

(19) **United States**

(12) **Patent Application Publication**

Fan et al.

(10) **Pub. No.: US 2009/0000194 A1**

(43) **Pub. Date:**

Jan. 1, 2009

(54) **SYSTEMS AND METHODS OF CONVERTING FUEL**

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(21) Appl. No.: **12/160,803**

(22) PCT Filed: **Jan. 12, 2007**

(86) PCT No.: **PCT/US07/00956**

§ 371 (c)(1),
(2), (4) Date: **Jul. 14, 2008**

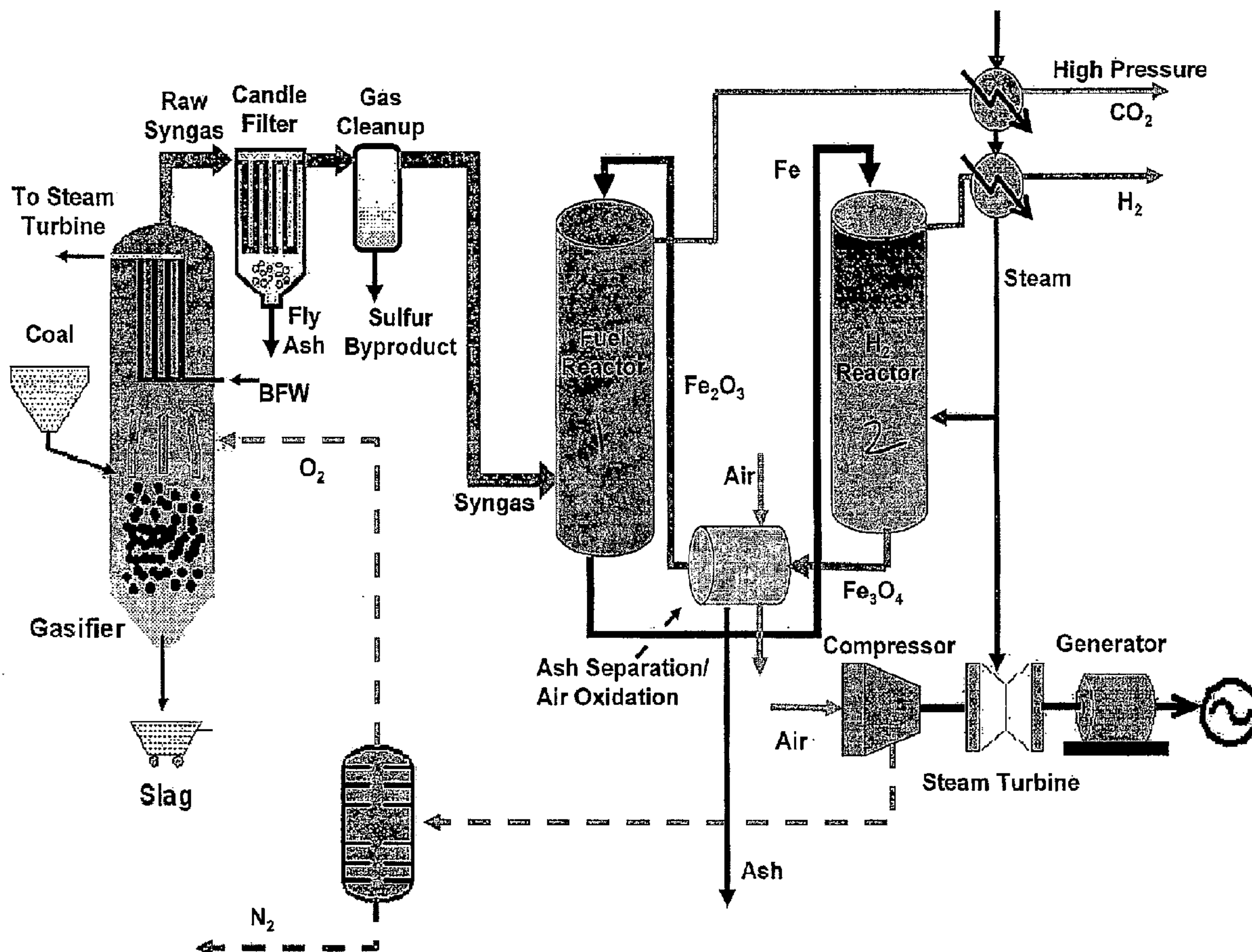
Related U.S. Application Data

(60) Provisional application No. 60/758,424, filed on Jan. 12, 2006, provisional application No. 60/758,507, filed on Jan. 12, 2006, provisional application No. 60/808,928, filed on May 26, 2006.

Publication Classification

(51) **Int. Cl.**
C10J 1/20 (2006.01)
(52) **U.S. Cl.** **48/199 R; 502/102; 501/94**
(57) **ABSTRACT**

Systems and methods for converting fuel are provided wherein the system comprises at least reactors configured to conduct oxidation-reduction reactions. The first reactor comprises a plurality of ceramic composite particles, wherein the ceramic composite particles comprises at least one metal oxide disposed on a support. The first reactor is configured to reduce the least one metal oxide with a fuel to produce a reduced metal or a reduced metal oxide. The second reactor is configured to oxidize the reduced metal or reduced metal oxide to produce a metal oxide intermediate. The system may also comprise a third reactor configured to oxidize the metal oxide intermediate to regenerate the metal oxide of the ceramic composite particles.



