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(54) **Title:** OXYGEN CARRYING MATERIALS

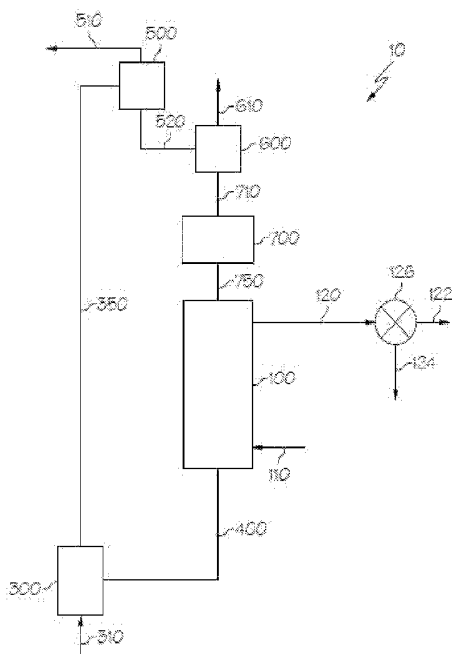


FIG. 1

(57) **Abstract:** In accordance with one embodiment of the present disclosure, an oxygen carrying material may include a primary active mass, a primary support material, and a secondary support material. The oxygen carrying material may include about 20% to about 70% by weight of the primary active mass, the primary active mass including a composition having a metal or metal oxide selected from the group consisting of Fe, Co, Ni, Cu, Mo, Mn, Sn, Ru, Rh, and combinations thereof. The oxygen carrying material may include about 5% to about 70% by weight of a primary support material. The oxygen carrying material may include about 1% to about 35% by mass of a secondary support material.

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OXYGEN CARRYING MATERIALS

This application claims the benefit of prior-filed U.S. Provisional Patent Application Ser. No. 61/484,982, filed May 11, 2011, the subject matter of which is hereby incorporated by reference in its entirety.

5 The present invention relates to oxygen carrying materials, and specifically to oxygen carrying materials that are associated with chemical looping systems.

 There is a constant need for clean and efficient energy generation systems. Most of the commercial processes that generate energy carriers such as steam, hydrogen, synthesis gas (syngas), liquid fuels and/or electricity are based on fossil fuels. 10 Furthermore, the dependence on fossil fuels is expected to continue in the foreseeable future due to the lower costs compared to renewable sources. Currently, the conversion of carbonaceous fuels such as coal, natural gas, and petroleum coke is usually conducted through a combustion or reforming process. However, combustion of carbonaceous fuels, especially coal, is a carbon intensive process that emits large quantities of carbon 15 dioxide to the environment. Sulfur and nitrogen compounds are also generated in this process due to the complex content in coal.

 Traditionally the chemical energy stored inside coal has been utilized by combustion with O₂, with CO₂ and H₂O as products. Similar reactions can be carried out if instead of oxygen, an oxygen carrying material is used in a chemical looping process. 20 For example, metal oxides such as Fe₂O₃ can act as suitable oxygen carrying materials. However, unlike combustion of fuel with air, there is a relatively pure sequestration ready CO₂ stream produced on combustion with metal oxide carriers. The reduced form of metal oxide may then be reacted with air to liberate heat to produce electricity or reacted with steam to form a relatively pure stream of hydrogen, which can then be used 25 for a variety of purposes.

 Chemical reactions between metal oxides and carbonaceous fuels, on the other hand, may provide a better way to recover the energy stored in the fuels. Several processes are based on the reaction of metal oxide particles with carbonaceous fuels to

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produce useful energy carriers. For example, Ishida et al. (U.S. Pat. No. 5,447,024) describes processes wherein nickel oxide particles are used to convert natural gas through a chemical looping process into heat, which may be used in a turbine. However, recyclability of pure metal oxides is poor and constitutes an impediment for its use in commercial and industrial processes. Moreover, this technology has limited applicability, because it can only convert natural gas, which is more costly than other fossil fuels. Another well known process is a steam-iron process, wherein coal derived producer gas is reacted with iron oxide particles in a fluidized bed reactor to be later regenerated with steam to produce hydrogen gas. This process however suffers from poor gas conversion rates due to improper contact between reacting solids and gases, and is incapable of producing a hydrogen rich stream.

One of the problems with the prior art in combustion looping systems has been the metal/metal oxide oxygen carrying material. For example, iron in the form of small particles may degrade and break up in the reactor. Iron oxide has little mechanical strength as well. After only a few redox cycles, the activity and oxygen carrying capacity of the metal/metal oxide may decline considerably. Replacing the oxygen carrying material with additional fresh metal/metal oxide makes the process more costly.

As demands increase for cleaner and more efficient systems of converting fuel, the need arises for improved systems, and system components therein, which will convert fuel effectively, while reducing pollutants.

The concepts of the present disclosure are generally applicable to oxygen carrying materials. In accordance with one embodiment of the present disclosure, an oxygen carrying material may comprise a primary active mass, a primary support material, and a secondary support material. The oxygen carrying material may comprise about 20% to about 70% by weight of the primary active mass, the primary active mass comprising a composition having a metal or metal oxide selected from the group consisting of Fe, Co, Ni, Cu, Mo, Mn, Sn, Ru, Rh, and combinations thereof. The oxygen carrying material may comprise about 5% to about 70% by weight of a primary support material. The primary support material may comprise a composition having at least one

metal, metal oxide, metal carbide, metal nitrate, metal halide, or combinations thereof; at least one ceramic or clay material, or salts thereof; at least one naturally occurring ore; or combinations thereof. The oxygen carrying material may comprise about 1% to about 35% by mass of a secondary support material. The secondary support material may
5 comprise a composition having at least one metal, metal oxide, metal carbide, metal nitrate, metal halide, or combinations thereof; at least one ceramic or clay material or salts thereof; at least one naturally occurring ore; or combinations thereof. The primary support material composition and the secondary support material composition may be different.

10 In accordance with another embodiment of the present disclosure, a system for converting fuel may comprise an oxygen carrying material, a first reactor comprising a moving bed and an inlet for providing fuel to the first reactor, wherein the first reactor is configured to reduce the oxygen carrying material with the fuel to produce a reduced oxygen carrying material, and a second reactor communicating with the first reactor and
15 an oxygen source, wherein the second reactor is configured to regenerate the oxygen carrying material by oxidizing the oxygen carrying material.

In accordance with another embodiment of the present disclosure, a method for synthesizing an oxygen carrying material may include forming a matrix comprising a primary active mass, a primary support, and a secondary support; drying the matrix; and
20 forming the matrix into particles of the oxygen carrying material.

The following detailed description of specific embodiments of the present disclosure can be best understood when read in conjunction with the following drawings, where like structure is indicated with like reference numerals and in which:

Fig. 1 is a schematic illustration of a system for converting fuel according to
25 one or more embodiments of the present invention;

Fig. 2 is a schematic illustration of another system for converting fuel according to one or more embodiments of the present invention;

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Fig. 3 is a chart that shows the enhanced reactivity of oxygen carrying materials according to one or more embodiments of the present invention;

Fig. 4 is a chart that shows the weight change percent over 100 redox cycles of oxygen carrying materials according to one or more embodiments of the present
5 invention;

Fig. 5 is a chart that shows the oxygen carrying capacity of oxygen carrying materials comprising ash according to one or more embodiments of the present invention; and

Fig. 6 is a chart that shows the oxygen carrying capacity of oxygen carrying
10 materials comprising a promoter according to one or more embodiments of the present invention.

Generally, the present disclosure is directed to oxygen carrying materials for use in systems for converting fuel by redox reactions of oxygen carrying material particles. In some embodiments, a reactor system may utilize a chemical looping process
15 wherein carbonaceous fuels may be converted to heat, power, chemicals, liquid fuels, and/or hydrogen (H₂). In the process of converting carbonaceous fuels, oxygen carrying materials within the system such as oxygen carrying particles may undergo reduction/oxidation cycles. The carbonaceous fuels may reduce the oxygen carrying materials in a reduction reactor. The reduced oxygen carrying materials may then be
20 oxidized by steam and/or air in one or more separate reactors. In some embodiments, oxides of iron may be preferred as at least one of the components in the oxygen carrying materials in the chemical looping system. In some embodiments, oxides of copper, cobalt and manganese may also be utilized in the system.

While various systems for converting fuel in which an oxygen carrying
25 materials may be utilized are described herein, it should be understood that the oxygen carrying materials described herein may be used in a wide variety of fuel conversion systems, such as those disclosed herein as well as others. It should also be understood that the oxygen carrying materials described herein may be used in any system which

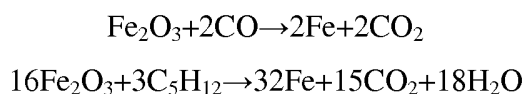
may utilize an oxygen carrying material. It should further be understood that while several fuel conversion systems that utilize an iron containing oxygen carrying material are described herein, the oxygen carrying material need not contain iron, and the reaction mechanisms described herein in the context of an iron containing oxygen carrying material may be illustrative to describe the oxidation states of oxygen carrying materials that do not contain iron throughout the fuel conversion process.

