of magnesium (Mg), aluminum (Al), manganese (Mn), calcium (Ca), lithium (Li), sodium (Na), nickel(Ni) and iron (Fe). In one embodiment, the ternary metal oxide comprises a metal compound selected from the group consisting of magnesium (Mg), aluminum (Al), manganese (Mn), calcium (Ca), lithium (Li), sodium (Na), nickel (Ni) and iron (Fe).

[0034] In one embodiment, the solvent used in the hydrolysis reaction comprises water.

[0035] In one embodiment, the carbonaceous reducing agent (20) comprises carbon-rich substances, for example carbon, graphite, charcoal, porous carbon, nano carbon, single and multi-wall carbon nanotube.

[0036] The supersonic quenching process (300) will be now discussed in detail with reference to FIG. 2 and FIG.3, which respectively illustrates an exemplary system of an embodiment of the present invention where the supersonic quenching process (300) is performed to optimize the formation of metal nitride from a carbothermic reduction of a metal oxide in the nitrogen atmosphere, and an exemplary supersonic quenching unit (1300), preferably a convergent-divergent nozzle aids in the supersonic quenching process (300).

[0037] As illustrated in FIG.2, the system (1000) comprises a reaction chamber (1100), a reaction mixture container (1200) being housed within the reaction chamber (1100) and a supersonic quenching unit (1300). The reaction mixture container holds a reaction mixture for undergoing a carbothermic reaction within the reaction chamber. The reaction mixture comprises metal oxide and a carbonaceous reducing agent. The supersonic quenching unit (1300) is operatively coupled with the reaction chamber (1100) to receive gaseous functional material (40) resulted from the reaction chamber (1100).

[0038] The reaction chamber (1100) is configured to allow carbothermic reduction of the reaction mixture in the presence of nitrogen at a temperature of 1400ºC to 1600ºC and a pressure of approximately 110kPa.. The resultant gaseous functional material (40) from the carbothermic reduction process may be in the form of metallic vapor. The metallic vapor comprises gaseous metal nitride. A stream of carrier gas (80), for example, argon gas or nitrogen gas may be introduced to the reaction chamber (1100) to carry and direct the metallic vapor from the reaction mixture container (1200) to the supersonic quenching unit (1300) where the metallic vapor is accelerated and expanded supersonically at a speed of at least 700 m/s, preferably ranging from 700m/s to 900m/s, more preferably ranging from 740 to 780 m/s, and most preferably 769 m/s, so that the metallic vapor is rapidly cooled or supersonically quenched and solidified into solid metal nitride without passing through a liquid phase. An additional stream (90), for example, nitrogen, is fed into the system through a conduit (1400) that is provided downstream at the exit point the supersonic quenching unit (1300). In one embodiment, the conduit (1400) is in fluid communication with the supersonic quenching unit (1300). The additional stream serves to adjust the fluid temperature, and this additional stream reacts with the coming fluid and forms metal nitride.

[0039] In one embodiment, the supersonic quenching unit (1300) comprises a convergent-divergent nozzle (1310). As illustrated in FIG.3, the exemplary convergent-divergent nozzle (1310) of the present invention comprises a convergent section (1311), a throat section (1313) positioned downstream of the convergent section (1311) and a divergent section (1312) positioned downstream of the throat section (1313). The convergent section (1311) comprises a decreasing cross-sectional area, tapering towards the throat section. The convergent section (1311) is configured to accelerate the gaseous functional material (40) comprises metal nitride or the metallic vapor received from a reaction chamber (1100) to a sonic speed as the metallic moves towards the throat section (1313). The throat section (1313) is located at the junction between the convergent section (1311) and the divergent section (1312). The throat section (1313) is the narrowest part of the convergent-divergent nozzle (1310). When the metallic vapor passes through the throat section (1313), the metallic vapor transitions from a subsonic speed to a supersonic speed of at least 700m/s. The divergent section (1312) follows the throat section (1313) and gradually increases in cross-sectional area from the throat section (1313). With this configuration, the divergent section (1312) decelerates the supersonic flow of the metallic vapor from the throat section (1313) and thereby causes a

significant drop in temperature in a short time, through an adiabatic expansion (i.e., expansion without heat exchange with the surrounding). In one embodiment, the cooling rate is about 550 ºC per second. This advantageously prevents the metallic vapor from condensing into a liquid or depositing on the wall of the convergent-divergent nozzle and directly allows the metallic vapor to solidify without phase change due to its extremely high cooling rate. Additionally, re-oxidation of metallic vapor can be prevented as the kinetic energy available for re-oxidation reactions has been significantly reduced in this supersonic quenching condition. Furthermore, this supersonic quenching process will cause the resultant metal nitride to be more brittle and to fracture. This would increase the surface area of the resultant metal nitride, and therefore potentially enhance the ammonia production rate.