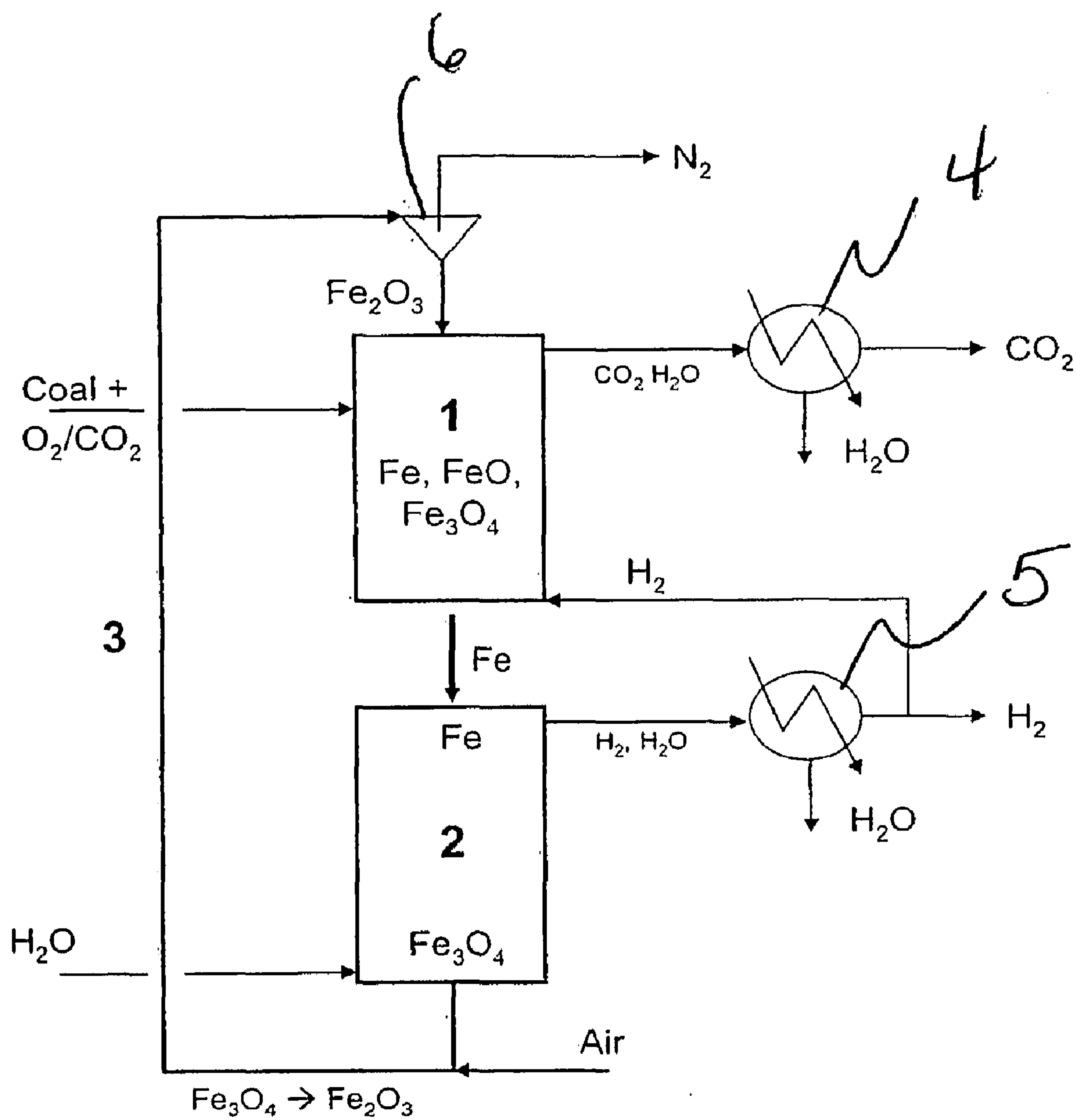


FIG. 1