Now referring to Fig. 1, embodiments of the systems described herein may be directed to a specific configuration wherein heat and/or power may be produced from solid carbonaceous fuels. In such a fuel conversion system 10, a reduction reactor 100 may be used to convert the carbonaceous fuels from an inlet stream 110 into a CO₂/H₂O rich gas in an outlet stream 120 using oxygen carrying materials. Oxygen carrying materials that enter the reduction reactor 100 from the solids storage vessel 700 through connection means 750 may contain oxides of iron with an iron valence state of 3+. Following reactions which take place in the reduction reactor 100, the metal such as Fe in the oxygen carrying material may be reduced to an average valence state between about 0 and 3+.

The oxygen carrying materials may be fed to the reactor via any suitable solids delivery device/mechanism. These solid delivery devices may include, but are not limited to, pneumatic devices, conveyors, lock hoppers, or the like.

The reduction reactor 100 generally may receive a fuel, which is utilized to reduce at least one metal oxide of the oxygen carrying material to produce a reduced metal or a reduced metal oxide. As defined herein, "fuel" may include: a solid carbonaceous composition such as coal, tars, oil shales, oil sands, tar sand, biomass, wax, coke etc; a liquid carbonaceous composition such as gasoline, oil, petroleum, diesel, jet fuel, ethanol etc; and a gaseous composition such as syngas, carbon monoxide, hydrogen, methane, gaseous hydrocarbon gases (C1-C6), hydrocarbon vapors, etc. For example, and not by way of limitation, the following equation illustrates possible reduction reactions:

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In this example, the metal oxide of the oxygen carrying material, Fe_2O_3 , is reduced by a fuel, for example, CO, to produce a reduced metal oxide, Fe. Although Fe
5 may be the predominant reduced composition produced in the reduction reaction of the reduction reactor 100, FeO or other reduced metal oxides with a higher oxidation state are also contemplated herein.

The reduction reactor 100 may be configured as a moving bed reactor, a series of fluidized bed reactors, a rotary kiln, a fixed bed reactor, combinations thereof, or
10 others known to one of ordinary skill in the art. Typically, the reduction reactor 100 may operate at a temperature in the range of about 400°C to about 1200°C and a pressure in the range of about 1 atm to about 150 atm; however, temperatures and pressures outside these ranges may be desirable depending on the reaction mechanism and the components of the reaction mechanism.

The $\text{CO}_2/\text{H}_2\text{O}$ rich gas of the outlet stream 120 may be further separated by a condenser 126 to produce a CO_2 rich gas stream 122 and an H_2O rich stream 124. The
15 CO_2 rich gas stream 122 may be further compressed for sequestration. The reduction reactor 100 may be specially designed for solids and/or gas handling, which is discussed herein. In some embodiments, the reduction reactor 100 may be configured as a packed
20 moving bed reactor. In another embodiment, the reduction reactor may be configured as a series of interconnected fluidized bed reactors, wherein oxygen carrying material may flow counter-currently with respect to a gaseous species.

Still referring to Fig. 1, the reduced oxygen carrying materials exiting the reduction reactor 100 may flow through a combustion reactor inlet stream 400 and may
25 be transferred to a combustion reactor 300. The reduced oxygen carrying material in the combustion reactor inlet stream 400 may be moved through a non-mechanical gas seal and/or a non-mechanical solids flow rate control device.

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To regenerate the metal oxide of the oxygen carrying materials, the system 10 may utilize a combustion reactor 300, which is configured to oxidize the reduced metal oxide. The oxygen carrying material may enter the combustion reactor 300 and may be fluidized with air or another oxidizing gas from an inlet stream 310. The iron in the oxygen carrying material may be re-oxidized by air in the combustion reactor 300 to an average valence state of about 3+. The combustion reactor 300 may release heat during the oxidation of oxygen carrying material particles. Such heat may be extracted for steam and/or power generation. In some embodiments, the combustion reactor 300 may comprise an air filled line or tube used to oxidize the metal oxide. Alternatively, the combustion reactor 300 may be a heat recovery unit such as a reaction vessel or other reaction tank.

The following equation lists one possible mechanism for the oxidation in the combustion reactor 300:



Following the oxidation reaction in the combustion reactor 300, the oxidized oxygen carrying materials may be transferred to a gas-solid separation device 500. The gas-solid separation device 500 may separate gas and fine particulates in an outlet stream 510 from the bulk oxygen carrying material solids in an outlet stream 520. The oxygen carrying material may be transported from the combustion reactor 300 to the gas-solid separation device 500 through solid conveying system 350, such as for example a riser. In one embodiment, the oxygen carrying material may be oxidized to Fe_2O_3 in the solid conveying system 350.

The bulk oxygen carrying material solids discharged from the gas-solid separation device 500 may be moved through a solids separation device 600, through connection means 710, and to a solids storage vessel 700 where substantially no reaction is carried out. In the solids separation device 600, oxygen carrying materials may be separated from other solids, which flow out of the system through an outlet 610. The

oxygen carrying material solids discharged from the solids storage vessel 700 may pass through a connection means 750 which may include another non-mechanical gas sealing device and finally return to the reduction reactor 100 to complete a global solids circulation loop.

5 In some embodiments, the oxygen carrying material particles may undergo numerous regeneration cycles, for example, 10 or more regeneration cycles, and even greater than 100 regeneration cycles, without substantially losing functionality. This system may be used with existing systems involving minimal design change.

10 Now referring to Fig. 2, in another embodiment, H₂ and/or heat/power may be produced from solid carbonaceous fuels by a fuel conversion system 20 similar to the system 10 described in Fig. 1, but further comprising an oxidation reactor 200. The configuration of the reduction reactor 100 and other system components in this embodiment follows the similar configuration as the previous embodiment shown in Fig. 1. The system of Fig. 2 may convert carbonaceous fuels from the reduction reactor inlet
15 stream 110 into a CO₂/H₂O rich gas stream 120 using the oxygen carrying materials that contain iron oxide with a valence state of about 3+. In the reduction reactor 100, the iron in the oxygen carrying material may be reduced to an average valence state between about 0 and 2+ for the H₂ production. It should be understood that the operation and configuration of the system 20 comprising an oxidation reactor 200 (a three reactor
20 system) is similar to the operation of the system 10 not comprising an oxidation reactor (a two reactor system), and like reference numbers in Figs. 1 and 2 correspond to like system parts.

25 Similar to the system of Fig. 1, the CO₂/H₂O rich gas in the outlet stream 120 of the system of Fig. 2 may be further separated by a condenser 126 to produce a CO₂ rich gas stream 122 and an H₂O rich stream 124. The CO₂ rich gas stream 122 may be further compressed for sequestration. The reduction reactor 100 may be specially designed for solids and/or gas handling, which is discussed herein. In some embodiments, the reduction reactor 100 may be operated in as packed moving bed reactor. In another embodiment, the reduction reactor may be operated as a series of

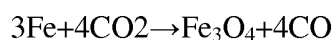
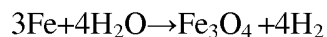
interconnected fluidized bed reactors, wherein oxygen carrying material may flow counter-currently with respect to a gaseous species.

The reduced oxygen carrying material exiting the reduction reactor 100 may be transferred, through a connection means 160, which may include a non-mechanical gas-sealing device 160, to an oxidation reactor 200. The reduced oxygen carrying materials may be re-oxidized with steam from an inlet stream 210. The oxidation reactor 200 may have an outlet stream 220 rich in H₂ and steam. Excessive/unconverted steam in the outlet stream 220 may be separated from the H₂ in the stream 220 with a condenser 226. An H₂ rich gas stream 222 and an H₂O rich stream 224 may be generated. The steam inlet stream 210 of the oxidation reactor 200 may come from condensed steam recycled in the system 20 from an outlet stream 124 of the reduction reactor 100.

In one embodiment, a portion of the solid carbonaceous fuel in the reduction reactor 100 may be intentionally or unintentionally introduced to the oxidation reactor 200, which may result in a H₂, CO, and CO₂ containing gas in an outlet stream 220. Such a gas stream 220 can be either used directly as synthetic gas (syngas) or separated into various streams of pure products. In the oxidation reactor 200, the reduced oxygen carrying materials may be partially re-oxidized to an average valence state for iron that is between 0 and 3+. In some embodiments, the reduction reactor 100 is configured to operate in a packed moving bed mode or as a series of interconnected fluidized bed reactors, in which oxygen carrying material may flow counter-currently with respect to the gaseous species.

The oxidation reactor 200, which may comprise the same reactor type or a different reactor type than the reduction reactor 100, may be configured to oxidize the reduced metal or reduced metal oxide to produce a metal oxide intermediate. As used herein, "metal oxide intermediate" refers to a metal oxide having a higher oxidation state than the reduced metal or metal oxide, and a lower oxidation state than the metal oxide of the oxygen carrying material. For example, and not by way of limitation, the following equation illustrates possible oxidation reactions in the oxidation reactor 200:

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In this example, oxidation in the oxidation reactor using steam may produce a
5 resultant mixture that includes metal oxide intermediates comprising predominantly
 Fe_3O_4 . Fe_2O_3 and FeO may also be present. Furthermore, although H_2O , specifically
steam, is the oxidant in this example, numerous other oxidants are contemplated, for
example, CO , O_2 , air, and other oxidizing compositions.

