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(71) Applicant: **EMPIRE TECHNOLOGY DEVELOPMENT LLC** [US/US]; 2711 Centerville Road, Suite 400, Wilmington, Delaware 19808 (US).

(72) Inventor: **THEVASAHAYAM, Arockiadoss**; C2E, SBI Officer's Qrts, Opp Race Course Ground, Thallakulam, Madurai, Tamilnadu 625002 (IN).

(74) Agent: **SRINIVAS, Harish**; Pepper Hamilton LLP, Suite 5000, 500 Grant Street, Pittsburgh, Pennsylvania 15219-2507 (US).

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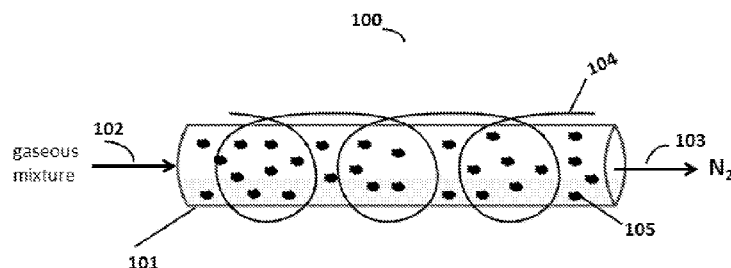


FIG. 1

(57) Abstract: Disclosed herein are methods and systems to isolate nitrogen from a mixture of gases. In an embodiment, a method of isolating nitrogen from a gaseous mixture involves contacting the gaseous mixture with a superparamagnetic catalyst to form a reaction mixture, and exposing the reaction mixture to a fluctuating magnetic field at ambient conditions.

METHODS AND SYSTEMS FOR ISOLATING NITROGEN FROM A GASEOUS MIXTURE

RELATED APPLICATION

[0001] This application claims priority to Indian Patent Application No. 3474/CHE/2014, filed July 14, 2014, entitled, “Methods and Systems for Isolating Nitrogen from a Gaseous Mixture,” the contents of which are herein incorporated by reference.

BACKGROUND

[0002] Nitrogen is frequently prepared by the fractional distillation of liquid air or by pressure swing adsorption (PSA) from atmospheric air. In the synthesis of nitrogen by PSA, the feed air is compressed and/or a vacuum pump is employed for reduction of bed pressure. Nitrogen recovery by PSA is rather low (40-50%) and the mechanical power required is very high.. In the air fractionation process, likewise, the feed air needs to be compressed (to about 100 psi) and cooled prior to distillation. Therefore, it is relatively expensive to isolate nitrogen by this method.

SUMMARY

[0003] Disclosed herein are methods and systems to purify nitrogen from a mixture of gases. In an embodiment, a method of isolating nitrogen from a gaseous mixture involves contacting the gaseous mixture with a superparamagnetic catalyst to form a reaction mixture, and exposing the reaction mixture to a fluctuating magnetic field.

[0004] In an additional embodiment, a method of making a catalyst involves contacting a paramagnetic oxide, cerium (IV) oxide, and a base. In some embodiments, the catalyst may be FeCe_2O_4 nanoparticles.

[0005] In a further embodiment, a reactor system for isolating nitrogen from a gaseous mixture includes a closed reaction vessel configured to receive a gaseous mixture

and a superparamagnetic catalyst, and at least one current carrying element arranged in proximity to a surface of the reaction vessel to provide a fluctuating magnetic field.

BRIEF DESCRIPTION OF THE FIGURES

[0006] FIG. 1 depicts a diagram of a reactor system to purify nitrogen from a mixture of gases according to an embodiment.

[0007] FIG. 2 represents a putative structure of FeCe_2O_4 according to an embodiment.

[0008] FIG. 3 depicts X-ray diffraction pattern of FeCe_2O_4 according to an embodiment. The XRD was acquired on a Xperts Pananalytical X-Ray diffractometer using Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 0.15418$ nm) with a scanning range (2θ) of 10 to 90. The peaks 2θ at 32.85, 46.724, 58.24, 67.70 and 77.19 correspond to iron cerium oxide (pcpdf files 36-1253).

DETAILED DESCRIPTION

[0009] This disclosure is not limited to the particular systems, devices and methods described, as these may vary. The terminology used in the description is for the purpose of describing the particular versions or embodiments only, and is not intended to limit the scope.

[0010] Disclosed herein are methods and systems for isolating or purifying nitrogen from a mixture of gases. In some embodiments, a method of isolating nitrogen from a gaseous mixture involves contacting the gaseous mixture with a superparamagnetic catalyst to form a reaction mixture, and exposing the reaction mixture to a fluctuating magnetic field at ambient conditions. The gaseous mixture may be air, flue gas, natural gas, or any combination thereof. In some embodiments, the gaseous mixture includes nitrogen, hydrogen,

oxygen, carbon dioxide, or any combination thereof. In other embodiments, the gaseous mixture may be compressed air.

