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(54) Title: CHEMICAL LOOPING SYSTEMS FOR CONVERSION OF LOW- AND NO-CARBON FUELS TO HYDROGEN

(57) Abstract: Disclosed herein are systems and methods for producing H2 from low carbon fuels (LCFs) using metal oxides in a chemical looping process.

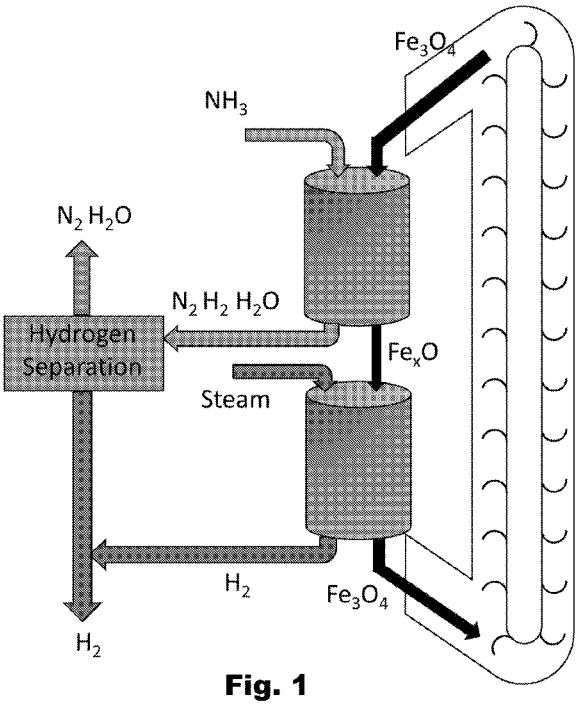

Fig. 1

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CHEMICAL LOOPING SYSTEMS FOR CONVERSION OF LOW- AND NO-CARBON FUELS TO HYDROGEN

CROSS-REFERENCE TO RELATED APPLICATION(S)

[0001] This patent application claims the benefit of priority to United States Provisional Application No. 62/341,294, filed on May 25, 2016, the entire contents of which are hereby incorporated by reference.

TECHNICAL FIELD

[0002] The intense debate on climate change triggered by greenhouse gas emissions from anthropogenic activities has led to extensive research efforts towards concepts like H_2 economy. H_2 as fuel burns without harmful emissions; however, the transportation of H_2 from its production site makes current large scale deployment a challenge. Several carbon-neutral or low carbon fuels (LCFs) have been investigated as sources of H_2 as they are more economical to transport over longer distances. Large scale utilization of these fuels is predicted to significantly improve the market penetration of utilization of H_2 as a fuel. This disclosure describes a low temperature process which utilizes a looping schematic for high-efficiency conversion of LCFs to H_2.

BACKGROUND

[0003] The traditional generation of H_2 from LCFs is based on catalytic thermal cracking, followed by a Pressure Adsorption for H_2 separation. LCFs include fuels such as ammonia (NH_3), hydrazine (N_2H_4), carbohydrazide (CH_6N_4O), hydrogen sulfide (H_2S), etc. Using NH_3 as an example, the conventional process suffers from several drawbacks including high energy consumption and operating temperature requirement for high efficiency thermal cracking (700 – 1100 °C); reduction in the overall H_2 production (~ 20% lower) and thermochemical efficiency reduction (at least 12.7 %) as a result of providing for the net endothermic heat of reaction. Many new technologies strive to achieve the thermal cracking by developing better catalysts (which will function at lower temperatures) or newer chemistries (such as Li-imide based high-efficiency reactions). The use of transition metals, rare earth metals, and alkaline earth metals as active sites for no-carbon based fuels decomposition to hydrogen has been thoroughly investigated before. Catalytic decomposition

of ammonia has been investigated over a variety of catalysts made from several active metals, and these have been investigated at a temperature range of 400-700 °C. The majority of the catalysts that are explored are mixed metal oxide catalysts operated at high space-velocities. These catalysts deal with a trade-off between low ammonia conversion and over-oxidation to H_2O, which leads to a loss of efficiency.[1] A method for utilizing aluminum oxide pellets with catalytically active metals deposited onto it to decompose ammonia at a temperature range of 500-700°C has also been proposed. The decomposition process has several technological limitations including efficient heat transfer and scale-up associated with heat release from the pellets.[2] A ruthenium based catalyst over carbon nanotube support has been one of the most effective catalysts for ammonia decomposition which is reported in the literature.[3] However, cost of making this novel catalyst might offset the economic feasibility of the process.[4] The amide-based approaches have the intrinsic limitation of being explosive, hazardous and lead to problems in ammonia based scale-up. Decomposition of ammonia over a lithium amide-imide catalyst has been investigated. However, due to low melting points of both the amide and the imide phase, it is not the most convenient catalyst to work within a fixed bed condition.[5]

SUMMARY

[0004] The present disclosure may overcome the limitations associated with the conventional LCF to H_2 processes by employing a novel looping based system. The disclosure provides specific conditions that enable the disclosed looping process to achieve high H_2 production and energy efficiencies in terms of the reactor design, reactor operating conditions, metal-oxide composition, and specific metal-oxide and LCF flowrates. Due to their relatively high hydrogen content, fuels such as ammonia (NH_3), hydrazine (N_2H_4), carbohydrazide (CH_6N_4O), hydrogen sulfide (H_2S), etc. can be classified as LCFs. This process utilizes a chemical looping scheme to convert efficiently LCF's to H_2 for its use as a fuel. It employs a metal oxide to break the LCF chemically into its constituent components one of them being H_2. Factors such as reactor design, reaction conditions have been considered along with metal oxide compositions in this invention disclosure.

[0005] In one aspect, disclosed herein is a system for converting a carbon-neutral or low-carbon fuel, the system comprising: a first reactor comprising a plurality of particles in which a primary metal oxide is disposed on a support, and an inlet for providing a carbon-neutral or low-carbon fuel, wherein the first reactor is configured to reduce the primary metal oxide to

produce a reduced metal or a reduced metal oxide; and a second reactor configured to oxidize at least a portion of the reduced metal or reduced metal oxide from the first reactor, to regenerate the primary metal oxide.

[0006] In some embodiments, the fuel is selected from the group consisting of ammonia, hydrazine, carbohydrazide, and hydrogen sulfide. In some embodiments, the fuel is ammonia.

[0007] In some embodiments, the system is configured to operate at a temperature of between 400 °C and 1190 °C. In some embodiments, the system is configured to operate at a pressure of between 1 atm and 30 atm. In some embodiments, the system is configured to operate at a GHSV of between 50 hr^{-1} and 5000 hr-1. In some embodiments, the first reactor comprises a co-current moving bed reactor, a counter-current moving bed reactor, a fluidized bed reactor, or a fixed bed reactor. In some embodiments, the second reactor comprises a co-current moving bed reactor, a counter-current moving bed reactor, a fluidized bed reactor, or a fixed bed reactor. In some embodiments, the inlet for the fuel is situated at the top, in the middle, or at the bottom of the first reactor.

[0008] In some embodiments, the primary metal oxide is Fe_3O_4. In some embodiments, wherein the support is selected from the group consisting of oxides of Ti, Al, Co, Cu, Mg, Mn, and Zn, or any combination thereof. In some embodiments, the support is $MgAl_2O_4$. In some embodiments, the system further comprises a hydrogen separation unit.

[0009] In another aspect, disclosed herein is a method of converting a carbon-neutral or low-carbon fuel, the method comprising: reducing a primary metal oxide in a reduction reaction between the fuel and the primary metal oxide, to produce a reduced metal or a reduced metal oxide, in a first reactor, thereby producing hydrogen; and oxidizing at least a portion of the reduced metal or reduced metal oxide with an oxidant, in a second reactor, thereby regenerating the primary metal oxide.

[0010] In some embodiments, the fuel is selected from the group consisting of ammonia, hydrazine, carbohydrazide, and hydrogen sulfide. In some embodiments, the fuel is ammonia.

[0011] In some embodiments, the method is conducted at a temperature of between 50 °C and 2000 °C. In some embodiments, the method is conducted at a pressure of between 1 atm and 30 atm. In some embodiments, the first reactor comprises a co-current moving bed reactor, a counter-current moving bed reactor, a fluidized bed reactor, or a fixed bed reactor. In some embodiments, the second reactor comprises a co-current moving bed reactor, a counter-current moving bed reactor, a fluidized bed reactor, or a fixed bed reactor. It should be noted that the specific configuration of a moving bed reactor can be achieved using a packed moving bed, staged fluidized bed, a downer and/or a rotary kiln. A fixed bed with

dynamic valve switching that approximate a simulated moving bed may also be used. The some embodiments, the method comprises introducing the fuel at the top, in the middle or at the bottom of the first reactor.