The oxidation reactor 200 may be configured as a moving bed reactor, a series
10 of fluidized bed reactors, a rotary kiln, a fixed bed reactor, combinations thereof, or
others known to one of ordinary skill in the art. Typically, the oxidation reactor 200 may
operate at a temperature in the range of about 400°C to about 1200°C and a pressure in
the range of about 1 atm to about 150 atm; however, one of ordinary skill in the art
would realize that temperatures and pressures outside these ranges may be desirable
15 depending on the reaction mechanism and the components of the reaction mechanism.

The oxidation reactor 200 may also comprise a moving bed with a
countercurrent contacting pattern of gas and solids. Steam may be introduced at the
bottom of the reactor and may oxidize the reduced Fe containing particles as the particles
move downwardly inside the oxidation reactor 200. In this embodiment, the product
20 formed may be hydrogen, which is subsequently discharged from the top of the oxidation
reactor 200. It will be shown in further embodiments that products such as CO and
syngas are possible in addition to hydrogen. Though Fe_2O_3 formation is possible in the
oxidation reactor 200, the solid product from this reactor may be mainly metal oxide
intermediate, Fe_3O_4 . The amount of Fe_2O_3 produced in the oxidation reactor 200 depends
25 on the oxidant used, as well as the amount of oxidant fed to the oxidation reactor 200.
The steam present in the hydrogen product of the oxidation reactor 200 may then be
condensed in order to provide for a hydrogen rich stream. At least part of this hydrogen
rich stream may be recycled back to the reduction reactor 100. In addition to utilizing the
same reactor type as the reduction reactor 100, the oxidation reactor 200 may similarly

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operate at a temperature between about 400°C to about 1200°C and pressure of about 1 atm to about 150 atm.

Still referring to Fig. 2, the partially re-oxidized oxygen carrying materials exiting the oxidation reactor 200 may flow through a combustion reactor inlet stream 400 and may be transferred to a combustion reactor 300. The reduced oxygen carrying material in the combustion reactor inlet stream 400 may be moved through a non-mechanical gas seal and/or a non-mechanical solids flow rate control device.

The oxygen carrying material may enter the combustion reactor 300 and may be fluidized with air or another oxidizing gas from an inlet stream 310. The iron in the oxygen carrying material may be re-oxidized by air in the combustion reactor 300 to an average valence state of about 3+. The combustion reactor 300 may release heat during the oxidation of oxygen carrying material particles. Such heat may be extracted for steam and/or power generation or used to compensate the process heat requirements.

Followed by the oxidation reactions in the combustion reactor 300, the oxidized oxygen carrying materials may be transferred in the same manner as the previous embodiment in Figure 1, such as through a solid conveying system 350 such as a riser, into a gas-solid separation device 500, to a solids separation device 600, and to solids storage vessel 700.

The reactors of the systems described herein may be constructed with various durable materials suitable to withstand temperatures of up at least 1200°C. The reactors may comprise carbon steel with a layer of refractory on the inside to minimize heat loss. This construction also allows the surface temperature of the reactor to be fairly low, thereby improving the creep resistance of the carbon steel. Other alloys suitable for the environments existing in various reactors may also be employed, especially if they are used as internal components configured to aid in solids flow or to enhance heat transfer within a moving bed embodiment. The interconnects for the various reactors can be of lock hopper design or rotary/star valve design to provide for a good seal. However, other interconnects as can be used.

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Various mechanisms can be used for solid transportation in the numerous systems disclosed herein. For example, in some embodiments the solid transportations systems described herein may be transport systems using a pneumatic conveyor driven by air, belt conveyors, bucket elevators, screw conveyors, moving beds and fluidized bed
5 reactors. The resultant depleted air stream may be separated from the particles and its high-grade-heat content recovered for steam production. After regeneration, the oxygen carrying material particle may not be substantially degraded and may maintain full particle functionality and activity.

Heat integration and heat recovery within the system and all system
10 components may be desirable. Heat integration in the system is specifically focused on generating the steam for the steam requirements of the oxidation reactor 200. This steam may be generated using the high grade heat available in the hydrogen, CO₂ and depleted air streams exiting the various system reactors 100,200,300, respectively. In one embodiment of the processes described herein, substantially pure oxygen may be
15 generated, in which part of the hydrogen may be utilized. The residence time in each reactor is dependent upon the size and composition of individual oxygen carrying material particles. For example, the residence time for a reactor comprising Fe based metal oxides may range from about 0.1 to about 20 hours.

In some embodiments, additional unwanted elements may be present in the
20 system. Trace elements like Hg, As, Se are not expected to react with Fe₂O₃ at the high temperatures of the process. As a result they are expected to be present in the CO₂ stream produced. If CO₂ is to be used as a marketable product, these trace elements may be removed from the stream. Various cleanup units, such as mercury removal units are contemplated herein. Similar options will need to be exercised in case the CO₂ stream is
25 let out into the atmosphere, depending upon the rules and regulations existing at that time. If it is decided to sequester the CO₂ for long term benign storage, e.g. in a deep geological formation, there may not be a need to remove these unwanted elements. Moreover, CO₂ may be sequestered via mineral sequestration, which may be more desirable than geological storage, because it may be safer and more manageable.

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Furthermore, sulfur may constitute an unwanted element, which must be accounted for in the system. In a solid fuel conversion embodiment, sulfur, which is present in coal, is expected to react with Fe_2O_3 and form FeS. Some FeS may release SO_2 in the combustion reactor 300. This will be liberated on reaction with steam in the oxidation reactor 300 as H_2S and will contaminate the hydrogen stream. During the condensation of water from this steam, most of this H_2S will condense out. The remaining H_2S can be removed using conventional techniques like amine scrubbing or high temperature removal using a Zn, Fe or a Cu based sorbent. Another method for removing sulfur may include the introduction of sorbents, for example, CaO, MgO, etc. Additionally, sorbents may be introduced into the reduction reactor 100 in order to remove the sulfur and to prevent its association with Fe. The sorbents may be removed from the system using ash separation device.

Although some embodiments of the present system are directed to producing hydrogen, it may be desirable for further treatment to produce ultra-high purity hydrogen. As would be familiar to one of ordinary skill in the art, some carbon or its derivatives may carry over from the reduction reactor 100 to the oxidation reactor 200 and contaminate the hydrogen stream. Depending upon the purity of the hydrogen required, it may be desirable to use a pressure swing adsorption (PSA) unit for hydrogen to achieve ultra high purities. The off gas from the PSA unit may comprise value as a fuel and may be recycled into the reduction reactor 100 along with coal, in solid fuel conversion embodiments, in order to improve the efficiency of hydrogen production in the system.

Further details regarding the operation of fuel conversion systems are described in Thomas (U.S. Patent No. 7,767,191), Fan (PCT/US10/48125), Fan (WO 2010/037011), and Fan (WO 2007/082089), all of which are incorporated herein by reference in their entirety.

The oxygen carrying material for use in a chemical looping system may comprise a ceramic framework. The ceramic framework may comprise a primary active mass and a support material. The support material may comprise a primary support

material. In some embodiments, the support material may further comprise a secondary support material. Without being bound by theory, it is believed that the support material enhances the longevity of the oxygen carrying material by providing stable reactivity and increased strength. In one embodiment, the oxygen carrying material contains between
5 about 10% to about 100% by weight of the ceramic framework. In another embodiment, the oxygen carrying material contains between about 40% to about 100% by weight of the ceramic framework. In another embodiment, the oxygen carrying material contains about 100% ceramic framework, wherein the oxygen carrying material does not substantially contain any materials other than the ceramic framework.

10 In a fuel conversion system, such as those depicted in Figs. 1 and 2, the active mass may serve to donate oxygen to the fuel for its conversion. It also may accept the oxygen from air/steam to replenish the oxygen lost. In one embodiment, the primary active mass may comprise a metal or metal oxide of Fe, Co, Ni, Cu, Mo, Mn, Sn, Ru, Rh, or a combination thereof. In another embodiment, the primary active mass may comprise
15 a metal or metal oxide of Fe, Cu, Ni, Mn, or combinations thereof. In yet another embodiment, the primary active mass may comprise a metal or metal oxide of Fe, Cu, or combinations thereof. In one embodiment, the oxygen carrying material contains between about 20% and about 70% by mass of the active mass material. In yet another embodiment, the oxygen carrying material contains between about 30% and about 65%
20 by mass of the active mass material.

In one embodiment, the oxygen carrying material may comprise a primary support material. Without being bound by theory, it is believed that in the ceramic framework, the support part of the oxygen carrying material, serves to provide strength to the particle and may help retain the reactivity of the oxygen carrying material. In one
25 embodiment, the primary support material may comprise a metal, metal oxide, metal carbides, metal nitrates, or metal halides of Li, Be, B, Na, Mg, Al, Si, K, Ca, Sc, Ti, V, Cr, Mn, Co, Zn, Ga, Ge, Rb, Sr, Y, Zr, Nb, Mo, Cd, In, Sn, Sb, Cs, Ba, La, Ce, Th. In another embodiment, the primary support material may comprise a ceramic or clay material such as, but not limited to, aluminates, aluminum silicates, aluminum

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phyllosilicates, silicates, diatomaceous earth, sepiolite, kaolin, bentonite, and combinations thereof. In yet another embodiment, the primary support material may comprise an alkali or alkine earth metal salt of a ceramic or clay material. In yet another embodiment, the primary support material may comprise a naturally occurring ore, such as, but not limited to, hematite, illmenite, or wustite. In one embodiment, the oxygen carrying material contains between about 5% and about 70% by mass of the primary support material. In another embodiment, the oxygen carrying material contains between about 30% and about 60% by mass of the primary support material.