[0011] FIG. 1 depicts an illustrative diagram of a reactor system **100** in accordance with an embodiment of the present disclosure. System **100** may be utilized for a one-step process for isolating nitrogen from air. The reactor system (or apparatus) **100** generally comprises a reaction vessel **101**, an inlet valve for gaseous mixture **102**, an outlet valve for nitrogen **103**, and a current carrying element **104**. Further, the catalyst FeCe_2O_4 **105** may be disposed within the reaction vessel.

[0012] In some embodiments, the reactor system **100** comprises at least one current carrying element **104** arranged in proximity to a surface of the reaction vessel and configured to provide a fluctuating magnetic field. Current carrying elements may be configured to generate magnetic fields of various strengths. The greater the current flow and coil density, the stronger the magnetic field. For instance, coil density may be high in order to produce a uniform magnetic field. In addition, the quantity of power required to achieve a particular magnetic field may depend on various factors, including the scale, structure, and location of the current carrying element with respect to the reaction vessel.

[0013] In other embodiments, the reactor system described herein may further comprise a thermoelectric couple, a pressure gauge, a temperature controller, a cooling system, a mechanical stirrer, or any combination thereof. In some embodiments, the current carrying element may be in close proximity to the reaction vessel. In other embodiments, the current carrying element may form a circular coil around a reaction vessel, as illustrated in FIG. 1. According to some embodiments, the strength of a magnetic field generated by the current carrying element may be about 0.1 millitesla to about 1 tesla, about 0.1 millitesla to about 0.5 tesla, about 0.1 millitesla to about 0.1 tesla, about 0.1 millitesla to about 10 millitesla, about 0.1 millitesla to about 1 millitesla, or any range between any two of these

values (including endpoints). The current carrying elements may be energized using various methods, including, without limitation, direct current, alternating current, and high-frequency alternating current. According to embodiments, the high-frequency alternating current may be about 25 hertz (Hz) to about 1 megahertz, about 25 hertz to about 500 kilohertz, or about 25 hertz to about 100 kilohertz. Specific examples include, but are not limited to, about 25 hertz, about 100 hertz, about 500 hertz, about 1 kilohertz, about 300 kilohertz, about 400 kilohertz, about 500 kilohertz, and about 1 megahertz, or any range between any two of these values (including endpoints). In some embodiments, the electric current may be in the range of about 0.1 ampere (A) to about 100 A, about 0.1 ampere to about 50 A, about 0.1 ampere to about 30 A, or about 0.1 ampere to about 1 A. Specific examples include, but are not limited to, about 0.1 A, about 5 A, about 10 A, about 20 A, about 50 A, and about 100 A, or any range between any two of these values (including endpoints).

[0014] The reactor system described herein may be a batch reactor system or a continuous flow reactor system. In some embodiments, the reaction vessel may be configured to maintain a constant pressure of gaseous mixture during the reaction process. For example, the gaseous mixture may be present at a pressure of about 0.5 atmosphere to about 1.5 atmospheres, about 0.5 atmosphere to about 1 atmosphere, or about 0.5 atmosphere to about 0.75 atmosphere. Specific examples include about 0.5 atmosphere, , about 0.75 atmosphere, about 1 atmosphere, about 1.25 atmospheres, and about 1.5 atmospheres, or any range between any two of these values (including endpoints).

[0015] The catalyst **105** that may be used in the reaction system **100** may be a superparamagnetic catalyst, such as FeCe_2O_4 , NiCe_2O_4 , or CoCe_2O_4 , or any combination thereof. In some embodiments, the catalyst may be in the form of nanoparticles. The catalyst described in the embodiments herein may be unsupported or may be supported over a surface of a support in a manner that maximizes the surface area of the catalytic reaction. A suitable

support may be selected from any conventional support, such as polymer membrane or a porous aerogel. For example, the catalyst may be coated on a polymer membrane and woven into a 3D mesh and introduced in the reactor system **100**.

[0016] In some embodiments, the catalyst described herein may be present in the reaction mixture at about 0.1 mole percent to about 1 mole percent, about 0.1 mole percent to about 0.5 mole percent, or about 0.1 mole percent to about 0.2 mole percent of the total reaction mixture. Specific examples include, but are not limited to, about 0.1 mole percent, about 0.2 mole percent, about 0.3 mole percent, about 0.4 mole percent, about 0.5 mole percent, about 0.6 mole percent, about 0.7 mole percent, about 0.8 mole percent, about 0.9 mole percent and about 1 mole percent, or any range between any two of these values (including endpoints).