[0012] In some embodiments, the primary metal oxide is Fe_3O_4. In some embodiments, wherein the support is selected from the group consisting of oxides of Ti, Al, Co, Cu, Mg, Mn, and Zn, or any combination thereof. In some embodiments, the support is $MgAl_2O_4$. In some embodiments, the method further comprises a step of separating the hydrogen from any co-products.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Figure 1 shows a process flow diagram of ATH technology for liquid fuel production.

[0014] Figure 2 shows a phase diagram of the Fe-NH_3-O system at 450 °C and 1 atm.

[0015] Figure 3 shows an operating line for the reducer reactor at 450 °C and 1 atm.

[0016] Figure 4 shows a phase diagram of the Fe-O-H_2 system at 450 °C and 1 atm.

[0017] Figure 5 shows the gas phase analysis of a fixed bed run with Fe_3O_4 and NH_3 at 600 °C and 1 atm at a GHSV of 500 hr^{-1}.

[0018] Figure 6 shows the gas phase analysis of a fixed bed run with Fe_3O_4 and NH_3 at 600 °C and 1 atm at a GHSV of 150 hr^{-1}.

[0019] Figure 7 shows the solid phase analysis of a fixed bed run with Fe_3O_4 and NH_3 at 600 °C and 1 atm at a GHSV of 500 hr^{-1}.

[0020] Figure 8 shows the solid phase analysis of a fixed bed run with Fe_3O_4 and NH_3 at 600 °C and 1 atm at a GHSV of 150 hr^{-1}.

[0021] Figure 9 shows the steady state composition of a simulated counter current moving bed with Fe_3O_4-$MgAl_2O_4$ system at 600 °C and 1 atm at a GHSV of 150 hr^{-1}.

[0022] Figure 10 shows the calculated equilibrium constant for experiments with different gas-solid contact pattern demonstrating controllability in reducer reactor performance

[0023] Figure 11 shows the normalized rate of weight change of Fe_3O_4 on reduction with ammonia for 400 °C and 600 °C.

[0024] Figure 12 shows the normalized rate of weight change of Fe_3O_4-$MgAl_2O_4$ on reduction with ammonia for 400 °C and 600 °C.

DETAILED DESCRIPTION

[0025] A process is proposed for deriving H_2 from low carbon fuels (LCF) with the use of metal oxide in a chemical looping system. This process employs the synergistic effect of utilizing thermodynamics while being able to harness the catalytic property of the metal oxide. The proposed process is flexible to several LCFs such as ammonia (NH_3), hydrazine (N_2H_4), carbohydrazide (CH_6N_4O), hydrogen sulfide (H_2S), etc., to utilize them as potential sources of H_2 generation. This process can be easily integrated with upcoming concepts like H_2 economy while reducing the carbon footprint for H_2 generation.

1. Definitions

[0026] The terms "comprise(s)," "include(s)," "having," "has," "can," "contain(s)," and variants thereof, as used herein, are intended to be open-ended transitional phrases, terms, or words that do not preclude the possibility of additional acts or structures. The singular forms "a," "and" and "the" include plural references unless the context clearly dictates otherwise. The present disclosure also contemplates other embodiments "comprising," "consisting of" and "consisting essentially of," the embodiments or elements presented herein, whether explicitly set forth or not.

[0027] The conjunctive term "or" includes any and all combinations of one or more listed elements associated by the conjunctive term. For example, the phrase "an apparatus comprising A or B" may refer to an apparatus including A where B is not present, an apparatus including B where A is not present, or an apparatus where both A and B are present. The phrases "at least one of A, B, . . . and N" or "at least one of A, B, . . . N, or combinations thereof" are defined in the broadest sense to mean one or more elements selected from the group comprising A, B, . . . and N, that is to say, any combination of one or more of the elements A, B, . . . or N including any one element alone or in combination with one or more of the other elements which may also include, in combination, additional elements not listed.

[0028] For the recitation of numeric ranges herein, each intervening number there between with the same degree of precision is explicitly contemplated. For example, for the range of 6-9, the numbers 7 and 8 are contemplated in addition to 6 and 9, and for the range 6.0-7.0, the number 6.0, 6.1, 6.2, 6.3, 6.4, 6.5, 6.6, 6.7, 6.8, 6.9, and 7.0 are explicitly contemplated.

[0029] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. In case of conflict, the present document, including definitions, will control. Preferred methods and

materials are described below, although methods and materials similar or equivalent to those described herein can be used in practice or testing of the present invention. All publications, patent applications, patents and other references mentioned herein are incorporated by reference in their entirety. The materials, methods, and examples disclosed herein are illustrative only and not intended to be limiting.

2. The Disclosure

[0030] The following section describes in detail the various configurations, methods and design of specific operating conditions disclosed as a part of this write-up.

[0031] The metal-oxide composition consists of two components, namely primary and secondary. In embodiments, the primary metal-oxide is Fe_3O_4. The primary metal-oxide should be able to crack LCF selectively. The secondary metal-oxide can be a combination of oxides of metals selected from Ti, Al, Co, Cu, Mg, Mn, Zn, etc., or even a combination complex like $MgAl_2O_4$. The secondary metal-oxide serves to strengthen the primary metal-oxide and can enhance reactivity by forming complexes which have a better thermodynamic selectivity than iron-oxide alone. The oxygen-carrier metal-oxide may contain a combination of primary and secondary metal-oxides in varying weight percentages accompanied by dopants to increase the overall activity of the metal oxide. The metal-oxide can be prepared by methods including but not limited to extrusion, pelletizing, co-precipitation, wet-impregnation, and mechanical compression. Techniques, like sintering the synthesized metal-oxide or adding a binder, can be used to increase the strength of the metal-oxide.

[0032] A model metal-oxide composition consists of a primary metal-oxide of Fe_3O_4 supported on a secondary metal oxide of the formula $MgAl_2O_4$. This complex can be Fe_3O_4 rich, $MgAl_2O_4$ rich or even have an overall non-stoichiometric support composition. The feedstock for this application can be any LCF including but not limited to ammonia, hydrazine hydrate, carbohydrazide, and hydrogen sulfide. In some embodiments, the LCF is ammonia. Figure 1 shows the conceptual schematic of the proposed configuration. The process configuration is described using ammonia as an example of LCF. As illustrated in Figure 1, the proposed process employs a novel metal-oxide reaction with NH_3 to produce a mixture of N_2, H_2, and H_2O at an operating temperature of 450 °C (450 °C used as an example temperature) in the reducer. The reduced metal-oxide then performs water-splitting to generate pure H_2 in the oxidizer resulting in a reduced energy penalty for separating N_2 and H_2 over the conventionally used thermal cracking of ammonia technology which forms one mixed stream of the cracked products. The net-combination of the reducer and combustor

performance is such that the total H_2 recovered from NH_3 feed is >99.99%. The H_2 can be further purified to fuel cell grade directly.

[0033] The proposed chemical looping reaction scheme can alleviate shortcomings in the conventional ammonia to hydrogen (ATH) process. Compared to the conventional technique, the ATH chemical looping process can increase the overall H_2 production efficiency by >20% and the thermochemical efficiency by >12.7%. The process platform is based on a co-current moving bed reactor system design to maximize NH_3 conversion to H_2 while minimizing the capital cost associated with the chemical looping reactor size. As discussed earlier conventional catalytic cracking techniques are limited by kinetics at temperatures of 450°C or lower, on the other hand, the co-current moving bed ATH process offers an effective control over the residence time of both the gas and solid phases and thus drives the reaction to thermodynamic equilibrium at 450°C. The temperature 450°C is used to illustrate the process, this can be further extended to temperatures up to 2000°C. Further, at these low operating temperatures, mechanical conveying systems can be employed between the reducer and combustor which can minimize the energy penalty and particle attrition for transporting the metal-oxide solids.

[0034] Figure 2 shows the thermodynamic phase diagram of the NH_3-Fe-O system at 450°C and 1 atm. The y-axis is the solids conversion of the Fe_2O_3 phase, wherein a solids conversion of 100% denotes complete oxygen transfer from Fe_2O_3 to NH_3. The NH_3 conversion is displayed in terms of the amount of H_2O production per mole of NH_3, with a value of 100% conversion denoting the formation of 1.5 moles H_2O per mole of NH_3.

[0035] Figure 3 shows the various operating conditions that can be obtained in the reducer reactor of the LCF to H_2 system. The choice of an operating condition for the reducer reactor system shown in Figure 1, 2 and 3 is made based on Figure 4, which shows the phase diagram of the H_2-O-Fe system.