[0040] In one embodiment, to achieve an efficient supersonic quenching of the gaseous functional material (40), or the metallic vapor, into a solid functional material (50) comprising solid metal nitride, without vapor condensation, the convergent-divergent nozzle (1310) may comprise a ratio of an outlet diameter of the divergent section (1312) to a throat diameter in a range of 2.1:1 to 2.28:1. In a preferred embodiment, the convergent-divergent nozzle (1310) may comprise a ratio of an outlet diameter of the divergent section (1312) to a throat diameter of about 2.28:1. The convergent-divergent nozzle (1310) may comprise a ratio of an inlet diameter of the convergent section (1311) to a throat diameter in a range of 3.75:1 to 4.28:1. In a preferred embodiment, the convergent-divergent nozzle (1310) comprises a ratio of an inlet diameter to a throat diameter of about 4.28: 1. In one embodiment, the inlet diameter may be ranging from 100-200 mm and the outlet diameter may be ranging from 250mm to 500mm. As used herein, the outlet diameter refers to the diameter of the cross-sectional area at the exit point of the divergent section (1312). The throat diameter refers to the diameter of the narrowest cross-sectional area within the convergent-divergent nozzle (1313). The inlet diameter refers to the diameter of the cross-sectional area at the entry point of the convergent section (1311).

[0041] In one embodiment, the convergent section (1311) may comprise a convergent section length ranging from 50-250mm. In a preferred embodiment, the convergent length may be about 150 mm. The convergent section length refers to the distance from the entry point of the convergent section (1311) to the throat section.

[0042] In one embodiment, the throat diameter may range from 20mm to 60mm. In a preferred embodiment, the throat diameter may be about 35 mm. As used herein, the throat

diameter refers to the diameter of the narrowest cross-sectional area within the convergent-divergent nozzle (1310).

[0043] In one embodiment, the throat section comprises a throat length ranging from 30 mm to 50 mm. In a preferred embodiment, the throat length may be about 35 mm. As used herein, the throat length refers to the distance across the narrowest section of the nozzle. This throat length is substantially minimized to ensure a sharp transition between the convergent section and divergent section.

[0044] In one embodiment, the divergent section comprises a divergent length ranging from 250 to 500mm. In a preferred embodiment, the divergent length may be about 150 mm. As used herein, the divergent length refers to the distance from the throat to the exit point of the divergent section.

[0045] In one embodiment, the convergent-divergent section (1310) comprises a conduit (1400), that is in fluid communication with and positioned downstream of the divergent section (1312). The conduit (1400) has a conduit length ranging from 500 mm to 2000 mm, from 700 mm to 1800 mm, from 900 mm to 1500 mm, from 600 mm to 1600 mm, from 800 mm to 1700 mm, or from 1000 mm to 1900 mm. In certain embodiments, the conduct length may be about 500 mm, about 600 mm, about 700 mm, about 800 mm, about 900 mm, about 1000 mm, about 1100 mm, about 1200 mm, about 1300 mm, about 1400 mm, about 1500 mm, about 1600 mm, about 1700 mm, about 1800 mm, about 1900 mm, or about 2000 mm. In a certain embodiment, the conduit breadth may be selected from any ranges of from 100 mm to 320 mm, from 150 mm to 300 mm, from 200 mm to 275 mm, or from 125 mm to 250 mm. As used herein, the conduit length refers to distance from one end of the conduit to the other end along its longest dimension. The conduit breath refers to the distance across the conduit perpendicular to its length.

[0046] In one embodiment, the convergent-divergent nozzle (1310) may be a de Laval nozzle. In one embodiment, the convergent-divergent nozzle (1310) may be made of a material comprising high density graphite or other materials having similar structural properties or functionality.