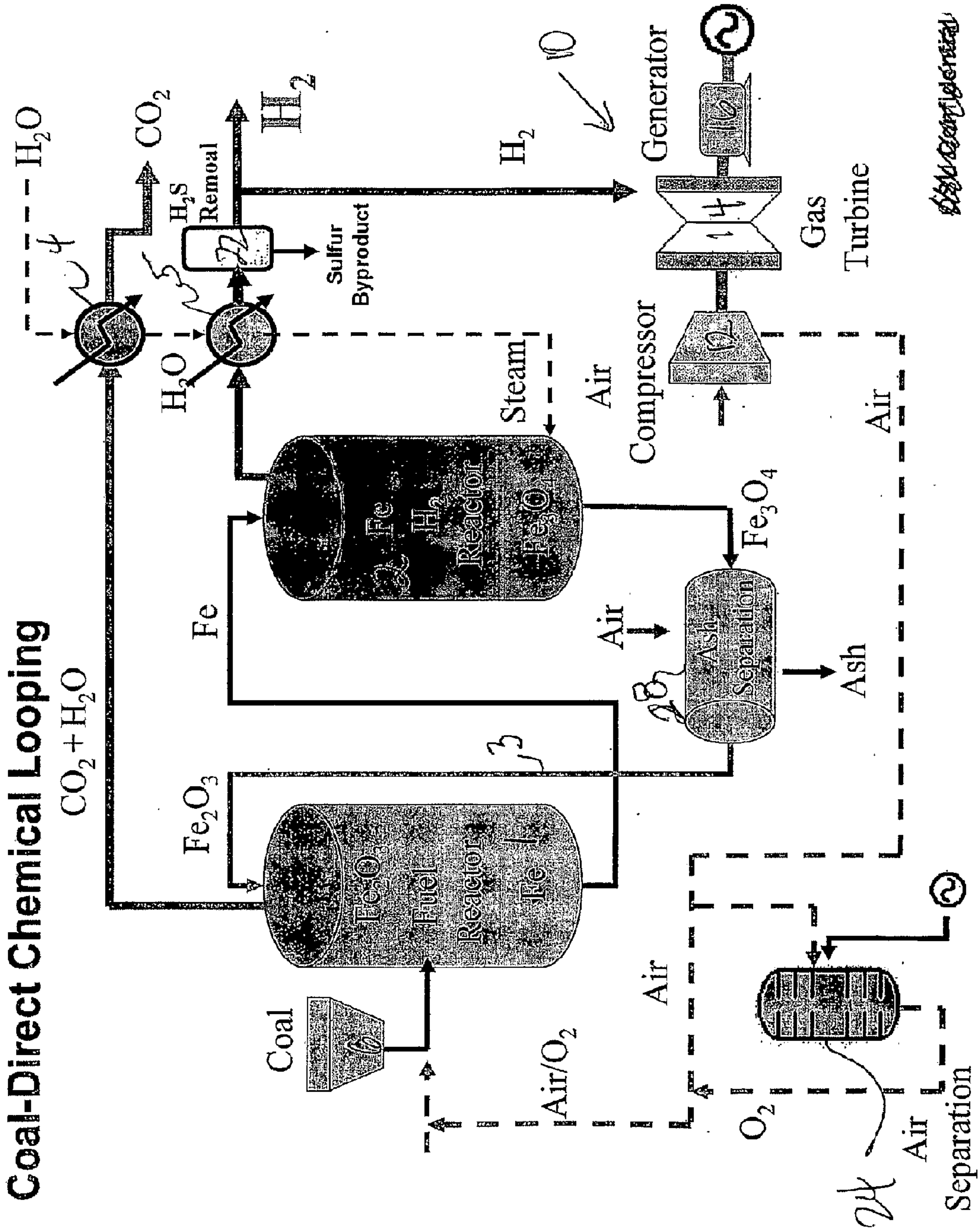


Fig. 7

Disclosed