[0036] Figure 4 shows that the steam re-oxidation from Fe (corresponding to 100% solids conversion) yields Fe_3O_4 (corresponding to 11% solids conversion) as the highest thermodynamically feasible oxidation state. This led to the choice of Fe_3O_4 as the input for the reducer reactor as shown in Figure 3. The operating line is chosen based on 11% solids conversion and yields a gas conversion of 13.4%, corresponding to an outlet gas composition of 0.201 moles H_2O, 1.29 moles of H_2, ~ 1.5 moles N_2 per mole of NH_3. This performance is constant beyond a Fe_3O_4/NH_3 ratio of 0.05. However, the operating condition depicted in Line A corresponds to a Fe_3O_4/NH_3 ratio of 0.4 to have good heat balance conditions in the

combined system. The oxygen lost as H_2O is recovered in the oxidizer, yielding an H_2 production efficiency of ≥ 99% (i.e. ≥1.495 moles of H_2 per mole of NH_3) based on Figure 4. The flexibility to operate under a wide range of Fe_3O_4/NH_3 ratios is important as the solids flowrate is used to transfer heat from the exothermic oxidizer reactor to the endothermic reducer reactor resulting in a near autothermal condition. This minimizes the thermal energy penalty for H_2 production. The reducer and the oxidizer both are proposed to be operated as packed moving bed type system to minimize physical attrition to the oxygen carrier particles. The operation of a counter-current moving bed oxidizer has advantages in terms of reducing the net steam consumption while adjusting the gas and solid phase residence times for reaching thermodynamic equilibrium. In the configuration proposed in Figure 1, a mechanical conveyor type system is proposed to transport the solids to the reducer reactor. The reducer and the oxidizer reactors can be operated as co-current and counter-current moving beds, fluidized beds or even fixed bed type systems. The temperature and pressure of operation for yielding a > 99% H_2 production efficiency can be between 400 °C to 800 °C, and 1 bar to 30 bar respectively. It should be noted that lower temperatures and pressures are preferred for commercial modules.

[0037] Figure 5 and Figure 6 shows the results of proof-of-concept laboratory studies using the iron-based catalytic metal oxide (Fe_3O_4) performed in a fixed bed system. This fixed bed represents the reducer section in the looping system. In Figures 5 and 6, the gas analysis of the outlet of the fixed bed is depicted. Both the fixed beds represented by Figures 5 and 6 were run at 600 °C and 1 atm pressure with a GHSV of 500 hr^{-1} and 150 hr^{-1} respectively. Spherical particles of Fe_3O_4 were used in the fixed bed for this test. For the fixed bed tests, spherical particles were synthesized from chemical grade compounds. These particles were then calcined under inert conditions at a temperature of 950 °C. The experiments with a GHSV of 500 hr^{-1} and 150 hr^{-1} have been referred to as Experiment A and B respectively.

[0038] Both the Figures 5 and 6 show a steady increase in the N_2 and H_2 concentration before reaching a steady state. The conversion for NH_3 goes up to approximately 65% and 62% for 500 hr^{-1} and 150 hr^{-1} respectively. Unlike the conventional catalytic NH_3 decomposition, H_2O also is a product which is in significant quantities. This loss of H_2 in the form of H_2O from the reducer is balanced out by the re-oxidation reaction in the oxidizer.

[0039] Figures 7 and 8 represent the solid composition on the top of the fixed bed. This was calculated from the X-Ray Diffraction (XRD) analysis done on the samples from 500 hr^{-1}

and 150 hr^{-1} GHSV for Figures 7 and 8 respectively. The particles form a core shell structure with respect to the reduced phases, as seen in Figures 7 and 8. The Fe layer is the dominant surface layer corresponding to a core-shell structure and the phase consistent with the calculated Equilibrium constant for both the GHSVs.

[0040] Figure 9 depicts the gas phase data of a simulated counter-current bed with Fe_3O_4-$MgAl_2O_4$ particles. These particles include 50% Fe_3O_4 and 50% $MgAl_2O_4$ by weight and are synthesized and sintered in the same way as the Fe_3O_4 particles. For a simulated counter-current moving bed, a solid profile of a counter-current moving bed was setup with 50% of the bed filled with reduced particles and 50% of them filled with the oxidized particles. The bed was setup in such a way that the reduced particles would meet the gas coming into the reactor and the gas exited the reactor with being in contact with the oxidized particles. For this Fe_3O_4-$MgAl_2O_4$ particles were reduced under hydrogen to yield Fe-$MgAl_2O_4$ particles, which would act as reduced particles.

[0041] As seen from Figure 9, an average ammonia conversion of 99.9% was achieved with the counter current moving bed configuration. The figure represents the mole fractions of the products and the unreacted ammonia during steady state run operation of the moving bed. This experiment has been referred to as Experiment C.

[0042] The steady state values for NH_3 reaction with Fe_3O_4 for different residence times and gas-solid contact pattern are plotted in terms of a NH_3 cracking equilibrium constant ($K_{NH3} = C_{NH3}/(C_{NH3} + C_{N2} + C_{H2} + C_{H2O})$. The experiments were carried out at 600 °C for demonstrating control over the equilibrium composition in terms of the equilibrium constant and different metal-oxide phases. Figure 10 shows the K_{NH3} calculated for these experimental runs for different thermodynamic contact patterns. Experiment A and B show a calculated equilibrium constant that is consistent with the final solids contact stage being Fe. Experiment C shows a calculated equilibrium constant that is consistent with the final solids contact stage being Fe_3O_4. These experimental data points show that the system performance can be controlled using different gas-solid contact pattern and yield further experimental proof for the thermodynamic performance.

[0043] Figures 11 and 12 show the normalized rate of reaction of the metal oxide and ammonia at 400 °C and 600 °C. Figure 11 represents the normalized rate of reaction of pure Fe_3O_4 and Figure 12 does the same for Fe_3O_4-$MgAl_2O_4$. For both the metal oxides, ammonia reacts with the metal oxide, reducing it in the process which can be measured as a decrease in weight of the metal oxide in a thermogravimetric analyzer. As there is a reduction in weight

the rate of weight change is a negative number, which has been considered in an absolute fashion in both Figures 11 and 12. These rates have been normalized with respect to the fresh active oxygen content. For the two Figures 11 and 12, the active oxygen that reacts with ammonia comes from Fe_3O_4.

[0044] Both Figures 11 and 12 are a proof of concept for ammonia decomposition at 400 °C, as there is an appreciable reduction of the metal oxide. From a kinetics standpoint, both Figures 11 and 12 show a higher reduction rate at 600 °C than 400 °C. The 400 °C graphs for both Figure 11 and 12 have a non-zero rate of reduction after the initial spike in the reaction. With a moving bed configuration, the residence time and the amount of metal oxide reduced can be very accurately controlled and thus a unit can be run within the bounds of the initial spike in the reaction ensuring efficient utilization of the kinetics of this system.

3. Embodiments

[0045] The following are embodiments of the disclosure.

[0046] (1) A system configuration is proposed, utilizing a low carbon fuel and an H_2 production efficiency of > 99% from these LCFs. The system configuration itself includes two primary reactors, a reducer and an oxidizer reactor each of which can be a co-current or a counter-current moving bed, fluidized bed or a fixed bed.

[0047] (2) A system configuration, in-conjunction with Embodiment 1, converts LCFs to H_2, using an (Fe) to LCF (C) molar ratio which can vary from 0.01 to 5.0. In certain embodiments, the molar ratio is about 0.01, about 0.05, about 0.1, about 0,15, about 0.2, about 0.25, about 0.3, about 0.35, about 0.4, about 0.45, about 0.5, about 0.55, about 0.6, about 0.65, about 0.7, about 0.75, about 0.8, about 0.85, about 0.9, about 1, about 1.5, about 2, about 2.5, about 3, about 3.5, about 4, about 4.5 or about 5 The temperature of operation can vary between 50 °C to 2000 °C. In certain embodiments, the temperature may vary between 400 °C to 1190 °C, The pressure of operation can vary between 1 atm and 30 atm. In certain embodiments, the pressure is about 1 atm, about 2 atm, about 3 atm, about 4 atm, about 5 atm, about 6 atm, about 7 atm, about 8 atm, about 9 atm, about 10 atm, about 11 atm, about 12 atm, about 13 atm, about 14 atm, about 15, atm, about 16 atm, about 17 atm, about 18 atm, about 19 atm, about 20 atm, about 21 atm, about 22 atm, about 23 atm, about 24 atm, about 25 atm, about 26 atm, about 27 atm, about 28 atm, about 29 atm, or about 30 atm.

[0048] (3) A reactor configuration is proposed, in conjunction with Embodiment 1, which has a flexible injection location for the LCF stream into the reactor system. The injection location can be situated on the top, middle or bottom section of the system, such that

sufficient residence time for reaching thermodynamic equilibrium for the final adjusted gas composition is achieved.

[0049] (4) A system configuration of the co-current moving bed reducer reactor can handle a variety of low or no carbon feedstocks, including but not limited to ammonia, hydrazine hydrate, carbohydrazide, hydrogen sulfide when used in conjunction with design considerations being satisfied for Embodiments 1 and 2. The invention reduces the energy input to separate and purify hydrogen from the product streams compared to conventional catalytic cracking process.