[0017] In some embodiments, the reaction mixture is exposed to a fluctuating magnetic field for about 30 minutes to about 3 hours. In some embodiments, the reaction mixture is exposed to a fluctuating magnetic field for about 30 minutes to about 2 hours. In some embodiments, the fluctuating magnetic field is applied for about 30 minutes to about 1 hour. In some embodiments, the reaction mixture is exposed to the fluctuating magnetic field for about 30 minutes, about 45 minutes, about 1 hour, about 1.5 hours, or about 3 hours, or any value or range of values between any of these values (including endpoints).

[0018] It is believed that the catalyst nanoparticles in the reaction mixture adsorb other gases in the mixture, leaving behind nitrogen, which exits the reaction vessel via an outlet. The obtained nitrogen gas is about 90% pure, about 95% pure, about 96% pure, about 97% pure, about 98% pure, about 99% pure, about 99.1% pure, about 99.5% pure, about 99.99% pure, or 100% pure. At the end of the reaction process, the superparamagnetic catalyst may be recovered by applying a magnetic field. For example, a bar magnet may be

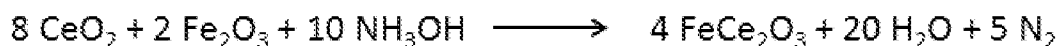
used to collect FeCe_2O_4 particles at the end of the reaction. The catalyst thus obtained can be reused.

[0019] Also disclosed herein are methods to make a catalyst. In some embodiments, the method involves contacting a paramagnetic oxide, cerium (IV) oxide, and a base. Non-limiting examples of paramagnetic oxides that may be used include, but are not limited to, iron oxide, nickel oxide, and cobalt oxide, or any combination thereof. In some embodiments, the base may be aqueous ammonia or hydrazine hydroxide, or a combination thereof.

[0020] In some embodiments, the catalyst FeCe_2O_4 may be prepared by contacting Fe_2O_3 , CeO_2 , and aqueous ammonia. Aqueous ammonia (ammonium hydroxide) may have a concentration of about 20 weight percent to about 50 weight percent, about 20 weight percent to about 40 weight percent, or about 20 weight percent to about 30 weight percent. Specific examples include, but are not limited to, about 20 weight percent, about 25 weight percent, about 30 weight percent, and about 50 weight percent, or any range between any two of these values (including their endpoints). In some embodiments, contacting may be accomplished by any suitable means, including mixing, stirring, combining, shaking, agitation, and the like. Fe_2O_3 , CeO_2 , and aqueous ammonia may be contacted for about 10 minutes to about 1 hour, about 10 minutes to about 45 minutes, about 10 minutes to about 30 minutes, or about 10 minutes to about 20 minutes. Specific examples include, but are not limited to, about 10 minutes, about 20 minutes, about 30 minutes, about 45 minutes, and about 1 hour, or any range between any two of these values (including their endpoints). In some embodiments, Fe_2O_3 and CeO_2 may be contacted in a molar ratio of about 1:6 to about 1:2, about 1:6 to about 1:3, about 1:6 to about 1:4, or about 1:6 to about 1:5. Specific examples include, but are not limited to, about 1:6, about 1:5, about 1:4, about 1:3, and about 1:2, or any range between any two of these values (including their endpoints). In some

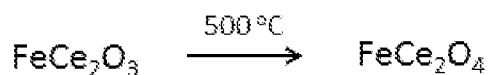
embodiments, CeO_2 , Fe_2O_3 , and ammonia may be contacted in a molar ratio of about 4:1:5, about 4:1:6, about 4:2:5, about 2:1:3, or about 1:1:1.

[0021] After the mixing step, the solvent is evaporated. This step may be performed by any known process in the art, such as heating, rotary evaporation, air drying, Soxhlet extraction, refluxing, or evaporating in an oven until the solvent is substantially evaporated. For example, the solvent may be heated to about 80 °C, about 100 °C, about 120 °C, or about 130 °C, using a reflux condenser. The reaction process may be outlined as follows:



[0022] In some embodiments, the FeCe_2O_3 obtained may further be subjected to the steps of washing, filtering, and drying. Drying may generally be performed in a hot air oven by heating to temperature of about 80-120 °C for 30-60 minutes. After drying, the FeCe_2O_3 powder may be heated in a furnace to a temperature of about 500 °C to about 800 °C. The heating may be carried out, for about 5 minutes to about 1 hour, about 5 minutes to about 45 minutes, about 5 minutes to about 30 minutes, or about 5 minutes to about 15 minutes. Specific examples include, but are not limited to, about 5 minutes, about 10 minutes, about 15 minutes, about 30 minutes, about 45 minutes, and about 1 hour, or any ranges between any two of these values (including their endpoints).

[0023] In some embodiments, the FeCe_2O_3 obtained after heating is subjected to ethanol washing in the presence of oxygen. This step converts FeCe_2O_3 to FeCe_2O_4 . This process may further impart a superparamagnetic property to the catalyst.