[0047] It is noted that, with the use of the supersonic quenching process (300) or the use of the supersonic quenching unit (1300), for example, the convergent-divergent nozzle (1310) of the present invention, the ammonia yield has been surprisingly increased, for example, a

kilogram of composite material comprises metal oxide can deliver a yield of at least 58% ammonium hydroxide. This high yield of ammonia as compared to the conventional ammonia production is largely attributed to the rapid cooling of the gaseous metal nitride when being accelerated and expanded at a supersonic speed of at least 700 m/s, preferably ranging from 700m/s to 900 m/s, and most preferably ranging from 740m/s to 780 m/s. The gaseous functional material is optimally maintained in its gaseous phase when it being accelerated and expanded at a supersonic speed. This advantageously avoids vapor deposition of the reactants and consequently enhance the ammonia yield since the formation of solid metallic nitride in the carbothermic reduction step has been significantly optimized.

[0048] The convergent-divergent nozzle (1310) designed in accordance with various embodiments of the present invention plays a critical role in the supersonic quenching process (300). The employment of the convergent-divergent nozzle in the supersonic quenching process (300) addresses the issues of reverse oxidation of metal nitride by maintaining an optimum vapor pressure, velocity, and temperature conditions thereby to achieve a rapid cooling of the gaseous metal nitride into solid metal nitride. The convergent-divergent nozzle (1310) prevents reoxidation of the gaseous metal nitride and significantly minimizes vapor deposition of the gaseous metal nitride in the reaction chamber (1100), thereby optimizing the formation of solid metal nitride during the supersonic quenching process (300). This eventually enhances the yield of ammonia in view of this optimized solid metal nitride being formed.

[0049] Various convergent-divergent nozzles (1310) with varying dimensions and configurations, i.e., Nozzle 1 -7, were prepared for experimenting with the supersonic quenching process (300) of the present invention. Fluid flow within these convergent-divergent nozzles (1310), i.e., Nozzle 1-7 were simulated and analyzed based on Computational Fluid Dynamics (CFD). The behavior of the reactant fluid flow within these exemplary convergent-divergent nozzles in the aspects of fluid pressure, temperature and velocity contours can be visualized from FIG.4a-FIG.10b.

[0050] Configuration details of each of the Nozzles 1 to 7 are provided in Table 1.

Table 1

	Nozzle 1	Nozzle 2	Nozzle 3	Nozzle 4	Nozzle 5	Nozzle 6	Nozzle 7
Inlet diameter	150 mm	120 mm	170 mm	150 mm	150 mm	150 mm	150 mm
Outlet diameter	80 mm	80 mm	80 mm	80 mm	80 mm	80mm	80 mm
Throat diameter	30 mm	30 mm	30 mm	40 mm	50 mm	40 mm	35 mm
Area Ratio	2.66	2.66	2.66	2	1.6	2	2.28
Pressure Inlet	1 bar	1 bar (100kPa)	1 bar (100kPa)	1 bar (100kPa)	1 bar (100kPa)	1 bar (100kPa)	1 bar (100kPa)
Inlet Temperature	1400 K (1126.85ºC)	1390 K (1116.85ºC)	1400 K (1126.85ºC)	1400 K (1126.85ºC)	1400 K (1126.85ºC)	1400 K (1126.85ºC)	1700K (1426.85ºC)
Temperature profile at the nozzle end	Not uniform. Blue:300K (26.85ºC) Green:780K (506.85ºC) Red:1400K (1126.85ºC)	Not uniform Blue: 300K (26.85ºC) Green: 780K (506.85ºC) Red: 1390K (1116.85ºC)	Not uniform Blue: 300K (26.85ºC) Green: 780K (506.85ºC) Red: 1390K (1116.85ºC)	Not uniform Blue:300K (26.85ºC) Green:780K (506.85ºC) Red:1400K (1126.85ºC)	Uniform Orange: 1300K (1026.85ºC) Red:1400K (1126.85ºC)	Uniform. Temperature is maintained at 1400K (1126.85ºC). Green:1400K (1126.85ºC)	Uniform. Temperature is maintained at 1470K (1196.85ºC) Green:1470K (1196.85ºC)
Conclusion	Majority is red colour 1400K (1126.85ºC) and **top** side of the nozzle is non uniform	Majority is red colour 1390K (1116.85ºC) and **bottom** side of the nozzle is non uniform	Inlet and outlet side same temperature and velocity	Outlet temperature also 1400K (1126.85ºC)	More uniform but the same inlet and outlet temperature	A slight reduction in outlet temperature obtained at the nozzle top and bottom wall	Inlet temperature higher than outlet temperature Mach no is also 2.4

[0051] Figure 4a is a CFD analysis visualizes how the reactant fluid flows through Nozzle 1 in term of flow velocity. As visualized, the flow velocity starts relatively low at the nozzle inlet (i.e., at around 3.0 m/s), gradually increases as it approaches the nozzle throat and then accelerates beyond the nozzle throat, leading to a flow velocity ranging from 11 m/s to 13 m/s at the nozzle exit. The velocity profile exhibits a snaking pattern, with fluctuations deviating from the nozzle centerline. Near specific sections of nozzle wall of the divergent section, the velocity drops sharply, with some regions reaching as low as 0-1 m/s.