[0050] It is understood that the foregoing detailed description and accompanying examples are merely illustrative and are not to be taken as limitations upon the scope of the disclosure. Various changes and modifications to the disclosed embodiments will be apparent to those skilled in the art. Such changes and modifications, including without limitation those relating to the chemical structures, substituents, derivatives, intermediates, syntheses, compositions, formulations, or methods of use of the invention, may be made without departing from the spirit and scope thereof.

REFERENCES

[0051] (1) Okamura, J, et. al. (2011). Ammonia decomposition catalysts and their production processes, as well as ammonia treatment method, US 2011/0176988 A1.

[0052] (2) Kodesch, K., Et. al. (2005), Ammonia cracker for production of hydrogen, US 6936363 B2.

[0053] (3) Yin S.F., et. al., A mini-review on ammonia decomposition catalysts for on-site generation of hydrogen for fuel cell applications, Applied Catalysis A: General, 2004, 277, 1–9

[0054] (4) T. E. Bell L. Torrente-Murciano, H_2 Production via Ammonia Decomposition Using Non-Noble Metal Catalysts: A Review, Top Catal, 2016, 59, 1438–1457

[0055] (5) Makepeace J. et. al., Ammonia decomposition catalysis using non-stoichiometric lithium imide, *Chem. Sci.*, 2015, 6, 3805.

CLAIMS

1. A system for converting a carbon-neutral or low-carbon fuel, the system comprising:

a first reactor comprising a plurality of particles in which a primary metal oxide is disposed on a support, and an inlet for providing a carbon-neutral or low-carbon fuel, wherein the first reactor is configured to reduce the primary metal oxide to produce a reduced metal or a reduced metal oxide; and a second reactor configured to oxidize at least a portion of the reduced metal or reduced metal oxide from the first reactor, to regenerate the primary metal oxide.

2. The system of claim 1, wherein the fuel is selected from the group consisting of ammonia, hydrazine, carbohydrazide, and hydrogen sulfide.

3. The system of claim 2, wherein the fuel is ammonia.

4. The system of any of claims 1-3, wherein the system is configured to operate at a temperature of between 50 °C and 2000 °C.

5. The system of any of claims 1-3, wherein the system is configured to operate at a pressure of between 1 atm and 30 atm.

6. The system of any of claims 1-3, wherein the system is configured to operate at a GHSV of between 50 hr^{-1} and 5000 hr^{-1}.

7. The system of any of claims 1-5, wherein the first reactor comprises a co-current moving bed reactor, a counter-current moving bed reactor, a fluidized bed reactor, or a fixed bed reactor.

8. The system of any of claims 1-6, wherein the second reactor comprises a co-current moving bed reactor, a counter-current moving bed reactor, a fluidized bed reactor, or a fixed bed reactor.

9. The system of any of claims 1-7, wherein the inlet for the fuel is situated at the top, in the middle, or at the bottom of the first reactor.

10. The system of any of claims 1-8, wherein the primary metal oxide is Fe_3O_4.

11. The system of any of claims 1-9, wherein the support is selected from the group consisting of oxides of Ti, Al, Co, Cu, Mg, Mn, and Zn, or any combination thereof.

12. The system of any of claims 1-10, wherein the support is $MgAl_2O_4$.

13. The system of any of claims 1-11, further comprising a hydrogen separation unit.

14. A method of converting a carbon-neutral or low-carbon fuel, the method comprising: reducing a primary metal oxide in a reduction reaction between the fuel and the primary metal oxide, to produce a reduced metal or a reduced metal oxide, in a first reactor, thereby producing hydrogen; and oxidizing at least a portion of the reduced metal or reduced metal oxide with an oxidant, in a second reactor, thereby regenerating the primary metal oxide.

15. The method of claim 13, wherein the fuel is selected from the group consisting of ammonia, hydrazine, carbohydrazide, and hydrogen sulfide.

16. The method of claim 14, wherein the fuel is ammonia.

17. The system of any of claims 13-15, comprising conducting the method at a temperature of between 50 °C and 5000 °C.

18. The method of any of claims 13-16, comprising conducting the method at a pressure of between 1 atm and 30 atm.

19. The method of any of claims 13-17, wherein the first reactor comprises a co-current moving bed reactor, a counter-current moving bed reactor, a fluidized bed reactor, or a fixed bed reactor.

20. The method of any of claims 13-18, wherein the second reactor comprises a co-current moving bed reactor, a counter-current moving bed reactor, a fluidized bed reactor, or a fixed bed reactor.

21. The method of any of claims 13-19, comprising introducing the fuel at the top, in the middle or at the bottom of the first reactor.

22. The method of any of claims 13-20, wherein the primary metal oxide is Fe_3O_4.

23. The method of any of claims 13-21, wherein the support is selected from the group consisting of oxides of Ti, Al, Co, Cu, Mg, Mn, and Zn, or any combination thereof.

24. The method of any of claims 13-22, wherein the support is $MgAl_2O_4$.

25. The method of any of claims 13-23, further comprising a step of separating the hydrogen from any co-products.

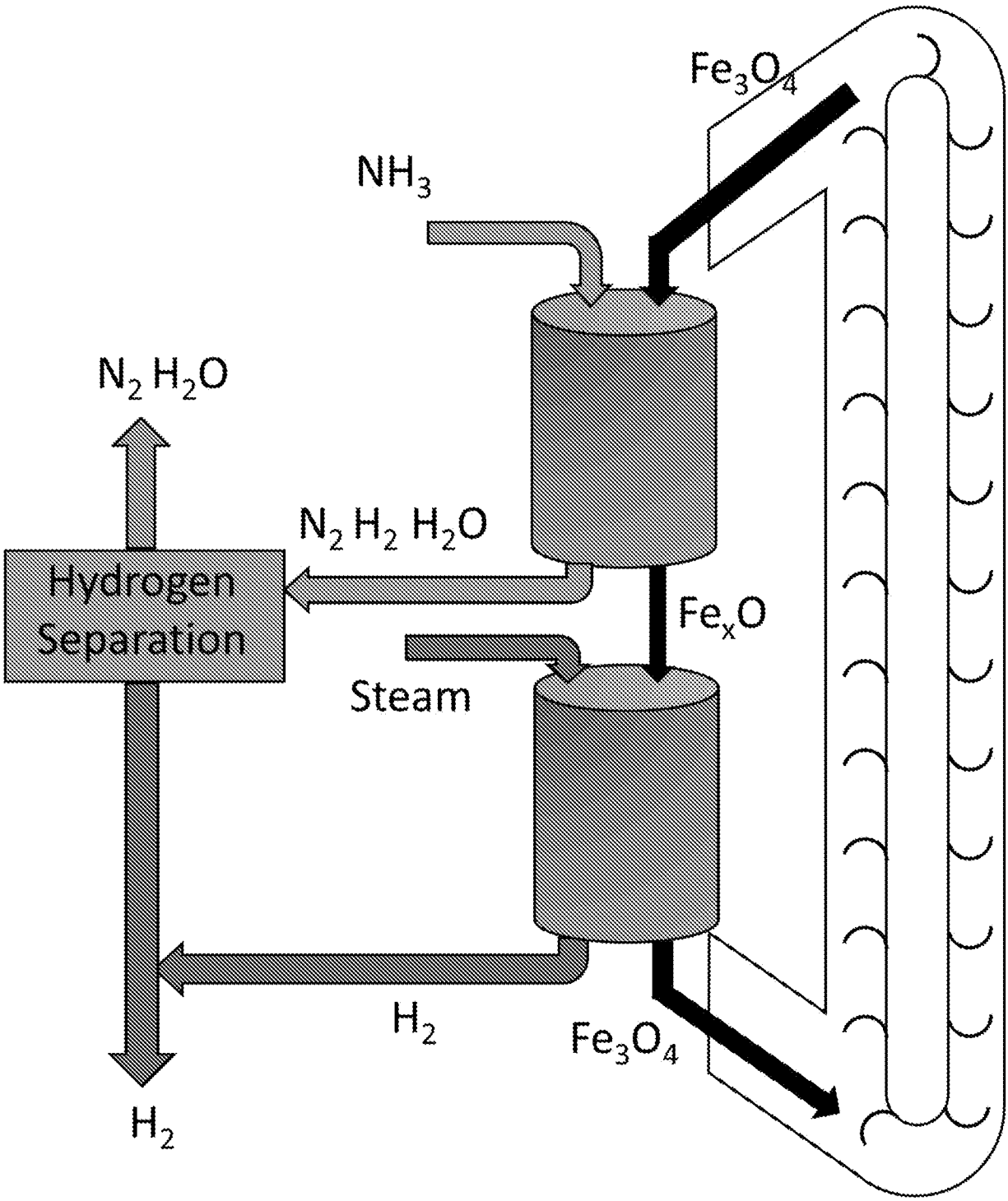
Fe_3O_4
NH_3
N_2 H_2O
N_2 H_2 H_2O
Hydrogen Separation
Fe_xO
Steam
H_2
Fe_3O_4
H_2