[0024] The FeCe_2O_4 catalyst obtained by the methods disclosed herein may be a nanoparticle having an average diameter of about 1 nanometer to about 50 nanometers, about

1 nanometer to about 40 nanometers, about 1 nanometer to about 25 nanometers, or about 1 nanometer to about 10 nanometers. Specific examples include, but are not limited to, about 1 nanometer, about 5 nanometers, about 15 nanometers, about 25 nanometers, and about 50 nanometers, or any range between any two of these values (including their endpoints). A putative structure of FeCe_2O_4 catalyst is shown in FIG. 2.

EXAMPLES

EXAMPLE 1: Preparation of FeCe_2O_4 catalyst

[0025] About 1 gram of Fe_2O_3 and 5 grams of CeO_2 were mixed and about 50 mL of ammonia solution was added drop by drop to the mixture of oxides at room temperature for about 30 minutes to form a solution. The solution was transferred to a reflux condenser and maintained at 120 °C until all the solvent was evaporated. The FeCe_2O_3 powder obtained was washed with distilled water until a pH of 7 was reached. The FeCe_2O_3 powder was dried in an hot air oven at 100 °C for 30 minutes. After drying, the FeCe_2O_3 powder was heated in a furnace for 10-15 minutes at 700 °C. The powdered material was removed and about 10 mL of ethanol was added immediately in the presence of atmospheric oxygen. Addition of ethanol to the hot powdered material instantly vaporized ethanol, thus imparting superparamagnetism to the catalyst. The FeCe_2O_4 catalyst prepared was characterized by X-ray diffraction and shows a polycrystalline structure (FIG. 3).

EXAMPLE 2: Isolating nitrogen gas from compressed air

[0026] About 500 milligrams of FeCe_2O_4 catalyst prepared in Example 1 was introduced in a closed reaction vessel, connected to an air compressor and an outlet connected to a gas collection chamber. Air was introduced into the reaction vessel and was exposed to a fluctuating magnetic field by supplying an electric current of 230V, 50 Hz, 240 mA for 60 minutes (magnetic field about 1000 μT). During the reaction process, the outlet

valve was opened to collect nitrogen that was released. The nitrogen gas that was obtained was 99% pure. The FeCe_2O_4 catalyst was recovered using simple magnets (0.03T) for reuse.

EXAMPLE 3: Isolating nitrogen from flue gas

[0027] About 500 milligrams of FeCe_2O_4 catalyst prepared in Example 1 is introduced in a closed reaction vessel, connected to a flue gas source and an outlet connected to a gas collection chamber. Flue gas is introduced into the reaction vessel and is exposed to a fluctuating magnetic field by supplying an electric current of 230V, 50 Hz, 240 mA for 75 minutes (magnetic field about 1000 μtesla). During the reaction process, the outlet valve is opened to collect nitrogen that is released. The nitrogen gas that is obtained is 98% pure. The FeCe_2O_4 catalyst is recovered using simple magnets (0.03T) for reuse.

EXAMPLE 4: Measurement of adsorption-desorption rates of oxygen to FeCe_2O_4 catalyst

[0028] About 100 milligrams of FeCe_2O_4 catalyst was placed in an enclosed chamber (250 mL vol) and exposed to various amounts of compressed air for 5 minutes. The initial pressure of compressed air was measured at the start of the experiment (A, Table 1). The chamber pressure after 5 minute exposure to 100 milligrams of FeCe_2O_4 was measured (B, Table 1), which indicated adsorption rate. To measure desorption, FeCe_2O_4 particles were kept in vacuum and subsequently exposed to hyperthermia for 5 minutes and the chamber pressure was measured (C, Table 1). The release of the adsorbed gas indicated the desorption rate.

TABLE 1

A: chamber pressure (mbar) at the start of the experiment	B: chamber pressure (mbar) after 5 minute exposure	C: chamber pressure (mbar) after hyperthermia
10	3.13	6.36
20	12.84	6.97
30	22.64	6.97
40	32.64	6.97

50	42.64	6.97
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[0029] In the above detailed description, reference is made to the accompanying drawings, which form a part hereof. In the drawings, similar symbols typically identify similar components, unless context dictates otherwise. The illustrative embodiments described in the detailed description, drawings, and claims are not meant to be limiting. Other embodiments may be used, and other changes may be made, without departing from the spirit or scope of the subject matter presented herein. It will be readily understood that the aspects of the present disclosure, as generally described herein, and illustrated in the Figures, can be arranged, substituted, combined, separated, and designed in a wide variety of different configurations, all of which are explicitly contemplated herein.