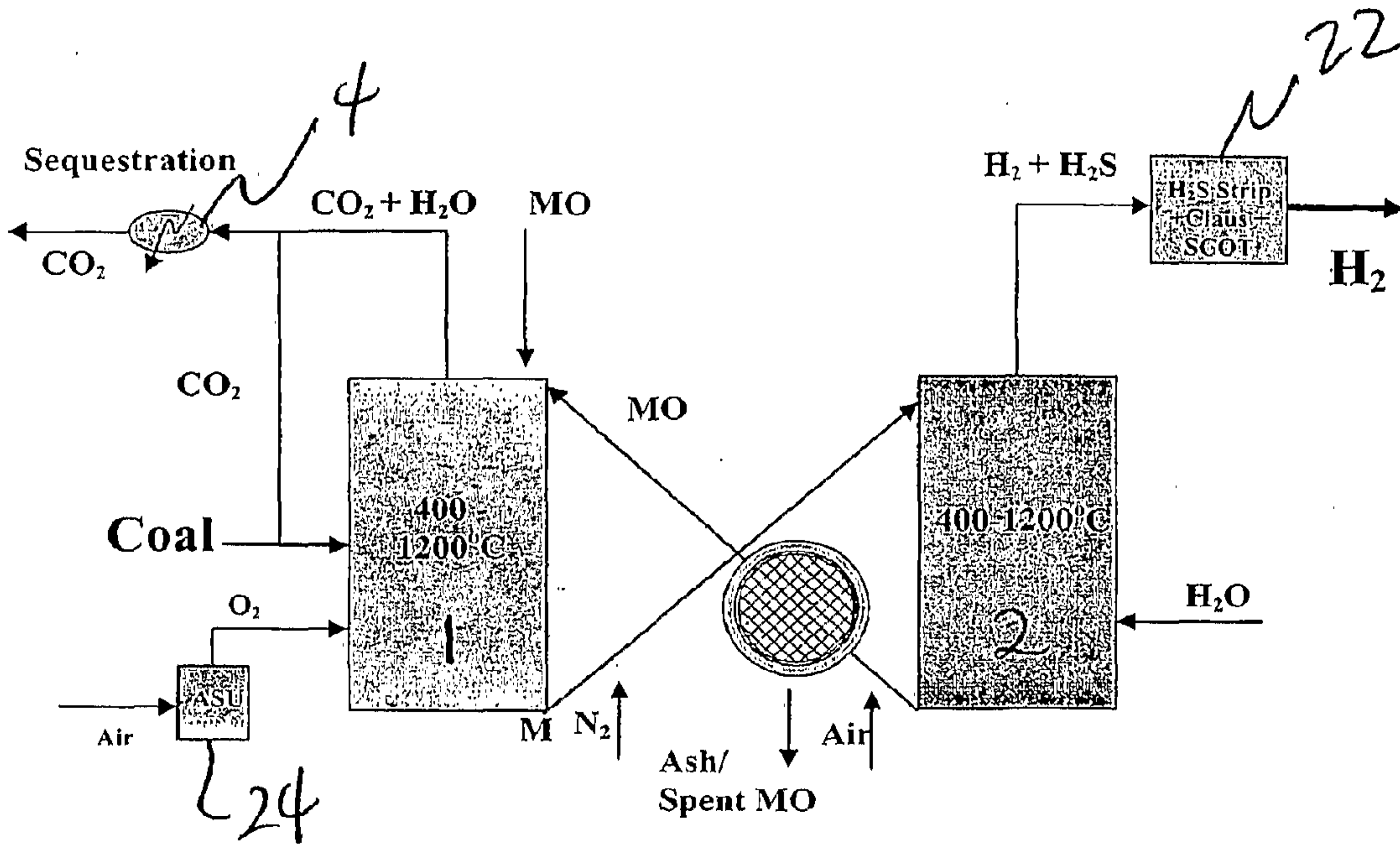


FIG. 3

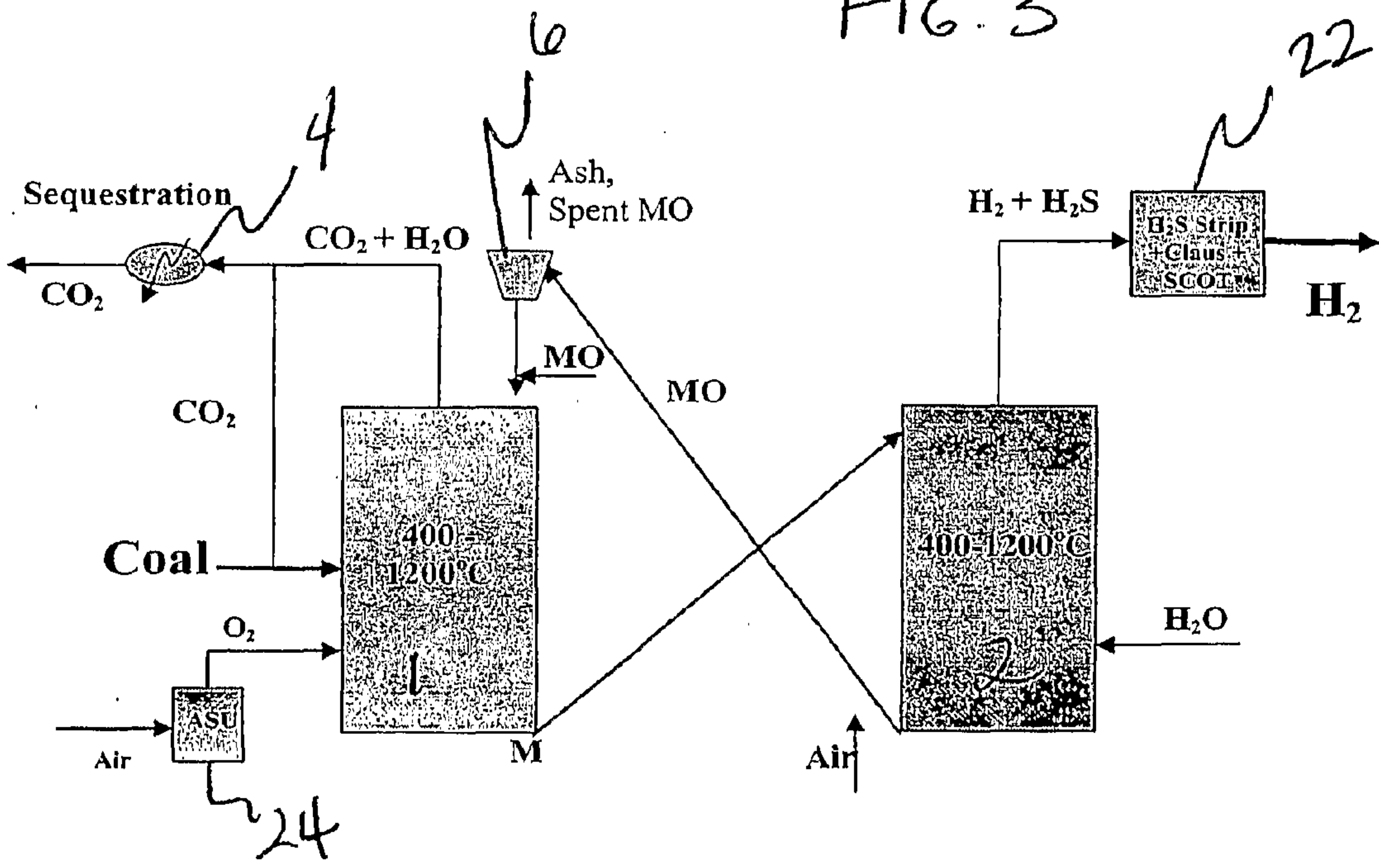