Fig. 1

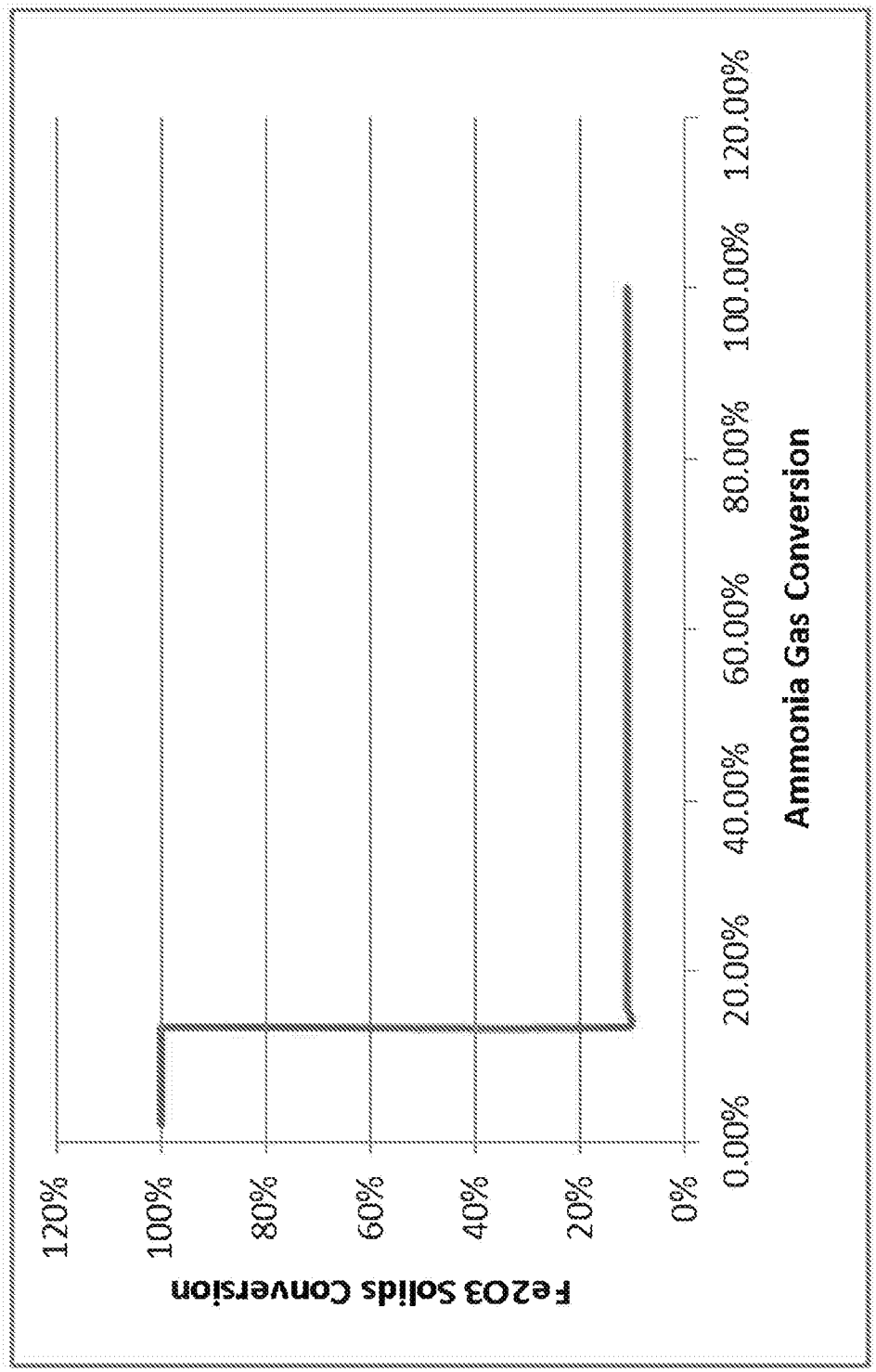
Fe2O3 Solids Conversion
120%
100%
80%
60%
40%
20%
0%
0.00%
20.00%
40.00%
60.00%
80.00%
100.00%
120.00%
Ammonia Gas Conversion

Fig. 2

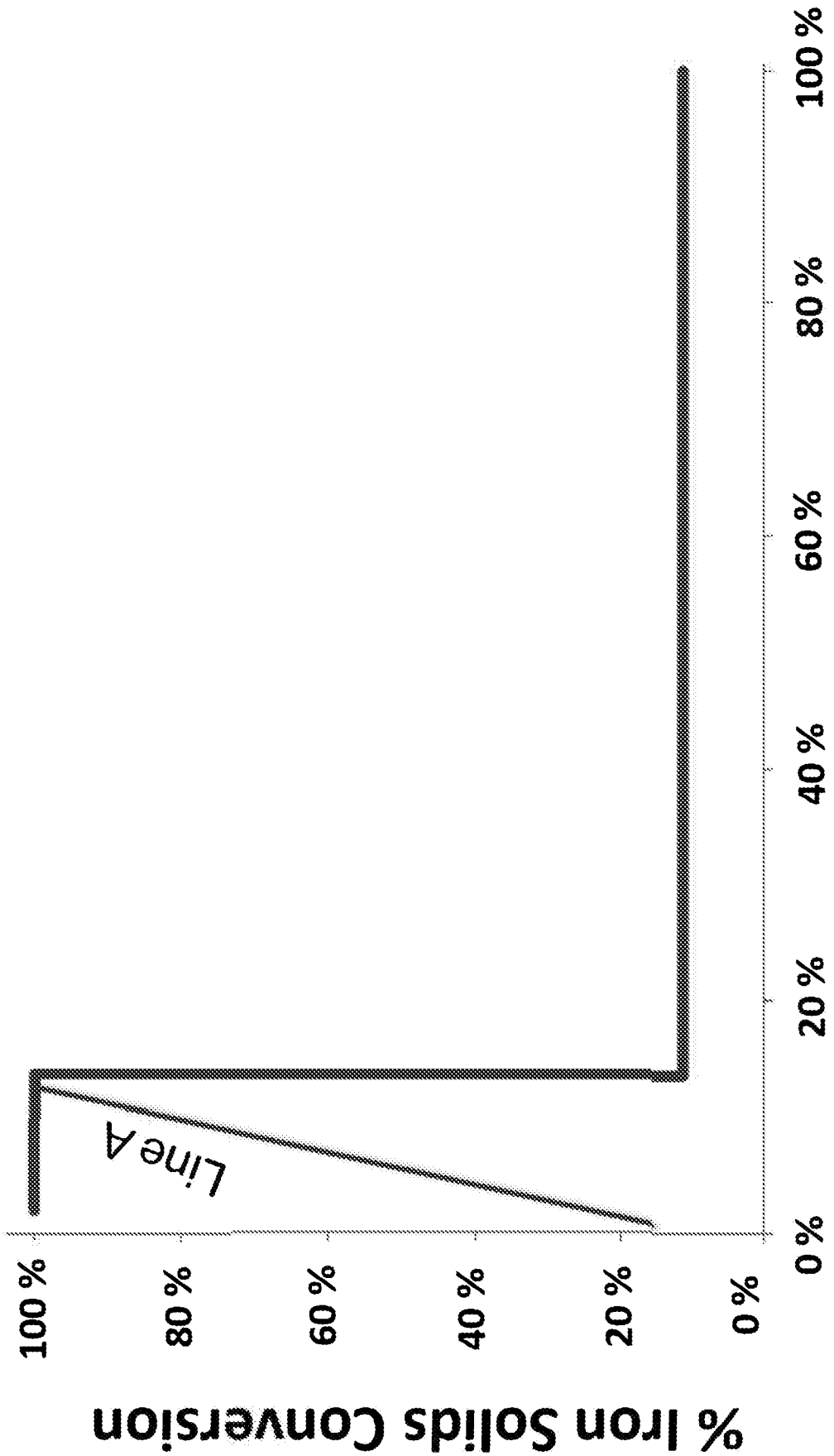
% Iron Solids Conversion
100 %
80 %
60 %
40 %
20 %
0 %
Line A
0 %
20 %
40 %
60 %
80 %
100 %
% Ammonia Gas Conversion