[0030] The present disclosure is not to be limited in terms of the particular embodiments described in this application, which are intended as illustrations of various aspects. Many modifications and variations can be made without departing from its spirit and scope, as will be apparent to those skilled in the art. Functionally equivalent methods and apparatuses within the scope of the disclosure, in addition to those enumerated herein, will be apparent to those skilled in the art from the foregoing descriptions. Such modifications and variations are intended to fall within the scope of the appended claims. The present disclosure is to be limited only by the terms of the appended claims, along with the full scope of equivalents to which such claims are entitled. It is to be understood that this disclosure is not limited to particular methods, reagents, compounds, compositions or biological systems, which can, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting.

[0031] As used in this document, the singular forms “a,” “an,” and “the” include plural references unless the context clearly dictates otherwise. Unless defined otherwise, all

technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art. Nothing in this disclosure is to be construed as an admission that the embodiments described in this disclosure are not entitled to antedate such disclosure by virtue of prior invention. As used in this document, the term “comprising” means “including, but not limited to.”

[0032] While various compositions, methods, and devices are described in terms of "comprising" various components or steps (interpreted as meaning "including, but not limited to"), the compositions, methods, and devices can also "consist essentially of" or "consist of" the various components and steps, and such terminology should be interpreted as defining essentially closed-member groups.

[0033] With respect to the use of substantially any plural and/or singular terms herein, those having skill in the art can translate from the plural to the singular and/or from the singular to the plural as is appropriate to the context and/or application. The various singular/plural permutations may be expressly set forth herein for sake of clarity.

[0034] It will be understood by those within the art that, in general, terms used herein, and especially in the appended claims (example, bodies of the appended claims) are generally intended as “open” terms (example, the term “including” should be interpreted as “including but not limited to,” the term “having” should be interpreted as “having at least,” the term “includes” should be interpreted as “includes but is not limited to,” etc.). It will be further understood by those within the art that if a specific number of an introduced claim recitation is intended, such an intent will be explicitly recited in the claim, and in the absence of such recitation no such intent is present. For example, as an aid to understanding, the following appended claims may contain usage of the introductory phrases "at least one" and "one or more" to introduce claim recitations. However, the use of such phrases should not be construed to imply that the introduction of a claim recitation by the indefinite articles "a" or

"an" limits any particular claim containing such introduced claim recitation to embodiments containing only one such recitation, even when the same claim includes the introductory phrases "one or more" or "at least one" and indefinite articles such as "a" or "an" (example, "a" and/or "an" should be interpreted to mean "at least one" or "one or more"); the same holds true for the use of definite articles used to introduce claim recitations. In addition, even if a specific number of an introduced claim recitation is explicitly recited, those skilled in the art will recognize that such recitation should be interpreted to mean at least the recited number (example, the bare recitation of "two recitations," without other modifiers, means at least two recitations, or two or more recitations). Furthermore, in those instances where a convention analogous to "at least one of A, B, and C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (example, "a system having at least one of A, B, and C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). In those instances where a convention analogous to "at least one of A, B, or C, etc." is used, in general such a construction is intended in the sense one having skill in the art would understand the convention (example, "a system having at least one of A, B, or C" would include but not be limited to systems that have A alone, B alone, C alone, A and B together, A and C together, B and C together, and/or A, B, and C together, etc.). It will be further understood by those within the art that virtually any disjunctive word and/or phrase presenting two or more alternative terms, whether in the description, claims, or drawings, should be understood to contemplate the possibilities of including one of the terms, either of the terms, or both terms. For example, the phrase "A or B" will be understood to include the possibilities of "A" or "B" or "A and B."

[0035] In addition, where features or aspects of the disclosure are described in terms of Markush groups, those skilled in the art will recognize that the disclosure is also

thereby described in terms of any individual member or subgroup of members of the Markush group.

[0036] As will be understood by one skilled in the art, for any and all purposes, such as in terms of providing a written description, all ranges disclosed herein also encompass any and all possible subranges and combinations of subranges thereof. Any listed range can be easily recognized as sufficiently describing and enabling the same range being broken down into at least equal halves, thirds, quarters, fifths, tenths, etc. As a non-limiting example, each range discussed herein can be readily broken down into a lower third, middle third and upper third, etc. As will also be understood by one skilled in the art all language such as “up to,” “at least,” and the like include the number recited and refer to ranges which can be subsequently broken down into subranges as discussed above. Finally, as will be understood by one skilled in the art, a range includes each individual member. Thus, for example, a group having 1-3 cells refers to groups having 1, 2, or 3 cells. Similarly, a group having 1-5 cells refers to groups having 1, 2, 3, 4, or 5 cells, and so forth.

[0037] Various of the above-disclosed and other features and functions, or alternatives thereof, may be combined into many other different systems or applications. Various presently unforeseen or unanticipated alternatives, modifications, variations or improvements therein may be subsequently made by those skilled in the art, each of which is also intended to be encompassed by the disclosed embodiments.