In one embodiment, the oxygen carrying material may comprise a secondary support material in addition to a primary support material. Without being bound by theory, it is believed that the addition of the secondary support material in the ceramic framework facilitates improved reactivity and strength of the oxygen carrying material. In one embodiment, the oxygen carrying material contains between about 1% and about 35% of the secondary support material. In one embodiment, the secondary support material may comprise a metal, metal oxide, metal carbides, metal nitrates, or metal halides of Li, Be, B, Na, Mg, Al, Si, K, Ca, Sc, Ti, V, Cr, Mn, Co, Zn, Ga, Ge, Rb, Sr, Y, Zr, Nb, Mo, Cd, In, Sn, Sb, Cs, Ba, La, Ce, Th. In another embodiment, the secondary support material may comprise a ceramic or clay material such as, but not limited to, aluminates, aluminum silicates, aluminum phyllosilicates, silicates, diatomaceous earth, sepiolite, kaolin, bentonite, and combinations thereof. In yet another embodiment, the secondary support material may comprise an alkali or alkine earth metal salt of a ceramic or clay material. In yet another embodiment, the secondary support material may comprise a naturally occurring ore, such as, but not limited to, hematite, illmenite, or wustite.

The oxygen carrying materials disclosed herein may display enhanced reactivity, recyclability, and strength. By way of comparison, some embodiments of oxygen carrying materials disclosed herein are compared with a "base case" oxygen carrying material that comprises 60 wt% Fe₂O₃ and 40 wt% TiO₂ (without a secondary support). Fig. 3 shows the enhanced reduction reactivity, based on the percentage of

reduction, of secondary supported oxygen carriers containing 50 wt% Fe_2O_3 , 25 wt% primary support material and 25 wt% secondary support material compared to the base case oxygen carrying material. The data in Fig. 3 was produced from an experiment wherein the reducing gas was 100ml/min of H_2 that was contacted with the oxygen carrying material at about 900°C under atmospheric conditions.

In one embodiment, the oxygen carrying material comprising a secondary support becomes mechanically stronger when exposed about 10 redox cycles. The mechanical strength is measured by using the process similar to the ASTM D4179 standard test method for single pellet crush strength of formed catalysts and catalyst carriers. The oxygen carrier pellets are placed between the crushing surface and a force gauge is used to measure the force required to crush the sample. The secondary supported oxygen that showed improved reduction reactivity also showed increased strength, as shown in Table 1.

Oxygen Carrier Candidate	Fresh carrier strength (N)	Post 10-cycles strength (N)	Change in Strength (%)
Base Case	63.64	58.04	-8.8
50wt% Fe_2O_3 , 25wt% TiO_2 , 25wt% SiO_2	68.28	126.8	85.71
50wt% Fe_2O_3 , 25wt% TiO_2 , 25wt% MgO	51.4	116.66	126.96
50wt% Fe_2O_3 , 25wt% Al_2O_3 , 25wt% MgO	33.28	76.66	130.35

Table 1

Fig. 4 shows the weight change percent of a secondary supported oxygen carrying material over 100 redox cycles, corresponding to the reactivity of the oxygen carrying material in a redox cycle. In one embodiment, the oxygen carrying material of Fig. 4 comprises 50wt% Fe_2O_3 , 40wt% TiO_2 and 10wt% MgO and does not lose more than about 5% of its carrying capacity when exposed to about 100 redox cycles. In one embodiment, the physical stability of the a secondary supported oxygen carrying material improves over redox cycles compared to a non secondary supported oxygen carrying material. For example, an oxygen carrying material comprising 50wt% Fe_2O_3 , 40wt% TiO_2 and 10wt% MgO had its strength improved about 65% over the base case

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oxygen carrying material over 50 redox cycles, and improved about 58% over the 100 redox cycles.

Without being limited by theory, it is believed that the improved physical stability of the secondary supported oxygen carriers may be associated with the volume expansion control. The redox performance of the oxygen carriers may result in the migration of the active metal phase. The reduction of iron oxide may cause a change in density in the oxygen carrying material and the oxygen migration may be controlled by the outward diffusion of iron ions. Therefore the denser iron grain center is shifted from its original location. The oxidation causes the volume to increase due to addition of mass. This continuous outward movement of the grain results in volume expansion. The volume expansion may cause the oxygen carrying material to become weaker. The addition of the primary support may assist to disperse the active metal phase and may prevent agglomeration of the iron phase and prevents deactivation. However, the volume expansion cannot be avoided. The secondary support material may serve to reduce the volume expansion rate by forming solid phase stabilizers that prevent the migration of iron to the surface.

In one embodiment, in addition to the ceramic framework, the oxygen carrying material may comprise a binder material. The addition of a binder material may increase the strength of the oxygen carrying material without substantial loss in reactivity. A ceramic/clay material may be used as a binder material. The binder material may help to increase the strength of the particle and may be inert under reactive conditions. In one embodiment, the oxygen carrying material contains between about 0.05wt% and about 20wt% by mass of the binder material. An Alkali or Alkaline earth metal salt may be used as a binding material to improve the physical integrity of a metal oxide in the ceramic framework. In one embodiment, the binding material may include bentonite, sodium silicate, potassium silicate, sepiolite, kaolin, or combination thereof.

In one embodiment, the oxygen carrying material may comprise ash. The ash may be derived from coal usage to maintain or improve the reactivity over multiple cycles. The presence of ash in the some fuel conversion systems may be unavoidable due

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to the direct introduction of coal/biomass into the reactor system. The ash is removed from the system along with the oxygen carrying material fines. The ash may be used in the oxygen carrying material as an inert material. The ash may comprise between about 0% and about 25% of the mass of the oxygen carrying material. The heterogeneous oxygen carrying material mixture containing the ceramic framework and ash may be prepared through one of the following synthesis techniques: mechanical mixing, slurry mixing, impregnation, sol-gel, co-precipitation, solution combustion. The presence of ash did not indicate any substantial detrimental effect on the particle reactivity and recyclability. An oxygen carrying material comprising of the base case of 60wt% Fe₂O₃ and 40wt% TiO₂ and containing varying amounts of ash was found to be reactive and recyclable, as shown in Fig. 5.

The novel oxygen carrying materials described in this invention disclosure are capable of maintaining stable oxygen donation capacity at temperature range from 600°C to 1250°C. In a preferred embodiment, the oxygen carrying material is made to undergo reduction and oxidation cycles between temperatures ranging from 700°C to 1250°C. In a more preferred embodiment, the oxygen carrying capacity is utilized in the temperature range of 750°C to 1050°C.

In one embodiment, in the ceramic framework, the use of multiple metal oxides as the primary active mass. The incorporation of multiple metal oxides as the primary active mass may bring unique benefits in chemical looping applications. Two or more primary and/or support metal cations and oxygen anion may form perovskite (ABO_{3-δ}) type of structure to achieve good oxygen anion conductivity and/or good structural stability. The preferred A site metal cations include the cations of Ca, Mg, Sr, Ba, Lanthium metals, and combinations thereof, the preferred B site metal cations include the cations of Ti, Al, Fe, Si, Mn, Co, and combination thereof. In one embodiment, iron is used as the B site metal and the molar ratio between iron and the total B site metal ranges between about 0.1 and about 1. In another embodiment, the aforementioned perovskite material is combined with a simple primary metal oxides and/or supports to achieve a heterogeneous metal oxide mixture through one of the following synthesis

techniques: mechanical mixing, slurry mixing, impregnation, sol-gel, co-precipitation, solution combustion. The heterogeneous mixture of the perovskite, primary metal oxide, and/or support can take the advantage of the high oxygen conductivity of perovskite, oxygen capacity of primary metal oxide, and structural and thermal stability of the support.

In another embodiment, two or more primary and/or support metal cations and oxygen anion form spinel or inverse spinel ($AB_2O_{4\delta}$) type of structure to achieve good structural stability and good reactivity. The preferred A site cations include the cations of Ca, Mg, Fe, Cu, Mn, Ni, Co, Cr, Ba, Sr, Zn, Cd, Ag, Au, Mo and combinations thereof, the preferred B site cations include the cations of Fe, Al, Mn, Cr, Si, B, Cr, Mo and combination thereof. Under a preferred embodiment, iron is used as the B site metal and the molar ratio between iron and the total A and B site metals ranges between 0.1 and 1. Under another preferred embodiment, the aforementioned spinel/anti-spinel material is combined with a simple primary metal oxides and/or supports to achieve a heterogeneous metal oxide mixture through one of the following synthesis techniques: mechanical mixing, slurry mixing, impregnation, sol-gel, co-precipitation, solution combustion.