Fig. 3

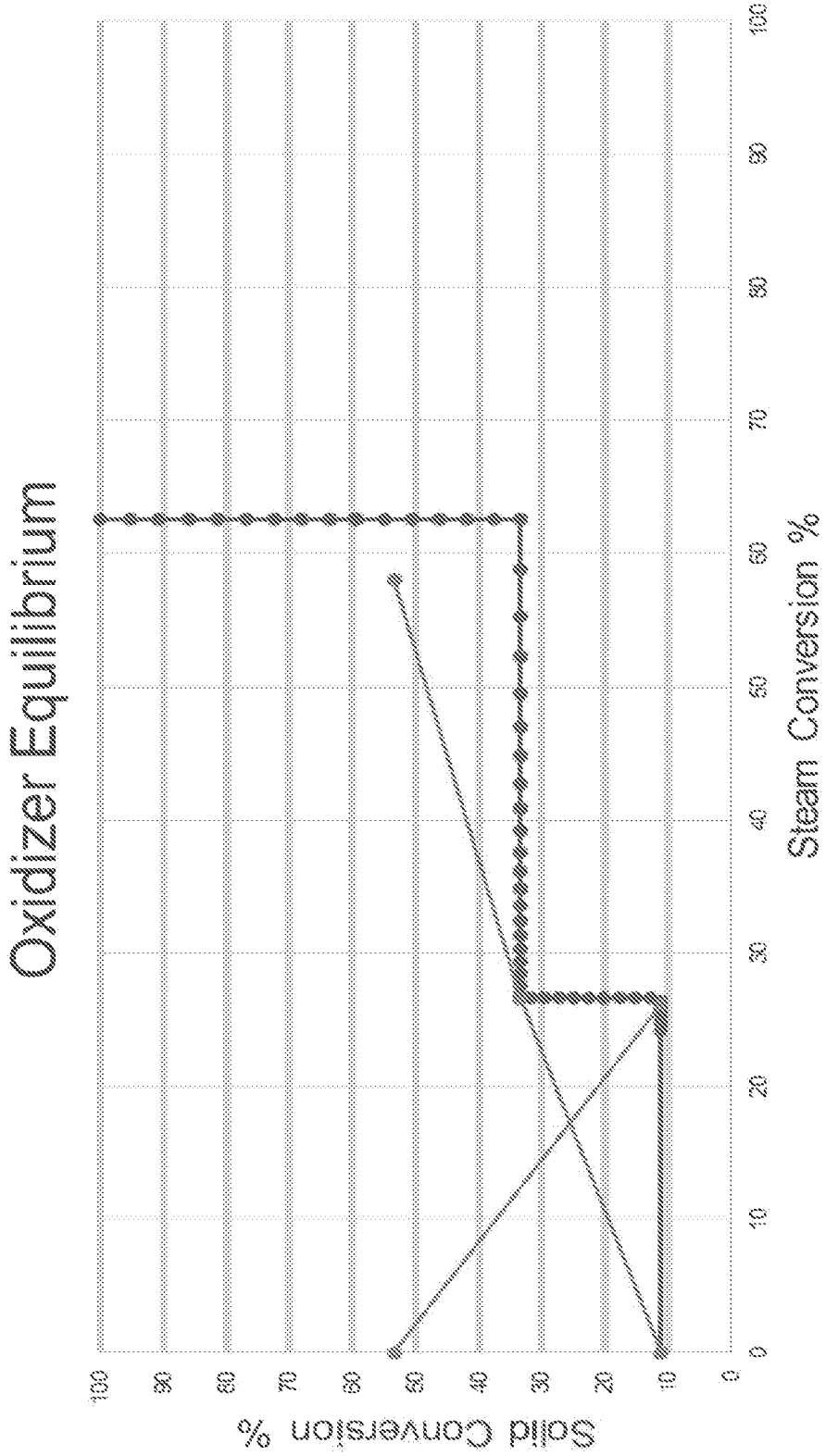
Oxidizer Equilibrium
Solid Conversion %
Steam Conversion %
100
90
80
70
60
50
40
30
20
10
0

Fig.4

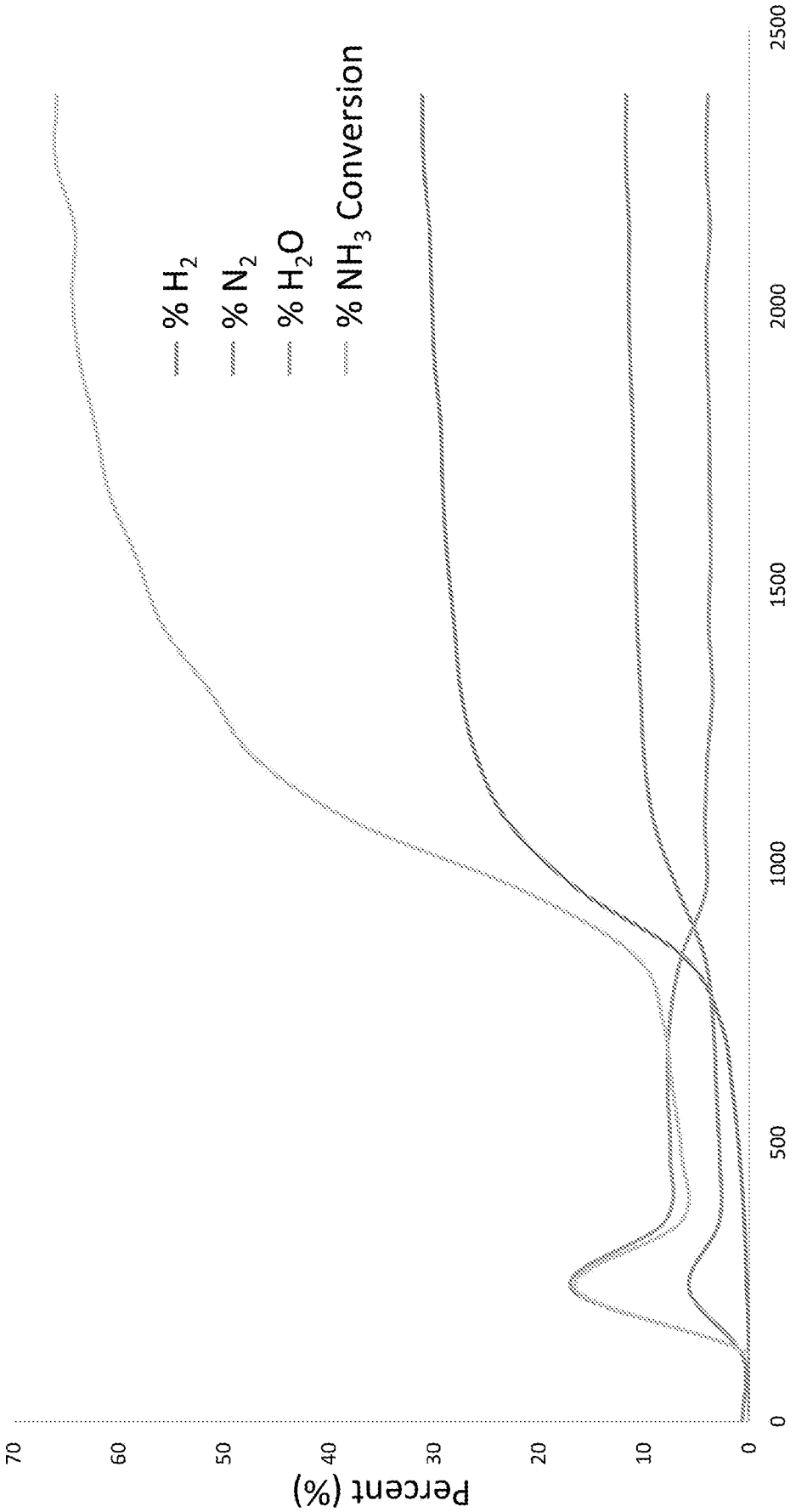
% H_2
% N_2
% H_2O
% NH_3 Conversion
Percent (%)
Time (s)
0
10
20
30
40
50
60
70
0
500
1000
1500
2000
2500

Fig. 5


% H_2
% N_2
% H_2O
% NH_3 Conversion
Percent(%)
Time (s)
0
10
20
30
40
50
60
70
0
1000
2000
3000
4000
5000
6000
7000