CLAIMS

What is claimed is:

1. A method of isolating nitrogen from a gaseous mixture, the method comprising:

 contacting the gaseous mixture with a superparamagnetic catalyst to form a reaction mixture; and

 exposing the reaction mixture to a fluctuating magnetic field.
2. The method of claim 1, wherein contacting the gaseous mixture with a superparamagnetic catalyst comprises contacting the gaseous mixture with FeCe_2O_4 .
3. The method of claim 1, wherein contacting the gaseous mixture with a superparamagnetic catalyst comprises contacting air, flue gas, natural gas, or any combination thereof with the superparamagnetic catalyst.
4. The method of claim 1, wherein contacting the gaseous mixture with a superparamagnetic catalyst comprises contacting nitrogen, hydrogen, oxygen, carbon dioxide, or any combination thereof with the superparamagnetic catalyst.
5. The method of claim 1, wherein contacting the gaseous mixture with the superparamagnetic catalyst comprises contacting the gaseous mixture and the superparamagnetic catalyst in a closed reaction vessel.
6. The method of claim 1, wherein exposing the reaction mixture to the fluctuating magnetic field comprises exposing the reaction mixture to the fluctuating magnetic field in a closed reaction vessel.
7. The method of claim 1, wherein exposing the reaction mixture to the fluctuating magnetic field comprises exposing the reaction mixture to the fluctuating magnetic field in a closed reaction vessel having at least one inlet and at least one outlet.

8. The method of claim 1, wherein exposing the reaction mixture to the fluctuating magnetic field further comprises maintaining a constant pressure in a reaction vessel during the exposing step.

9. The method of claim 8, wherein maintaining the constant pressure in the reaction vessel comprises maintaining a constant pressure of about 0.5 atmosphere to about 1.5 atmospheres in the reaction vessel.

10. The method of claim 1, wherein contacting the gaseous mixture with the superparamagnetic catalyst to form a reaction mixture comprises contacting the gaseous mixture with the superparamagnetic catalyst which is present at about 0.1 mole percent to about 1 mole percent of the reaction mixture.

11. The method of claim 1, wherein contacting the gaseous mixture with the superparamagnetic catalyst comprises contacting the gaseous mixture with nanoparticles of FeCe_2O_4 .

12. The method of claim 11, wherein contacting the gaseous mixture with the superparamagnetic catalyst comprises contacting the gaseous mixture with FeCe_2O_4 nanoparticles coated on a polymer membrane.

13. The method of claim 1, wherein exposing the reaction mixture to the fluctuating magnetic field comprises exposing the reaction mixture to the fluctuating electromagnetic field generated by an electrical current of about 0.1 ampere (A) to about 100 A, and a frequency of about 25 hertz to about 1 megahertz.

14. The method of claim 13, wherein exposing the reaction mixture to the fluctuating magnetic field comprises exposing the reaction mixture to the fluctuating electromagnetic field of about 0.1 millitesla to about 1 tesla.

15. The method of claim 1, wherein exposing the reaction mixture to the fluctuating magnetic field comprises exposing the reaction mixture to the fluctuating magnetic field for about 30 minutes to about 3 hours.

16. The method of claim 1, further comprising performing the contacting and the exposing steps by a batch process or a continuous process.

17. A method of making a catalyst, the method comprising contacting a paramagnetic oxide, cerium (IV) oxide, and a base.

18. The method of claim 17, wherein contacting the paramagnetic oxide, cerium (IV) oxide, and the base comprises contacting iron oxide, nickel oxide, cobalt oxide, or any combination thereof with cerium (IV) oxide and the base.

19. The method of claim 17, wherein contacting the paramagnetic oxide, cerium (IV) oxide, and the base comprises contacting paramagnetic oxide and cerium (IV) oxide with aqueous ammonia, hydrazine hydroxide, or any combination thereof.

20. The method of claim 17, wherein contacting the paramagnetic oxide, cerium (IV) oxide, and the base comprises contacting paramagnetic oxide, cerium (IV) oxide, and FeCe_2O_4 to form nanoparticles of FeCe_2O_4 .

21. The method of claim 17, wherein contacting the paramagnetic oxide, cerium (IV) oxide, and the base comprises contacting Fe_2O_3 , CeO_2 , and aqueous ammonia.

22. The method of claim 21, wherein contacting the paramagnetic oxide, cerium (IV) oxide, and the base comprises contacting the paramagnetic oxide, cerium (IV) oxide, and the base for about 10 minutes to about 1 hour.

23. The method of claim 17, wherein contacting the paramagnetic oxide, cerium (IV) oxide, and the base comprises contacting CeO_2 , Fe_2O_3 , and aqueous ammonia in a molar ratio of about 4:1:5.