FIG. 4

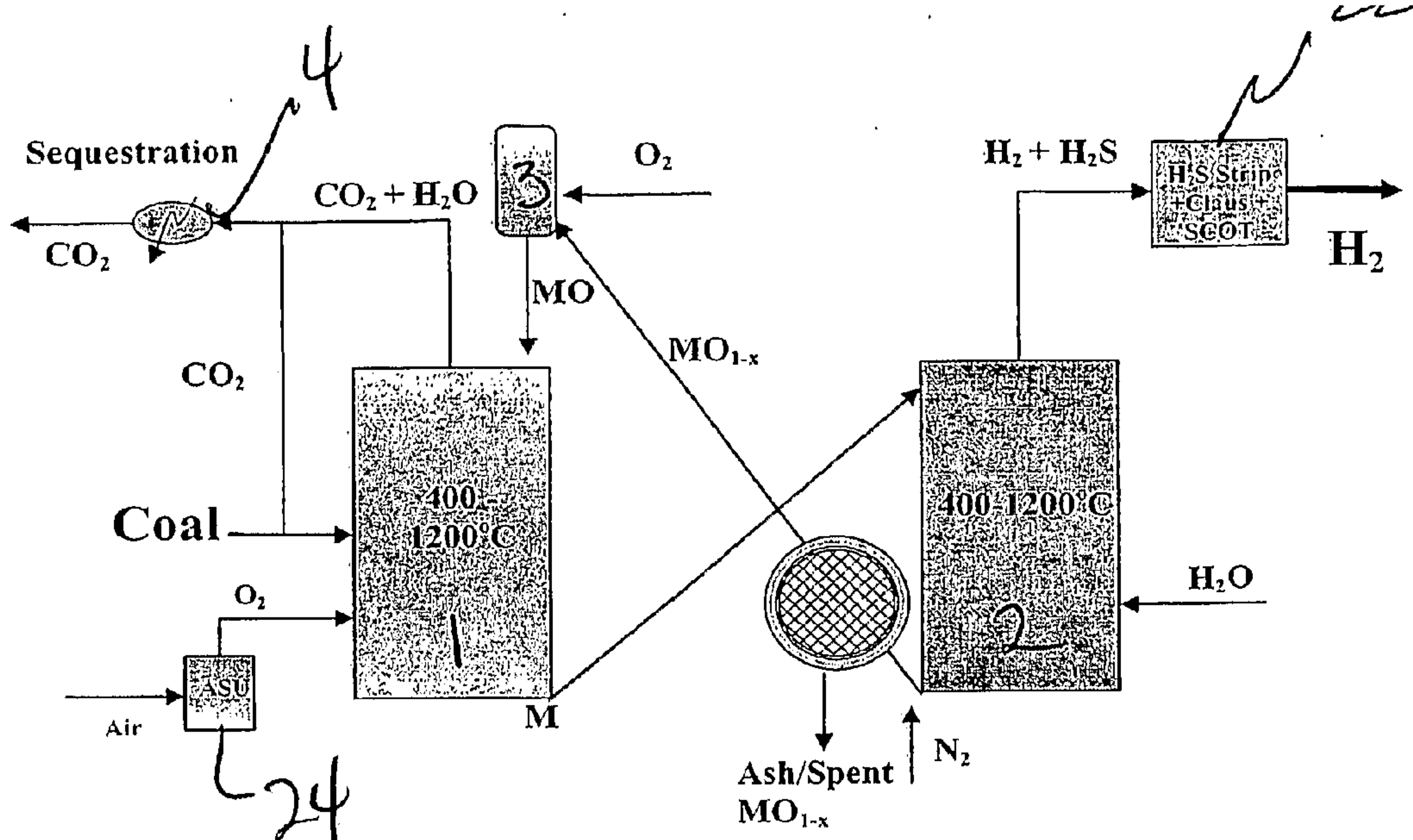


FIG. 5