Fig. 6

Component	Mole %
Fe_3O_4	40.44%
FeO	52.04%
Fe	6.60%
Fe_4N	0.92%

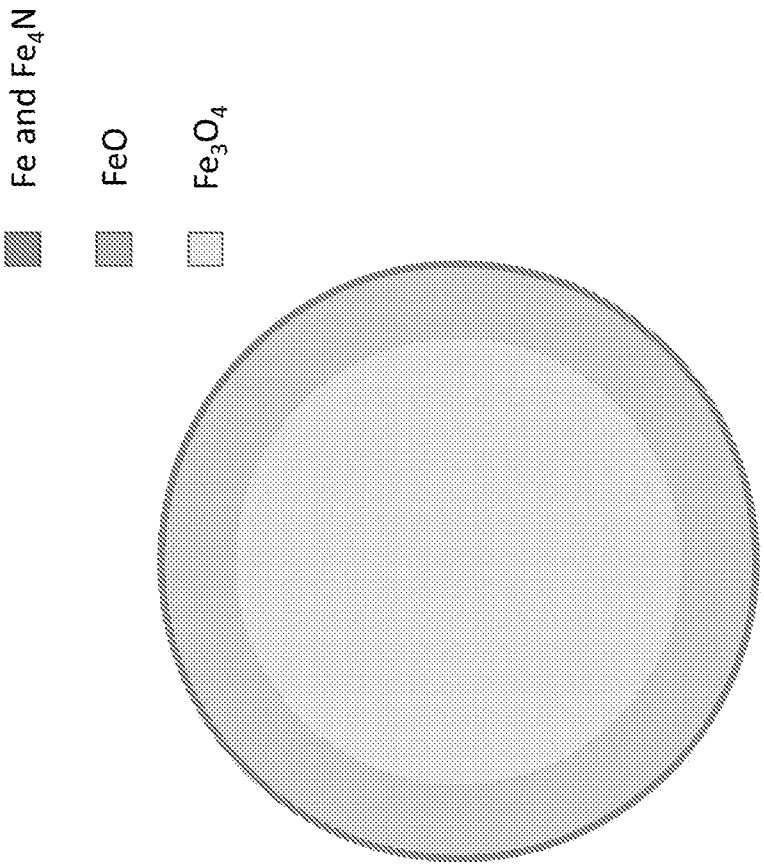

Fig. 7

Component	Mole %
Fe_3O_4	32.03%
FeO	28.09%
Fe	36.36%
Fe_4N	3.52%

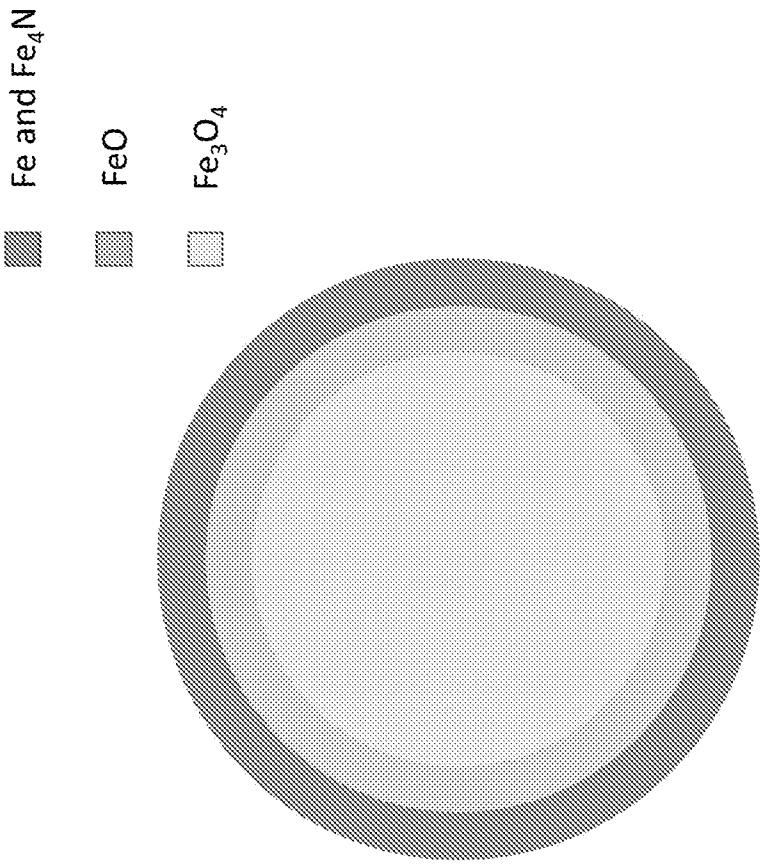

Fig. 8

Component	Mole fraction
H_2	0.706
H_2O	0.0481
N_2	0.259
NH_3	0.0005

Fig. 9

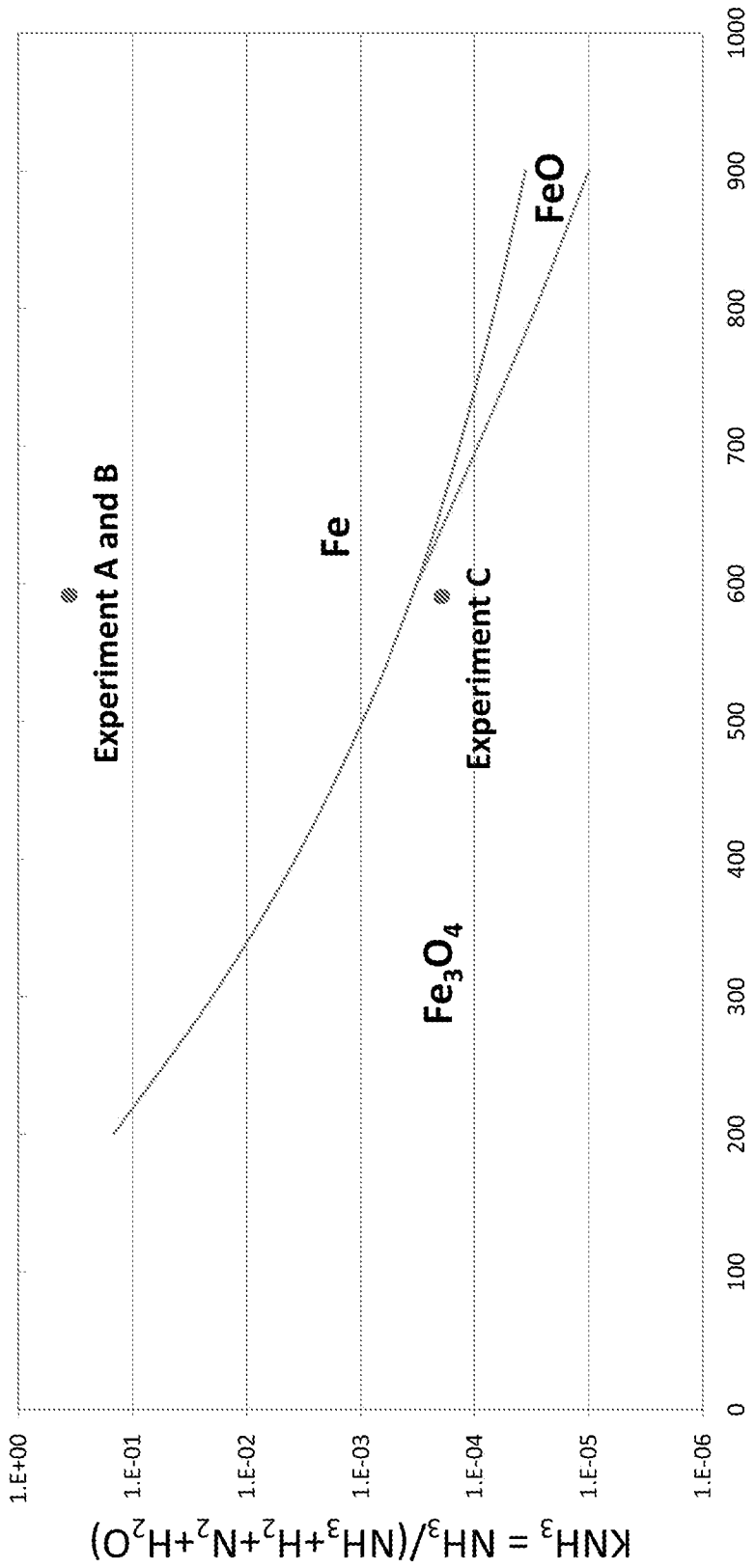
Experiment A and B
Fe
Experiment C
FeO
Fe_3O_4
Temperature (°C)
$KNH_3 = NH_3/(NH_3+H_2+N_2+H_2O)$
1.E+00
1.E-01
1.E-02
1.E-03
1.E-04
1.E-05
1.E-06
0
100
200
300
400
500
600
700
800
900
1000