[0052] Referring to Figure 4b, which provides a temperature profile of the reactant fluid passing through Nozzle 1, it is observed that the flow in Nozzle 1 is initially at a temperature of at least 1400K (1126.85ºC) at the nozzle inlet. As the flow accelerates beyond the nozzle throat, the flow temperature remains consistently high, comparable to the inlet conditions. However, at the nozzle exit, a sharp temperature drop is observed near the upper corner adjacent to the nozzle wall. The fluid temperature at the nozzle exit, near the upper corner adjacent to the nozzle wall is around 300-780 K (26.85ºC to 506.85ºC).

[0053] Similar to Nozzle 1, as shown in Figure 5a, the flow velocity in Nozzle 2 starts relatively slows at the nozzle inlet (i.e., at around 3 m/s). As the flow approaches and passes through the nozzle throat, the flow velocity gradually increases and then significantly accelerates to 13-16 m/s. As the flow transitions further, at the exit of the nozzle, the flow velocity drops sharply to 7-8 m/s. The velocity profile exhibits a snaking pattern, with the fluid oscillates across the centerline of the nozzle. When the flow approaches the exit, a notable temperature drop is observed near the lower wall in the divergent section. The flow velocity near the wall in the divergent section is 0-3 m/s.

[0054] The temperature profile of Nozzle 2 is shown in Figure 5b. It is observed that the fluid temperature at the nozzle inlet is at least 1390K (1116.85ºC), and the fluid temperature is maintained as the fluid flows beyond to the nozzle throat and then to the nozzle exit. However, at the nozzle exit, a significant reduction in temperature is observed (i.e. 300-780K or 26.85ºC to 506.85ºC) is observed near the lower corner adjacent to the nozzle wall of the divergent section.

[0055] Similar to both Nozzle 1 and 2, Nozzle 3 has uneven fluid flow distribution. As shown in Figure 6a, the flow starts at a velocity of 1-3m/s and gradually increases to 13-15 m/s when

the flow passes through the nozzle throat and exits the nozzle. The velocity profile exhibits a snaking pattern with the fluid oscillates across the centerline of divergent section of the nozzle. The fluid in some regions near the nozzle walls experiences a drastic reduction in velocity (i.e., at a flow velocity of around 0-8m/s.).

[0056] In the aspect of temperature profile, as shown in Figure 6b, the fluid temperature in Nozzle 3 is constant at 1400K (1126.85ºC) as the fluid progresses from the inlet nozzle to the outlet nozzle, except that at the nozzle exit, a drastically low temperature of 300-780K (26.85ºC to 506.85ºC) is observed near the upper corner adjacent to the upper nozzle wall.

[0057] Figure 7a shows that the flow in Nozzle 4 starts at a velocity of 3-4 m/s at the nozzle inlet. As the flow progresses beyond the nozzle throat and reaches the nozzle exit, a snaking flow pattern at a velocity of 11-13 m/s is observed, with the fluid oscillating across the centerline of the divergent section of the nozzle. It is also observed that near the nozzle walls of the divergent section, the fluid flow velocity has drastically dropped to 0-3 m/s.

[0058] Figure 7b shows that the fluid temperature in Nozzle 4 is constant at 1400K (1126.85ºC) as the fluid progresses from the inlet nozzle to the outlet nozzle. However, at the nozzle exit, near the upper corner adjacent to the nozzle wall, the fluid temperature has drastically dropped to 0-1100 K (-273.15ºC to 826.85ºC).

[0059] Nozzle 5 has a more uniform fluid velocity and temperature profiles as compared to Nozzle 1-4. As shown in Figure 8a, the flow starts at a relatively low velocity at around 6 m/s at the nozzle inlet and steadily increases at a velocity of 15-16 m/s when the flow passes through and beyond the nozzle throat. As the flow progresses further and reaches the nozzle exit, the velocity has dropped to around 10-12 m/s. No snaking fluid pattern is observed.