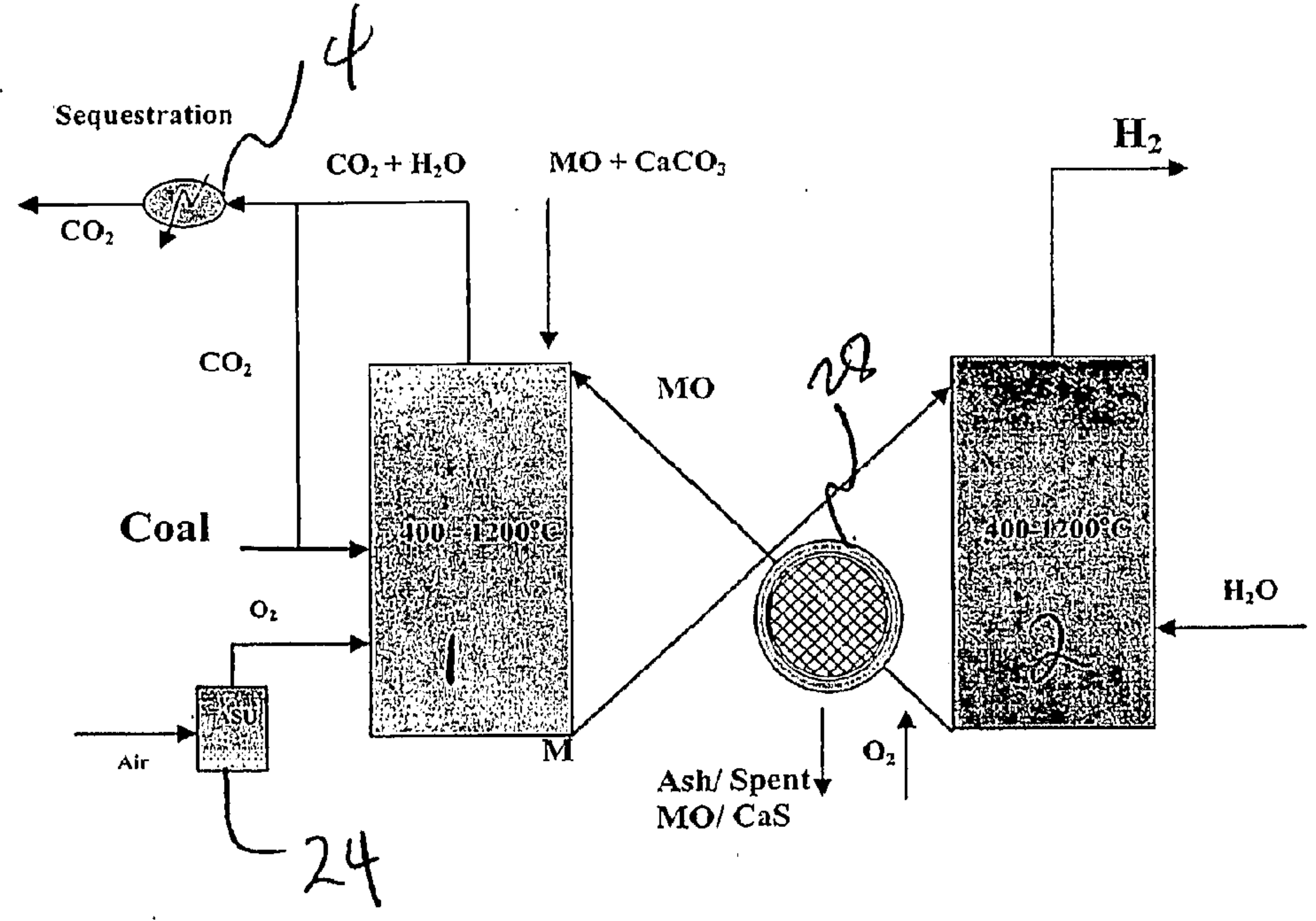


FIG. 6