24. The method of claim 23, further comprising isolating the catalyst by evaporating a solvent.

25. The method of claim 24, wherein isolating the catalyst further comprises washing the catalyst, filtering the catalyst, and drying the catalyst.

26. The method of claim 25, wherein drying the catalyst further comprises heating the catalyst to a temperature of about 500 °C to about 800 °C.

27. The method of claim 26, wherein heating the catalyst further comprises heating the catalyst for about 5 minutes to about 30 minutes.

28. The method of claim 27, wherein heating the catalyst further comprises contacting the catalyst with ethanol to convert the catalyst to a superparamagnetic catalyst.

29. A reactor system for isolating nitrogen from a gaseous mixture, the reactor comprising:

a closed reaction vessel configured to receive a gaseous mixture and a super paramagnetic catalyst; and

at least one current carrying element arranged in proximity to a surface of the reaction vessel to provide a fluctuating magnetic field.

30. The reactor system of claim 29, wherein the catalyst is FeCe_2O_4 nanoparticles.

31. The reactor system of claim 29, wherein the reactor system is a batch reactor system or a continuous reactor system.

32. The reactor system of claim 29, further comprising at least one inlet valve and at least one outlet valve.

33. The reactor system of claim 32, wherein the inlet valve is configured to allow the gaseous mixture into the reaction vessel.

34. The reactor system of claim 29, wherein the reaction vessel is configured to maintain a constant pressure of the during a reaction process.

35. The reactor system of claim 29, further comprising a gaseous mixture and at least one superparamagnetic catalyst.

36. The reactor system of claim 29, further comprising nitrogen.

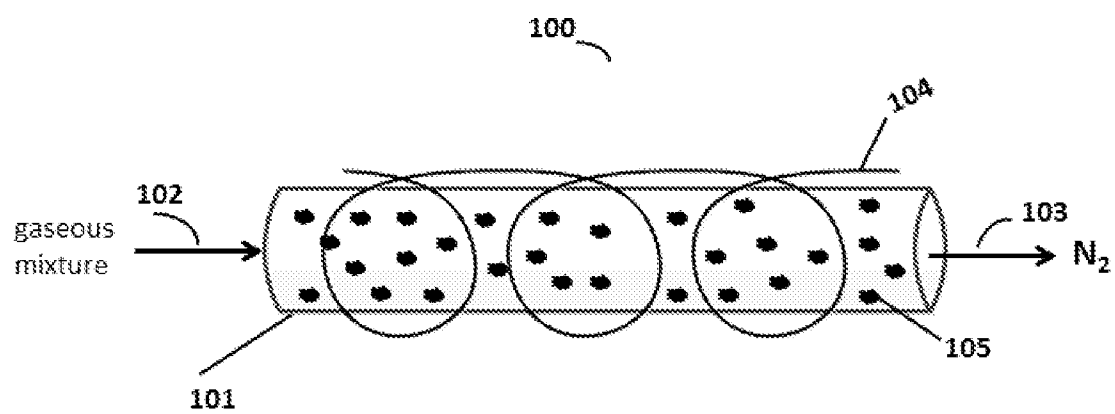


FIG. 1

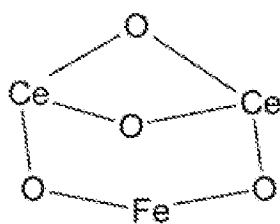


FIG. 2

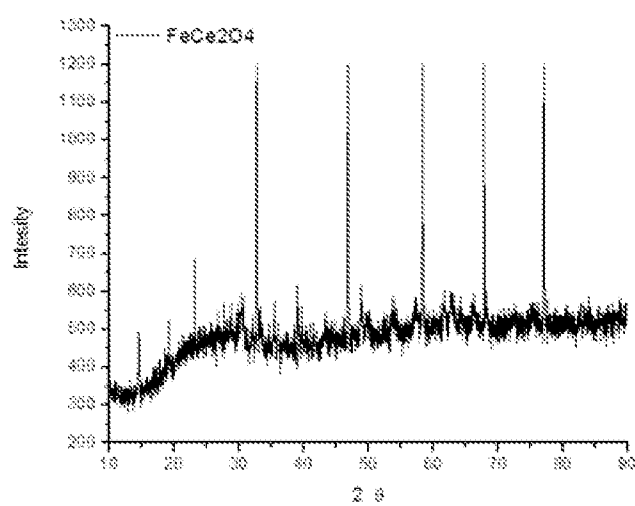


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 15/40285

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: claims 1-16, directed to a method of isolating nitrogen from a gaseous mixture, the method comprising: contacting the gaseous mixture with a superparamagnetic catalyst to form a reaction mixture.