In yet another embodiment, a heterogeneous metal oxide mixture consisting of one or more of the following primary oxygen donors: oxides of copper, manganese, nickel, cobalt, iron, and the aforementioned perovskite and spinel/anti-spinel materials is prepared using one of the following synthesis techniques: mechanical mixing, slurry mixing, impregnation, sol-gel, co-precipitation, solution combustion. Under a preferred embodiment, the mixture contains at least 10% (wt.) oxides of iron and one or more of the following metal oxides: oxides of copper, nickel, manganese, and cobalt. One embodiment containing the active phase comprised of the mixtures of the oxides of iron and copper displayed stable reactivity over multiple cycles.

In yet another embodiment, one or more of the members of alkali and Group III elements are added to the complex metal oxides to enhance the strength and reactivity

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of the aforementioned metal oxides. In a preferred embodiment, Li, Na, K, B, or combinations thereof is used.

In another embodiment, the oxygen carrying material may be used in combination with a promoter. The oxygen carrying material disclosed herein may
5 comprise promoters such as, but not limited to, mixed metals, metal oxides, metal nitrites, metal halides, metal carbides, or combinations thereof as promoters to increase reactivity and strength. A promoter may improve methane conversion to CO₂ and H₂O. The addition of certain promoters may significantly improve the oxygen carrying material performance. Small quantities of promoter material incorporated into the
10 oxygen carrying material can help improve the kinetic reaction rates between the oxygen carrying material and the reactive gases. The preferred weight % of the promoters introduced into the oxygen carrying material ranges between about 0.01% to about 10%. In one embodiment, the promoters are introduced into the oxygen carrying materials after the synthesis of the oxygen carrying material by using the impregnation techniques
15 like wet-impregnation, dry impregnation or incipient wet impregnation method. In another embodiment, the promoters are introduced into the oxygen carrying material during the synthesis of the heterogeneous oxygen carrying material mixture containing the ceramic framework prepared by one of the following synthesis techniques: mechanical mixing, slurry mixing, impregnation, sol-gel, co-precipitation, solution
20 combustion.

The oxidation of methane into CO₂ and water occurs at a slower rate compared to the oxidation of other gaseous fuels like H₂ and CO. This makes improving the reactivity of the oxygen carrying material with methane a useful strategy to maintain lower residence time required in the reactors. The promoters selected for this purpose
25 can be pure metal, oxides, nitrates or halides of the Lanthanide series elements, group IIIB, IVB, VB, VIB elements or a combination thereof. In one embodiment, the addition of dopants improved the methane oxidation rates of the oxygen carrying material, as shown in Figure 6. The data of Fig. 6 was produced from an experiment wherein CH₄ at

100ml/min was contacted with the oxygen carrying material at about 900°C. In one embodiment, the dopants that may be oxides of ceria and/or zirconia.

The reduction rate of the oxygen carrying materials may play a direct role on the oxygen carrying material residence time in the reducer reactor. Faster rates may result in improved cost benefits for the process. The promoters selected for this purpose
5 can be pure metal, oxides, nitrates or halides of the Ni, Cu, Mn, Cr, Zr, Mo, Ag, Au, Zn, Sn, Pt, Ru, Rh, Re or a combination thereof. In one such preferred embodiment, the addition of Nickel oxides in small quantities resulted in faster reduction rates of the oxygen carrying materials with reducing gases.

10 The air oxidation rate of the oxygen carrying materials may play a direct role on the combustor reactor size. The higher rates may result in improved cost benefits for the process. The promoters selected for this purpose may be a pure metal, oxides, nitrates or halides of the Lanthanide and Actinide series elements, group IA, IIA, IIIA, IVA elements or a combination thereof. In one embodiment, the addition of dopants in small
15 quantities reduced the time taken to achieve complete oxidation with air from 30 minutes to less than 10 minutes. The dopants may be oxides of lithium and boron and combinations thereof. In one embodiment, the addition of 5wt% LiBO₂ to the secondary supported oxygen carrier comprising of 50wt% Fe₂O₃, 40wt% TiO₂ and 10wt% MgO resulted in the reduction of time required for complete oxidation from 30 minutes to 26
20 minutes. In another embodiment, the addition of 10wt% LiBO₂ to the secondary supported oxygen carrier comprising of 50wt% Fe₂O₃, 40wt% TiO₂ and 10wt% MgO resulted in complete oxidation within 6 minutes.

The reactivity and recyclability of the oxygen carrying material may not be compromised by the addition of small quantities of promoters. For example, a pellet with
25 boron oxide as the promoter may not deteriorate the recyclability of the oxygen carrying material. In one embodiment, substantially no loss in reactivity is observed over 42 cycles with an oxygen carrier comprised of 50wt% Fe₂O₃, 40wt% TiO₂ and 10wt% MgO mixed with 5wt% of B₂O₃.

In one embodiment, the oxygen carrying material may be synthesized by making the ceramic framework that comprises the active metal/metals, primary support material and secondary support material, and the remaining additional material into a well-mixed matrix prepared by one of the following synthesis techniques: mechanical
5 mixing, slurry mixing, impregnation, sol-gel, co-precipitation, solution combustion. The result of such action is a homogenous powder mixture.

The homogenous powder mixture may then be processed to arrive at the final oxygen carrying material. The post mixture formation processing involves multiple steps. The first step, if required, is drying at temperatures in the range from about 50°C
10 to about 450°C for a given time period that ranges between about 1 to about 14 hours.

The mixture may then be modified to the given particle size range of about 0.5mm to about 7mm in diameter using particle formation techniques such as, but not limited to, pelletization, extrusion, or granulation. To facilitate the smoother modification of the mixture into the given size, certain other materials may be added to
15 the homogenous mix. The special material that is added can be a binder material such as clay, ceramics, starch, glucose, sucrose or a combination thereof. They can also be lubricant materials such as, but not limited to magnesium stearate, licowax, and combinations thereof. The formed pellet may then be introduced to the sintering step.

The sintering of the pellets may result in increase in strength of the oxygen
20 carrying materials which is crucial for longevity of operation of the chemical looping systems. The pellets are sintered at temperatures in the range of about 450°C to about 1300°C for extended time periods in the range of about 1 to about 48 hours.

The fines generated from the chemical looping unit due to attrition may be re-
used to make the oxygen carrying material. In this embodiment, the fines may be mixed
25 with the fresh oxygen carrying material mixture synthesized using techniques such as, but not limited to, mechanical mixing, slurry mixing, impregnation, sol-gel, co-precipitation, solution combustion. This mixture of fines and fresh particles may be calcined together to form stronger particles. The weight % of fines in the mixture may

range between about 0 – 100%. The oxygen carrying material made from 100% fines was found to be reactive and recyclable with substantially no deterioration of reactivity after about 5 redox cycles. The oxygen carrying material made from 100% fines were also up to 34% stronger than a fresh oxygen carrying material synthesized from chemical
5 grade raw materials.

It is noted that recitations herein of a component of the present disclosure being “configured” in a particular way, to embody a particular property, or function in a particular manner, are structural recitations, as opposed to recitations of intended use. More specifically, the references herein to the manner in which a component is
10 “configured” denotes an existing physical condition of the component and, as such, is to be taken as a definite recitation of the structural characteristics of the component.

For the purposes of describing and defining the present invention it is noted that the term “substantially” is utilized herein to represent the inherent degree of uncertainty that may be attributed to any quantitative comparison, value, measurement,
15 or other representation. The term “substantially” is also utilized herein to represent the degree by which a quantitative representation may vary from a stated reference without resulting in a change in the basic function of the subject matter at issue.

Having described the subject matter of the present disclosure in detail and by reference to specific embodiments thereof, it is noted that the various details disclosed
20 herein should not be taken to imply that these details relate to elements that are essential components of the various embodiments described herein, even in cases where a particular element is illustrated in each of the drawings that accompany the present description. Rather, the claims appended hereto should be taken as the sole representation of the breadth of the present disclosure and the corresponding scope of the
25 various embodiments described herein. Further, it will be apparent that modifications and variations are possible without departing from the scope of the appended claims. More specifically, although some aspects of the present disclosure are identified herein as preferred or particularly advantageous, it is contemplated that the present disclosure is not necessarily limited to these aspects.

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CLAIMS

1. An oxygen carrying material comprising:

5 about 20% to about 70% by weight of a primary active mass, the primary active mass comprising a composition having a metal or metal oxide selected from the group consisting of Fe, Co, Ni, Cu, Mo, Mn, Sn, Ru, Rh, and combinations thereof;

about 5% to about 70% by weight of a primary support material, the primary support material comprising a composition having:

10 (i) at least one metal, metal oxide, metal carbide, metal nitrate, metal halide, or combinations thereof;

(ii) at least one ceramic or clay material, or salts thereof;

(iii) at least one naturally occurring ore; or

(iv) combinations thereof; and

15 about 1% to about 35% by mass of a secondary support material, the secondary support material comprises a composition having:

(i) at least one metal, metal oxide, metal carbide, metal nitrate, metal halide, or combinations thereof;

(ii) at least one ceramic or clay material or salts thereof;

(iii) at least one naturally occurring ore; or

20 (iv) combinations thereof;

wherein the primary support material composition and the secondary support material composition are different.