[0060] Now turning to Figure 8b, the fluid temperature in Nozzle 5 is constantly maintained at 1400K (1126.85ºC) when the fluid progresses from the inlet nozzle to the nozzle exit. The fluid temperature at the inlet nozzle and the outlet nozzle are identical (i.e., 1400K or 1126.85ºC).

[0061] As shown in Figure 9a, it is observed that, within Nozzle 6, as the fluid progresses from the inlet nozzle to the nozzle throat, the fluid velocity is accelerated from 355 m/s to a supersonic speed of 1207 m/s. The fluid flow experiences a progressive reduction of velocity as it further progresses and reaches the nozzle exit. The exit flow velocity is around 780 m/s.

[0062] Figure 9b visualizes the temperature profile of the fluid flow in Nozzle 6. Within the main flow regions, that is the centerline of the divergent section of the nozzle, it can be observed that the temperature is consistently constant at 1400K (1126.85ºC) as the fluid flows from the nozzle inlet, then the nozzle throat and reaches the nozzle exit. The fluid temperature is slightly reduced at the nozzle exit (i.e., having a temperature of around 1300K (1026.85ºC)). Despite this, a narrow thermal boundary layer near the nozzle wall at the nozzle exit exhibits substantially lower temperature, for example, at 263 to 420 K (-10.15ºC to 146.85ºC).

[0063] Figure 10a is a CFD results of Nozzle 7 in the aspect of flow velocity throughout the nozzle. This CFD result demonstrates that the fluid flow accelerated to at least 945 m/s when it passes through the nozzle throat from the nozzle inlet. The fluid flow experiences a significant increase in velocity (i.e., around 1100 m/s) when it transitions further to the mid trunk of the nozzle and the fluid flow progressively slows down and exits at a velocity of around 769 m/s.

[0064] Turning to Figure 10b, it can be observed that Nozzle 7 experiences a gradual reduction in the temperature as the fluid flows from the nozzle inlet to the nozzle exit via the nozzle throat. At the nozzle inlet , the fluid temperature is initially at 1700K(1426.85ºC), and it is gradually reduced to around 1472K (1198.85ºC) when exiting the nozzle.

[0065] Both Nozzle 6 and 7 are suitable for use as a supersonic quenching unit in the ammonia production in accordance with an embodiment of the present invention. Nozzle 7 is most preferred, in one embodiment of the present invention.

[0066] Embodiments of the Present Invention

Embodiment 1: A method for producing ammonia, comprising: (a) carbothermic reduction of a composite material comprising a metal oxide using a carbonaceous reducing agent in a nitrogen atmosphere to form a functional material in a gaseous state; and (b) subjecting the gaseous functional material to a supersonic quenching process whereby the gaseous functional material is supersonically cooled to directly form a solid functional material.

Embodiment 2: The method of **Embodiment 1**, wherein the gaseous functional material is supersonically cooled at a fluid flow speed of at least 700 m/s.

Embodiment 3: The method of **Embodiment 1**, further comprising (c) hydrolyzing the solid functional material with a solvent thereby regenerating a composite material comprising a metal oxide and forming hydrous ammonia.

Embodiment 4: The method of **Embodiment 3**, further comprising (d) subjecting the hydrous ammonia to a heat treatment thereby generating anhydrous ammonia.

Embodiment 5: The method of **Embodiment 3**, further comprising (e) recycling the regenerated composite material to (a) through (b) to form solid functional material.

Embodiment 6: The method of **Embodiment 1** or **Embodiment 2**, wherein (b) subjecting the gaseous functional material to a supersonic quenching process comprises using a convergent-divergent nozzle.

Embodiment 7: The method of **Embodiment 6**, wherein using a convergent-divergent nozzle comprises using a convergent-divergent nozzle having a ratio of an exit diameter to a throat diameter in a range of 2: 1 to 2.28:1.

Embodiment 8: The method of **Embodiment 6** or **7**, wherein the convergent-divergent nozzle comprises a ratio of an exit diameter to a throat diameter of about 2.28: 1.

Embodiment 9: The method of any one of **Embodiments 6 to 8**, wherein the convergent-divergent nozzle comprises a ratio of an inlet diameter to a throat diameter in a range of 3.75:1 to 4.28:1.

Embodiment 10: The method of any one of **Embodiments 6 to 9**, wherein the convergent-divergent nozzle comprises a ratio of an inlet diameter to a throat diameter of about 4.28: 1.