Group II: claims 17-28, directed to a method of making a catalyst

Group III: claims 29-36, directed to a reactor system for isolating nitrogen from a gaseous mixture, the reactor comprising a closed reaction vessel configured to receive a gaseous mixture

Continue on first sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-16

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 15/40285

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B01D 53/02 (2015.01)

CPC - B01D 53/26; B01D 53/261 and F24F 2003/144

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)

IPC(8) - B01D 53/02 (2015.01)

CPC - B01D 53/26; B01D 53/261 and F24F 2003/144

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
 CPC - CPC= B01J2208/00469, B01J12/00, B01J2208/0038, B01J20/28004, B01D53/12, B01D53/02, B01D15/02, B01J2208/0038, C07D277/56, B01J2208/00433, G01N24/08, G01R33/44, G01N27/74, G01R33 (Search terms- See below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 PatBase and Google. Search terms: nitrogen, nitrous, superparamagnetic, catalyst, paramagnetic, catalyst, super, magnetic, field, fluctuate, variable, oscillate, vibrate, gas, gaseous, separation, isolation, remove, react, absorb, fece2o4, ferrous, cerium, oxide and ceria.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 1,553,737 A (Allingham) 15 September 1925 (15.09.1925) Entire document, especially Fig 2 and pg 2, ln 16-98.	1-16
Y	US 4,668,379 A (Rosensweig et al.) 26 May 1987 (26.05.1987) Entire document, especially col 3, ln 34-36; col 5, ln 34-36; col 6, ln 45-48; col 9, ln 43-58 and col 11, ln 65 to col 12, ln 2	1-16
Y	Niu et al. 'The corrosion of a Fe-15 wt.% Ce alloy in Coal Gasification Type Atmospheres at 600 to 800 deg. C'; (Published 2002), Journal of Phase Equilibria; February 2002, Volume 23, Issue 1, pp 61-67 url:< http://link.springer.com/article/10.1361/105497102770332225#> Entire document, especially pg 65, col 1, para 2.	2, 11 and 12
A	US 2009/0230347 A1 (Pridohl et al.) 17 September 2009 (17.09.2009) Entire document, especially para [0035] and [0040]	1

☐ Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"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

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

06 November 2015

Date of mailing of the international search report

15 DEC 2015

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents

P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300

PCT OSP: 571-272-7774

Continue from Box III

The inventions listed as Groups I-III do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special technical features:

The special technical feature of Group I is a method of isolating nitrogen from a gaseous mixture, the method comprising: contacting the gaseous mixture with a superparamagnetic catalyst to form a reaction mixture which is not required by groups II-III

The special technical feature of Group II is a method of making a catalyst, the method comprising contacting a paramagnetic oxide, cerium (IV) oxide, and a base, which is not required by groups I and III

The special technical feature of Group III is a reactor system for isolating nitrogen from a gaseous mixture, the reactor comprising: a closed reaction vessel configured to receive a gaseous mixture and a super paramagnetic catalyst; and at least one current carrying element arranged in proximity to a surface of the reaction vessel to provide a fluctuating magnetic field, which is not required by groups I and II

Common technical features:

Groups I-III share the technical feature of a catalyst. However, this shared technical feature does not provide a contribution over the prior art because this shared technical features as being anticipated by US 5,190,635 A to Hettner as Hettner teaches a catalyst, in particular a superparamagnetic catalyst (col 8, ln 32-35 'Following is an example of a typical catalytic cracking process operating commercially with a catalyst containing a high level of superparamagnetic material.').

Groups I and III share the technical feature of isolating nitrogen from a gaseous mixture, the method comprising: contacting the gaseous mixture with a superparamagnetic catalyst to form a reaction mixture; and exposing the reaction mixture to a fluctuating magnetic field

However, this shared technical feature does not provide a contribution over the prior art because this shared technical feature is being obvious over US 2009/0230347 A1 to Pridohl et al. (hereinafter 'Pridohl') as PridFohl discloses the feature of isolating gases from a gaseous mixture (para [0040] 'the powder formed (superparamagnetic material para [0038] 'Preparation of the Superparamagnetic Powders') are cooled in a known manner and separated off from the stream of waste gases') and the method comprising: contacting the gaseous mixture with a superparamagnetic catalyst to form a reaction mixture (para [0040] 'After the reaction, the reaction gases and the powder formed (superparamagnetic material) are cooled in a known manne' -After the formation of the superparamagnetic material the material is still exposed to gases) and exposing the reaction mixture to a fluctuating (alternating) magnetic field (para [0035] 'preferably, for heating, the formulation according to the invention is exposed to a magnetic alternating field'). However, Pridohl does not disclose isolating nitrogen. While Pridohl does not specify isolating nitrogen, it would have been obvious to one of ordinary skill in the art to isolate nitrogen, as the nitrogen could then be reused in the process or in another process.

Groups I-III, therefore, lack unity under PCT Rule 13.2, because they do not share a same or corresponding special technical feature providing a contribution over the prior art.