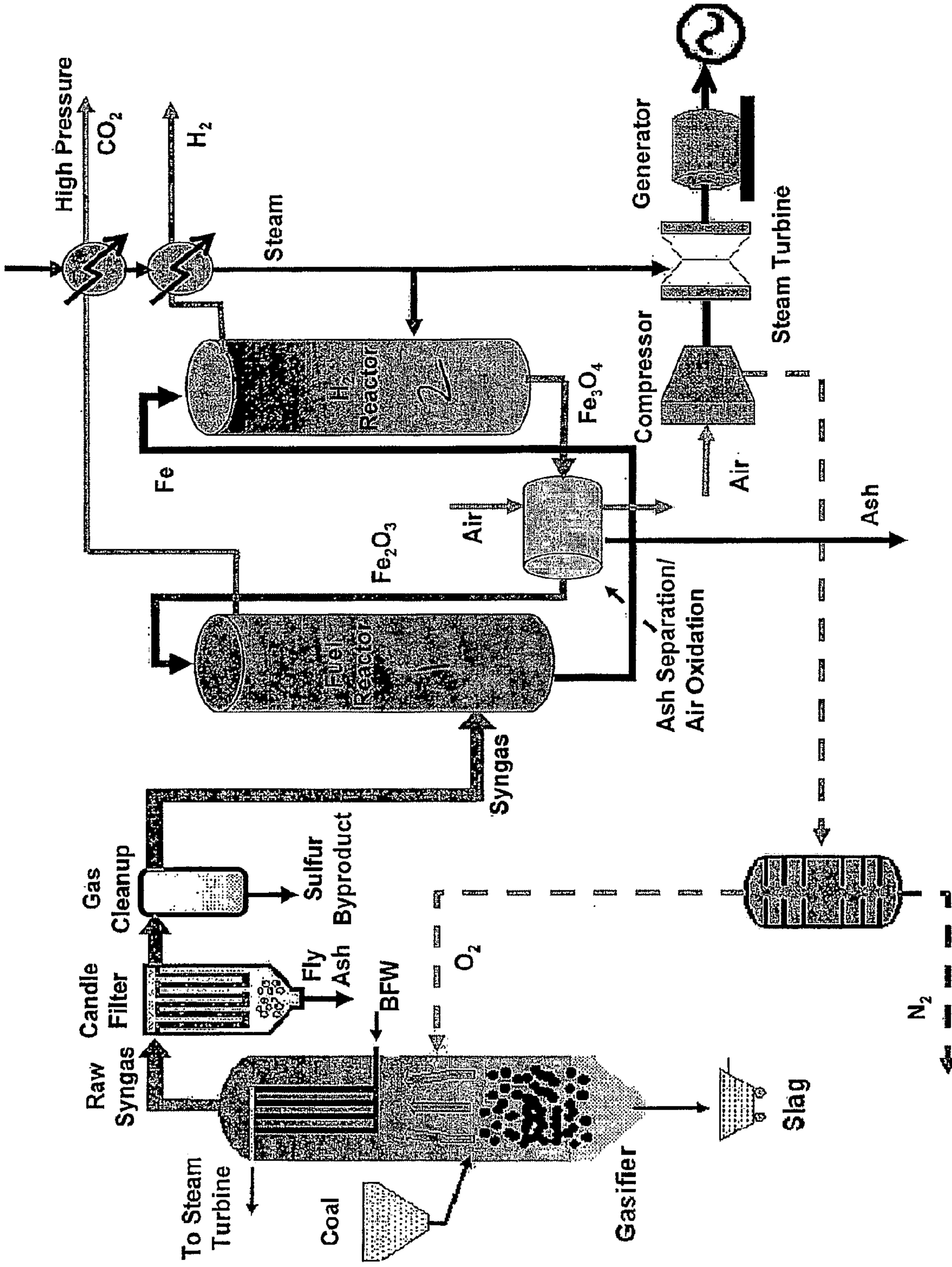


Figure 7

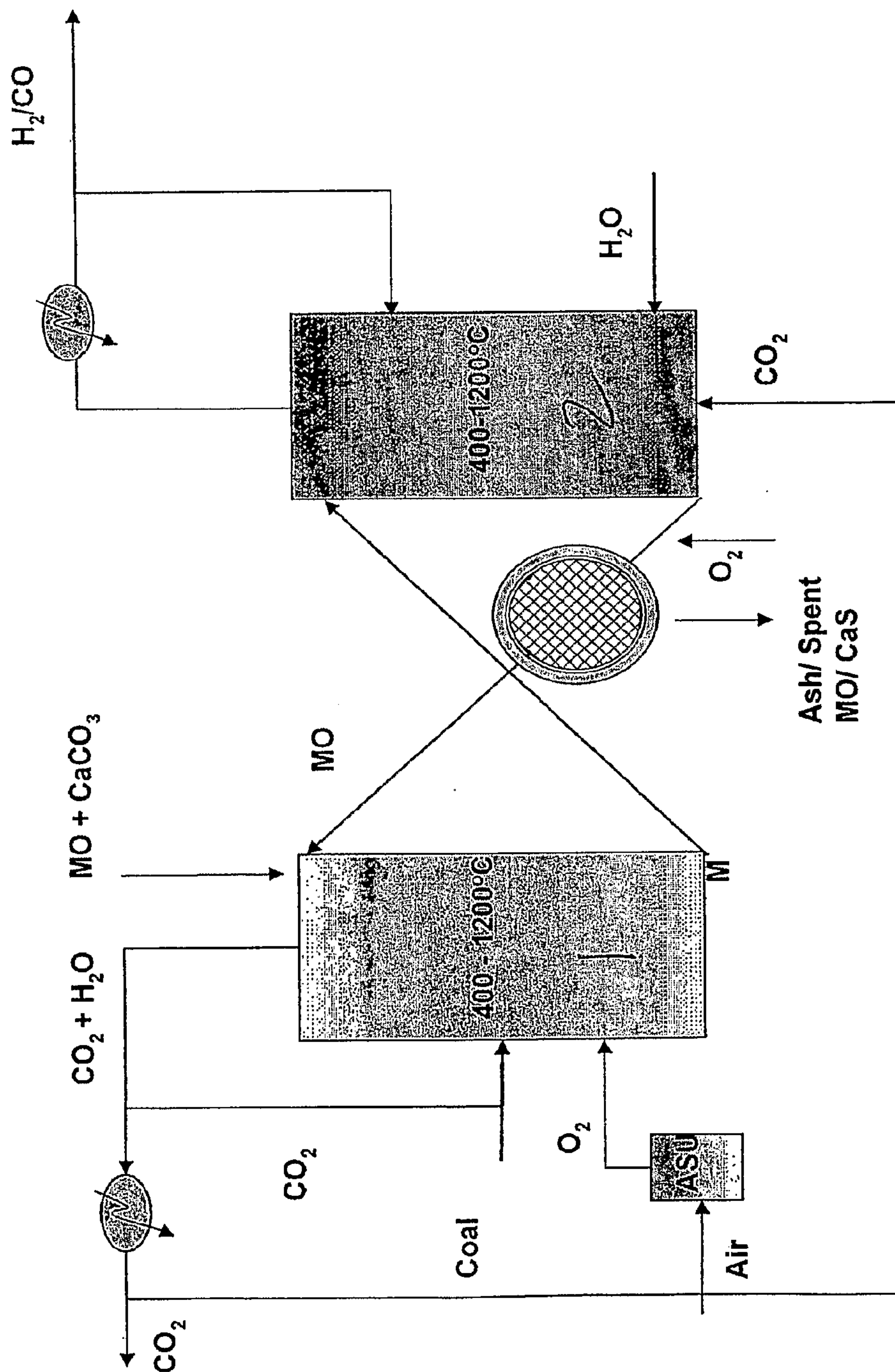