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2. The oxygen carrying material of claim 1, wherein the at least one metal, metal oxide, metal carbide, metal nitrate, or metal halide comprise metal elements selected from the group consisting of Li, Be, B, Na, Mg, Al, Si, K, Ca, Sc, Ti, V, Cr, Mn, Co, Zn, Ga, Ge, Rb, Sr, Y, Zr, Nb, Mo, Cd, In, Sn, Sb, Cs, Ba, La, Ce, Th, and combinations thereof;
- 5
3. The oxygen carrying material of claim 1, wherein the oxygen carrying material contains between about 30% and about 65% by mass of the primary active mass, the oxygen carrying material contains between about 30% and about 60% by mass of the primary support material, and the oxygen carrying material contains between about 5% and about 25% by mass of the
- 10 secondary support material.
4. The oxygen carrying material of claim 1, wherein the primary active mass comprises an oxide of Fe.
- 15 5. The oxygen carrying material of claim 1, wherein the primary support material comprises a metal, metal oxide, metal carbide, metal nitrate or metal halide of Li, Be, B, Na, Mg, Al, Si, K, Ca, Sc, Ti, V, Cr, Mn, Co, Zn, Ga, Ge, Rb, Sr, Y, Zr, Nb, Mo, Cd, In, Sn, Sb, Cs, Ba, La, Ce, Th.
- 20 6. The oxygen carrying material of claim 5, wherein the primary support material comprises an oxide of Ti.
7. The oxygen carrying material of claim 1, wherein the secondary support material comprises a metal, metal oxide, metal carbide, metal nitrate or metal halide of Li, Be, B, Na, Mg, Al, Si, K, Ca, Sc, Ti, V, Cr, Mn, Co, Zn, Ga, Ge, Rb, Sr, Y, Zr, Nb, Mo, Cd, In, Sn, Sb, Cs, Ba, La, Ce, Th.

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8. The oxygen carrying material of claim 7, wherein the secondary support material comprises an oxide of Mg.
9. The oxygen carrying material of claim 1, wherein the oxygen carrying material further
5 comprises a binder material.
10. The oxygen carrying material of claim 1, wherein the oxygen carrying material further comprises ash.
- 10 11. The oxygen carrying material of claim 1, wherein the oxygen carrying material further comprises a promoter.
12. The oxygen carrying material of claim 11, wherein the promoter comprises mixed metals, metal oxides, metal nitrites, metal halides, metal carbides, or combinations thereof.
- 15
13. The oxygen carrying material of claim 1, wherein the oxygen carrying material is formed into particles and substantially all of the particles have a diameter between about .5 mm and about 7 mm.
- 20 14. The oxygen carrying material of claim 1, wherein the primary active mass comprises at least two different metal oxides selected from the group comprising metal oxides of Fe, Co, Ni, Cu, Mo, Mn, Sn, Ru, Rh.

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15. The oxygen carrying material of claim 1, wherein the oxygen carrying material does not lose more than about 5% of its carrying capacity when exposed to about 100 redox cycles.
16. The oxygen carrying material of claim 1, wherein the oxygen carrying material becomes
5 mechanically stronger when exposed about 10 redox cycles.
17. The oxygen carrying material of claim 1, wherein the primary active mass comprises an oxide of Fe, the primary support material comprises an oxide of Ti, the oxygen carrying material contains between about 30% and about 65% by mass of the primary active mass, the oxygen
10 carrying material contains between about 30% and about 60% by mass of the primary support material, and the oxygen carrying material contains between about 5% and about 25% by mass of the secondary support material.
18. A system for converting fuel comprising:
- 15 an oxygen carrying material of claim 1;
- a first reactor comprising a moving bed and an inlet for providing fuel to the first reactor, wherein the first reactor is configured to reduce the oxygen carrying material with the fuel to produce a reduced oxygen carrying material; and
- a second reactor communicating with the first reactor and an oxygen source, wherein the
20 second reactor is configured to regenerate the oxygen carrying material by oxidizing the oxygen carrying material.

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19. The system for converting fuel of claim 18, wherein the oxygen carrying material does not lose more than about 5% of its carrying capacity when exposed to about 100 redox cycles.
20. The system for converting fuel of claim of claim 18, further comprising a third reactor,
5 wherein the third reactor is situated between the first reactor and the second reactor and in communicating with the first reactor and the second reactor, and is configured to oxidize at least a portion of the reduced oxygen carrying material from said first reactor to produce an oxygen carrying material intermediate and hydrogen.
- 10 21. A method for synthesizing oxygen carrying material of claim 1 comprising:
forming a matrix comprising a primary active mass, a primary support, and a secondary support;
drying the matrix; and
forming the matrix into particles of the oxygen carrying material of claim 1.