Fig. 10

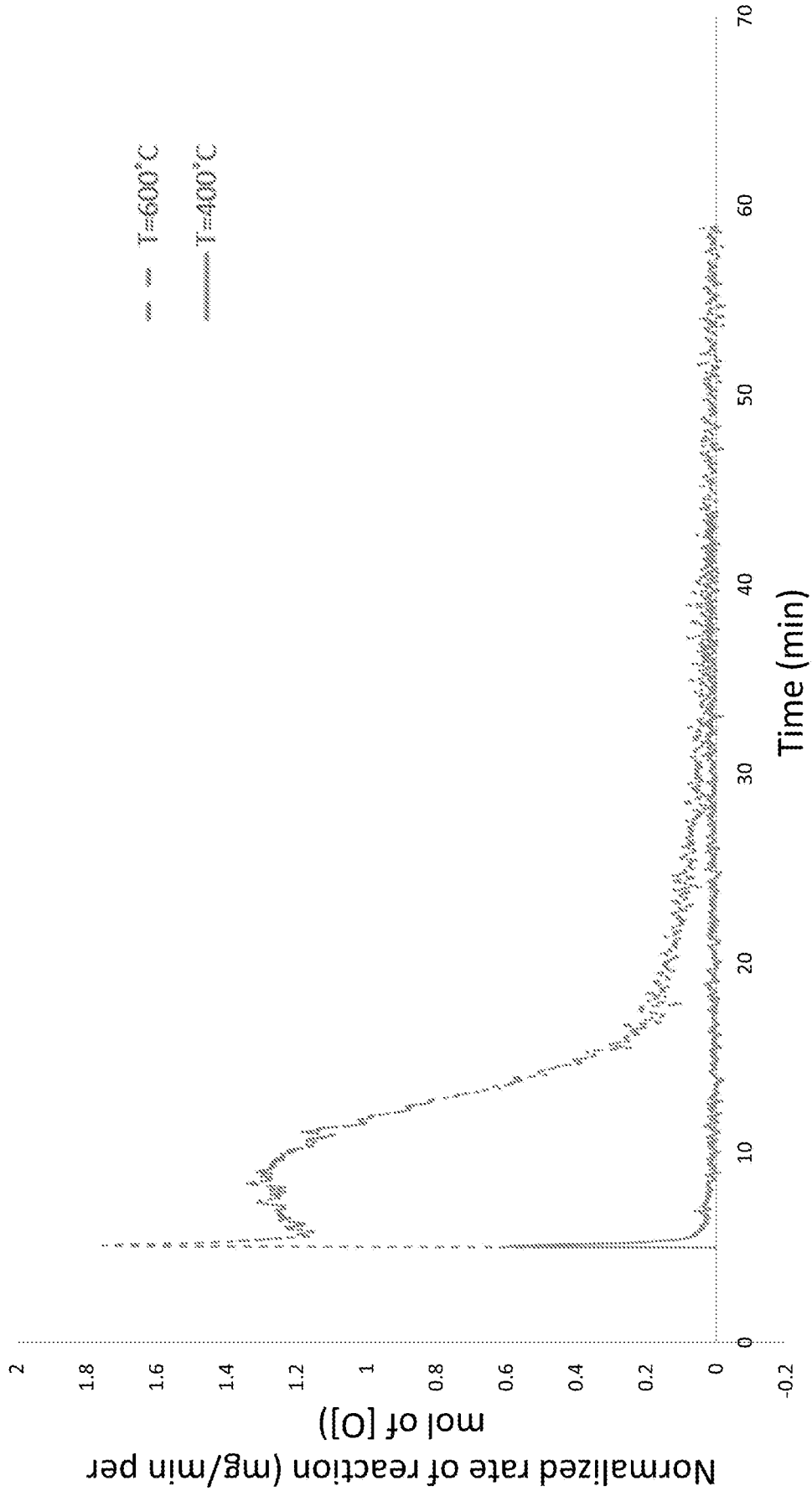
Normalized rate of reaction (mg/min per mol of [O])
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
0
10
20
30
40
50
60
70
Time (min)
T=600°C
T=400°C

Fig. 11

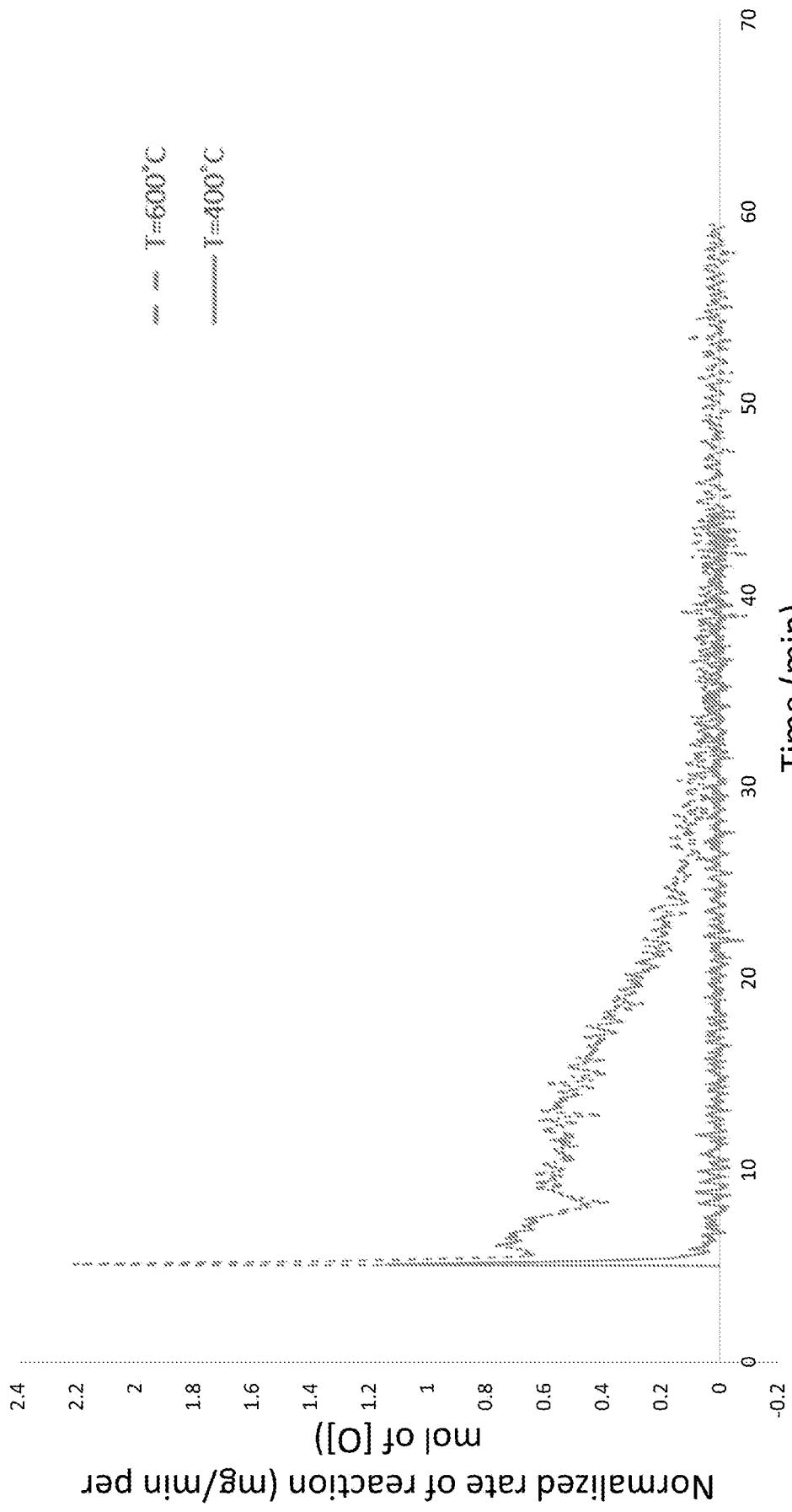
T=600°C
T=400°C
Normalized rate of reaction (mg/min per mol of [O])
Time (min)
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
0
10
20
30
40
50
60
70

Fig. 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 17/34503

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C01B 3/02, C01B 31/00, H01M 8/06 (2017.01)
CPC - Y02P 20/145, C01B 2203/84, C01B 2203/0485, C10J 2300/093

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)
See Search History Document

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/0175533 A1 (THOMAS et al.) 11 August 2005 (11.08.2005); para [0008] [0011] [0018] [0037] [0057]	1-6, 14-16
A	US 2011/0024687 A1 (WHITE et al.) 03 February 2011 (03.02.2011); entire document	1-6, 14-16
A	US 2011/0176988 A1 (OKAMURA et al.) 21 July 2011 (21.07.2011); entire document	1-6, 14-16
A	US 2004/0152790 A1 (CORNARO et al.) 05 August 2004 (05.08.2004); entire document	1-6, 14-16
A	US 2004/0154223 A1 (POWELL et al.) 12 August 2004 (12.08.2004); entire document	1-6, 14-16
A	US 2015/0093557 A1 (THE OHIO STATE UNIVERSITY) 02 April 2015 (02.04.2015); entire document	1-6, 14-16
A	US 2014/0275297 A1 (BABCOCK & WILCOX POWER GENERATION GROUP. INC.) 18 September 2014 (18.09.2014); entire document	1-6, 14-16

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* 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	Date of mailing of the international search report
20 July 2017	15 AUG 2017
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

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 17/34503

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.: 7-13, 17-25
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:

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.:

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.