Embodiment 11: The method of any one of the preceding **Embodiments**, wherein the metal oxide is a binary metal oxide or a ternary metal oxide.

Embodiment 12: The method of any one of the preceding **Embodiments**, the carbonaceous reducing agent is selected from a group consisting of carbon, graphite, charcoal, porous carbon, nano carbon, single and multi-wall carbon nanotube.

Embodiment 13: The method of any one of the preceding **Embodiments**, wherein the metal oxide comprises metal oxide nanoparticles having a particle size of equal to or less than 100nm.

Embodiment 14: The method of **Embodiment 13**, wherein the metal oxide nanoparticles comprise a particle size in a range of 20nm to 30nm.

Embodiment 15: An apparatus for producing ammonia comprising: a reaction chamber configured to carry out carbothermic reduction of a composite material comprising metal oxide with a carbonaceous reducing agent in a nitrogen atmosphere to form a functional material in a gaseous state; and a supersonic quenching unit operatively coupled with the reaction chamber and configured to supersonically cool the gaseous functional material to directly form solid functional material.

Embodiment 16: The apparatus of **Embodiment 15**, wherein the supersonic quenching unit is configured to supersonically cool the gaseous functional material at fluid flow speed of at least 700 m/s.

Embodiment 17: The apparatus of **Embodiment 15 or 16**, wherein the supersonic quenching unit comprises a convergent-divergent nozzle.

Embodiment 18: The apparatus of **Embodiment 17**, wherein the convergent-divergent nozzle comprises a ratio of an exit diameter to a throat diameter in a range of 2.1: 1 to 2.28:1.

Embodiment 19: The apparatus of **Embodiment 17 or 18**, wherein the convergent-divergent nozzle comprises a ratio of an exit diameter to a throat diameter of about 2.28: 1.

Embodiment 20: The apparatus of any one of **Embodiments 17 to 19**, wherein the convergent-divergent nozzle comprises a ratio of an inlet diameter to a throat diameter in a range of 3.75:1 to 4.28:1.

Embodiment 21: The apparatus of any one of **Embodiments 17 to 20**, wherein the convergent-divergent nozzle comprises a ratio of an inlet diameter to a throat diameter of about 4.28:1.

Embodiment 22: The apparatus of any one of **Embodiments 15 to 20**, wherein the supersonic quenching unit is operatively coupled with a conduit.

[0067] The embodiments herein and the various features and advantageous details thereof are explained with reference to the non-limiting embodiments in the description. Descriptions of well-known components and processing techniques are omitted so as to not unnecessarily

obscure the embodiments herein. The examples or cases used herein are intended merely to facilitate an understanding of ways in which the embodiments herein may be practiced and to further enable those of skill in the art to practice the embodiments herein. Accordingly, the examples should not be construed as limiting the scope of the embodiments herein.

[0068] The foregoing description of the specific embodiments will so fully reveal the general nature of the embodiments herein that others can, by applying current knowledge, readily modify and/ or adapt for various applications such specific embodiments without departing from the generic concept, and, therefore, such adaptations and modifications should and are intended to be comprehended within the meaning and range of equivalents of the disclosed embodiments. It is to be understood that the phraseology or terminology employed herein is for the purpose of description and not of limitation. Therefore, while the embodiments herein have been described in terms of preferred embodiments, those skilled in the art will recognize that the embodiments herein can be practiced with modification within the spirit and scope of the embodiments as described herein.

[0069] The use of the expression "at least" or "at least one" suggests the use of one or more elements or ingredients or quantities, as the use may be in the embodiment of the disclosure to achieve one or more of the desired objects or results. Any discussion of documents, acts, materials, devices, articles and the like that has been included in this specification is solely for the purpose of providing a context for the disclosure. It is not to be taken as an admission that any or all of these matters form a part of the prior art base or were common general knowledge in the field relevant to the disclosure as it existed anywhere before the priority date of this application.

[0070] While considerable emphasis has been placed herein on the particular features of this disclosure, it will be appreciated that various modifications can be made, and that many changes can be made in the preferred embodiments without departing from the principles of the disclosure. These and other modifications in the nature of the disclosure or the preferred embodiments will be apparent to those skilled in the art from the disclosure herein, whereby it is to be distinctly understood that the foregoing descriptive matter is to be interpreted merely as illustrative of the disclosure and not as a limitation.