15

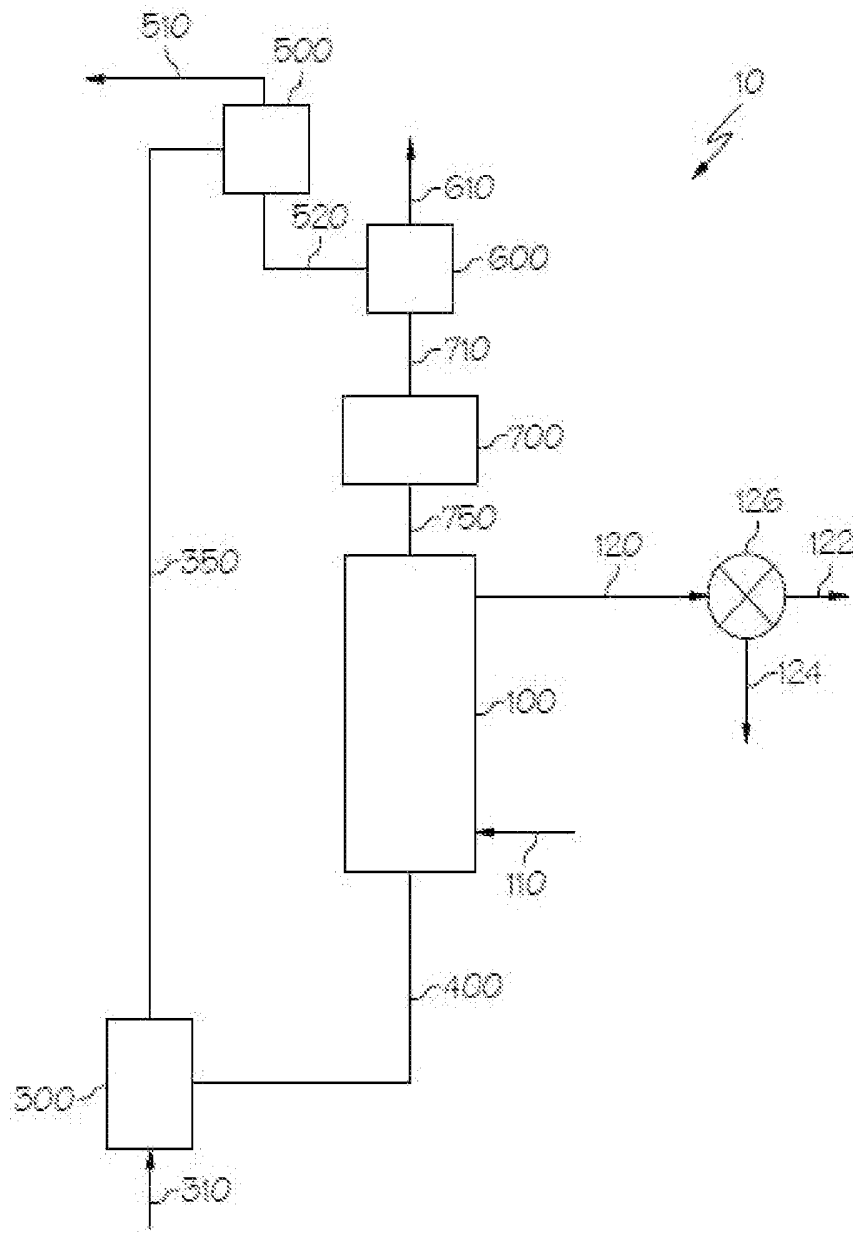


FIG. 1

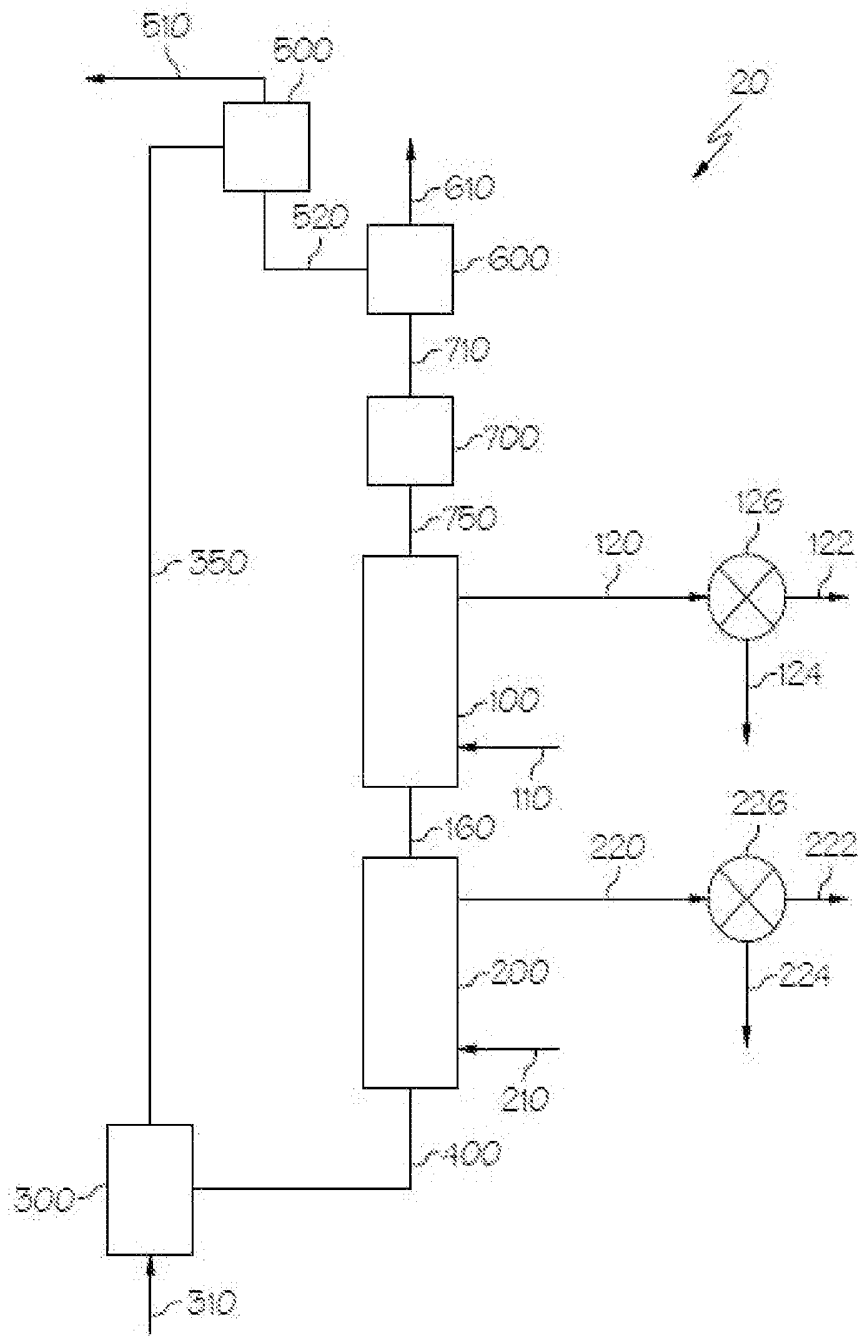


FIG. 2

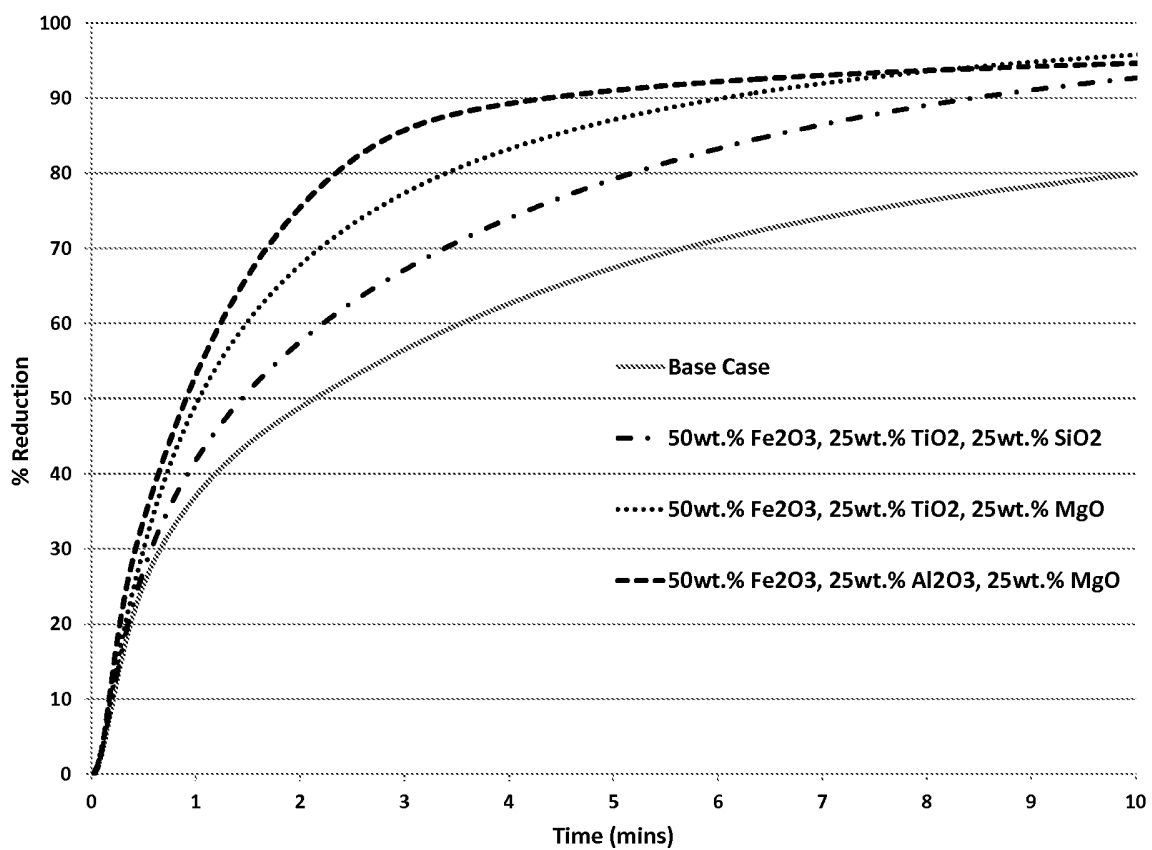


FIG. 3

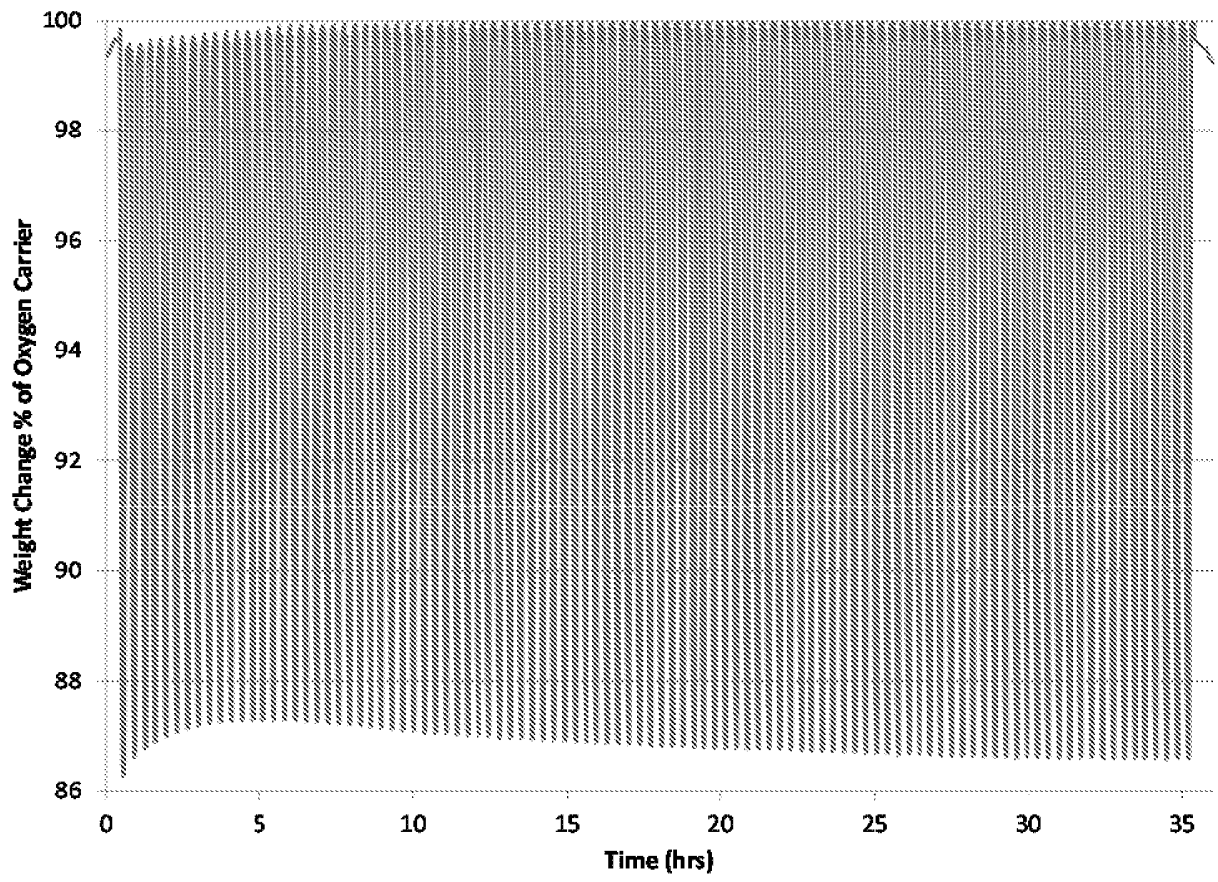


FIG. 4

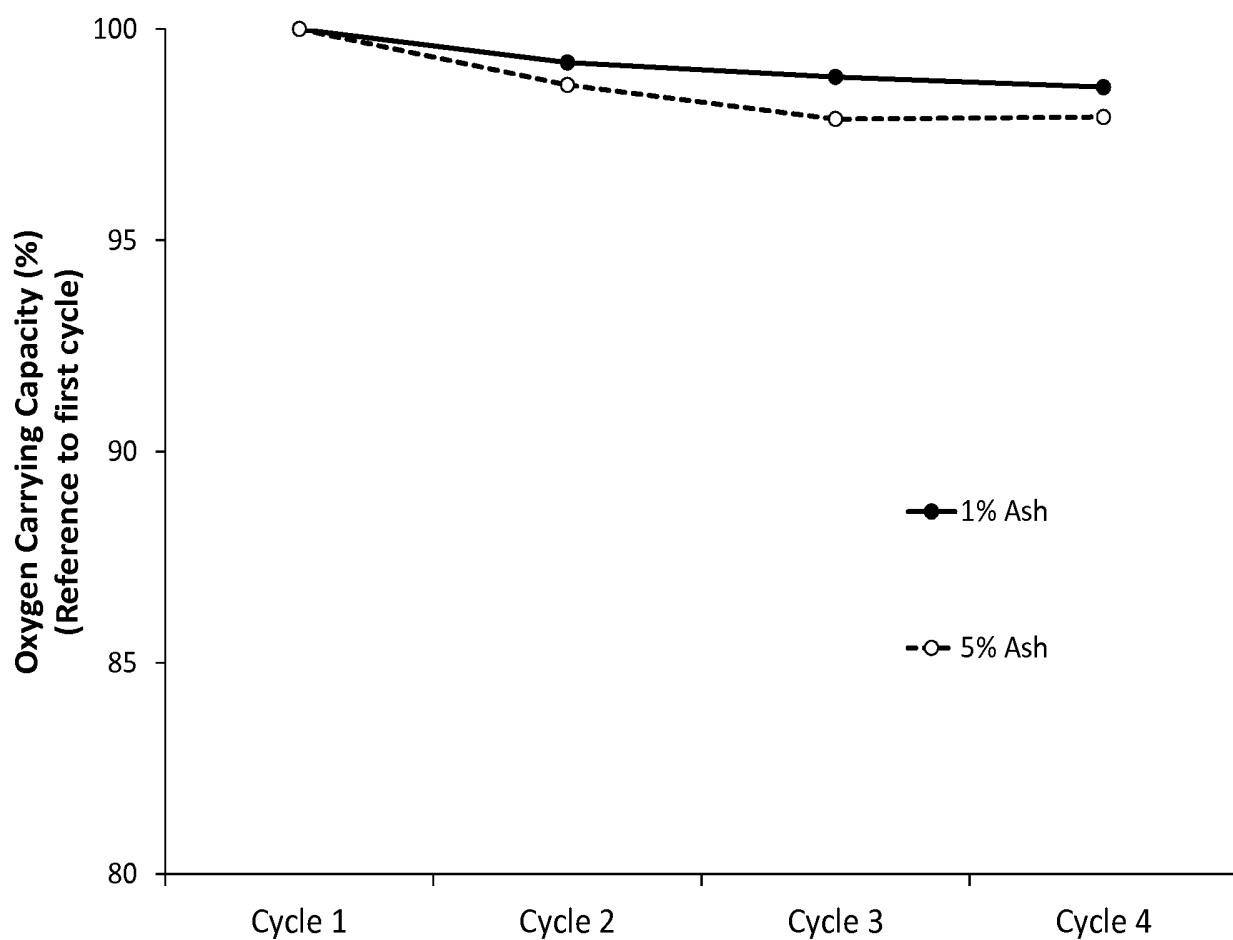


FIG. 5

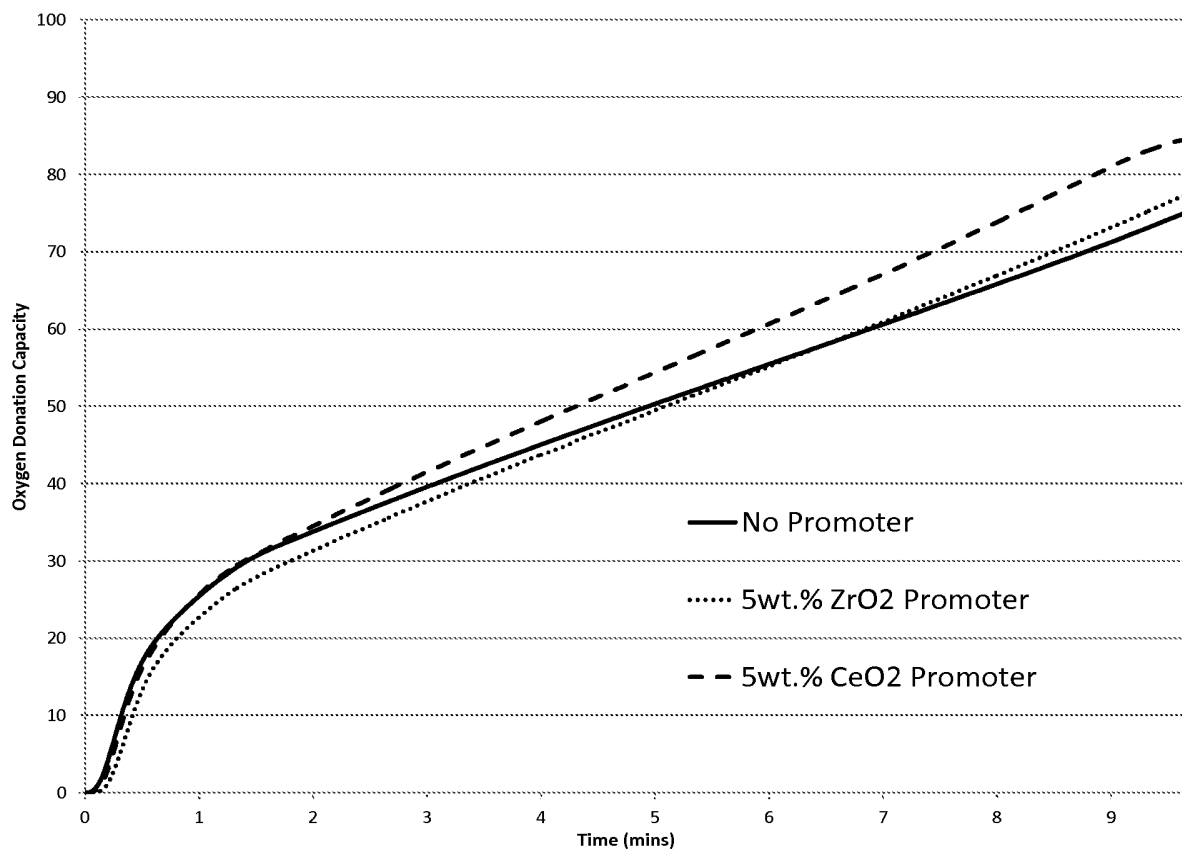


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/37557

A. CLASSIFICATION OF SUBJECT MATTER
 IPC(8) - F02C 1/08; F01K 3/18; F02C 1/00; F01K 3/00 (2012.01)
 USPC - 60/775; 60/39.461; 60/39.464; 60/781
 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) - F02C 1/08; F01K 3/18; F02C 1/00; F01K 3/00 (2012.01)
 USPC - 60/775; 60/39.461; 60/39.464; 60/781

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 PubWEST (PGPB,USPT,USOC,EPAB,JPAB) Terms - redox oxidize oxidized reduced reducing third reactor promoter ceramic ash TiO2
 pellet looping oxygen carrying materials
 Google - redox looping pellet binder metal-oxide TiO2 third-reactor steam hydrogen; oxygen carrying materials reactor binder metal-oxide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X — Y	US 2005/0175533 A1 (THOMAS, ET AL.) 11 August 2005 (11.08.2005), paras [0015], [0020], [0044], [0046], [0059]-[0060], [0062], [0067]	1-7a, 9-14, 16-20 ----- 7b, 8, 15
Y	US 2009/0000194 A1 (FAN, ET AL.) 01 January 2009 (01.01.2009), paras [0038]-[0039]	7b, 15
Y	US 2007/0049489 A1 (BECUE, ET AL.) 01 March 2007 (01.03.2007), para [0020]	8
A	US 2011/0054049 A1 (LAMBERT, ET AL.) 03 March 2011 (03.03.2011), entire document	1-20
A	US 5,447,024 A (ISHIDA, ET AL.) 05 September 1995 (05.09.1995), entire document	1-20

Further documents are listed in the continuation of Box C.

* Special categories of cited documents:	“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
“A” document defining the general state of the art which is not considered to be of particular relevance	“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
“E” earlier application or patent but published on or after the international filing date	“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
“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)	“&” document member of the same patent family
“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	

Date of the actual completion of the international search 31 July 2012 (31.07.2012)	Date of mailing of the international search report 13 AUG 2012
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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. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774
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