Figure 8

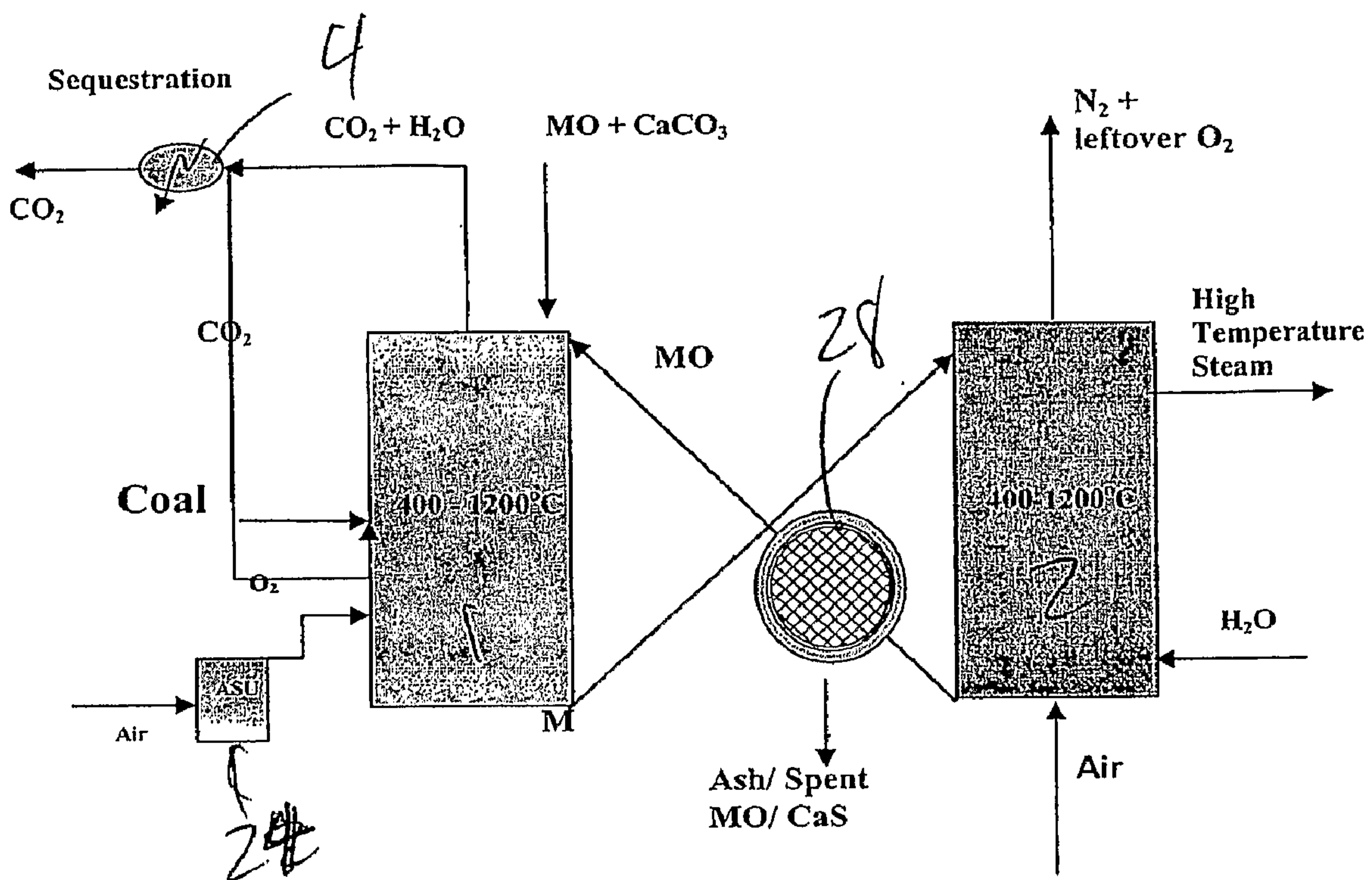
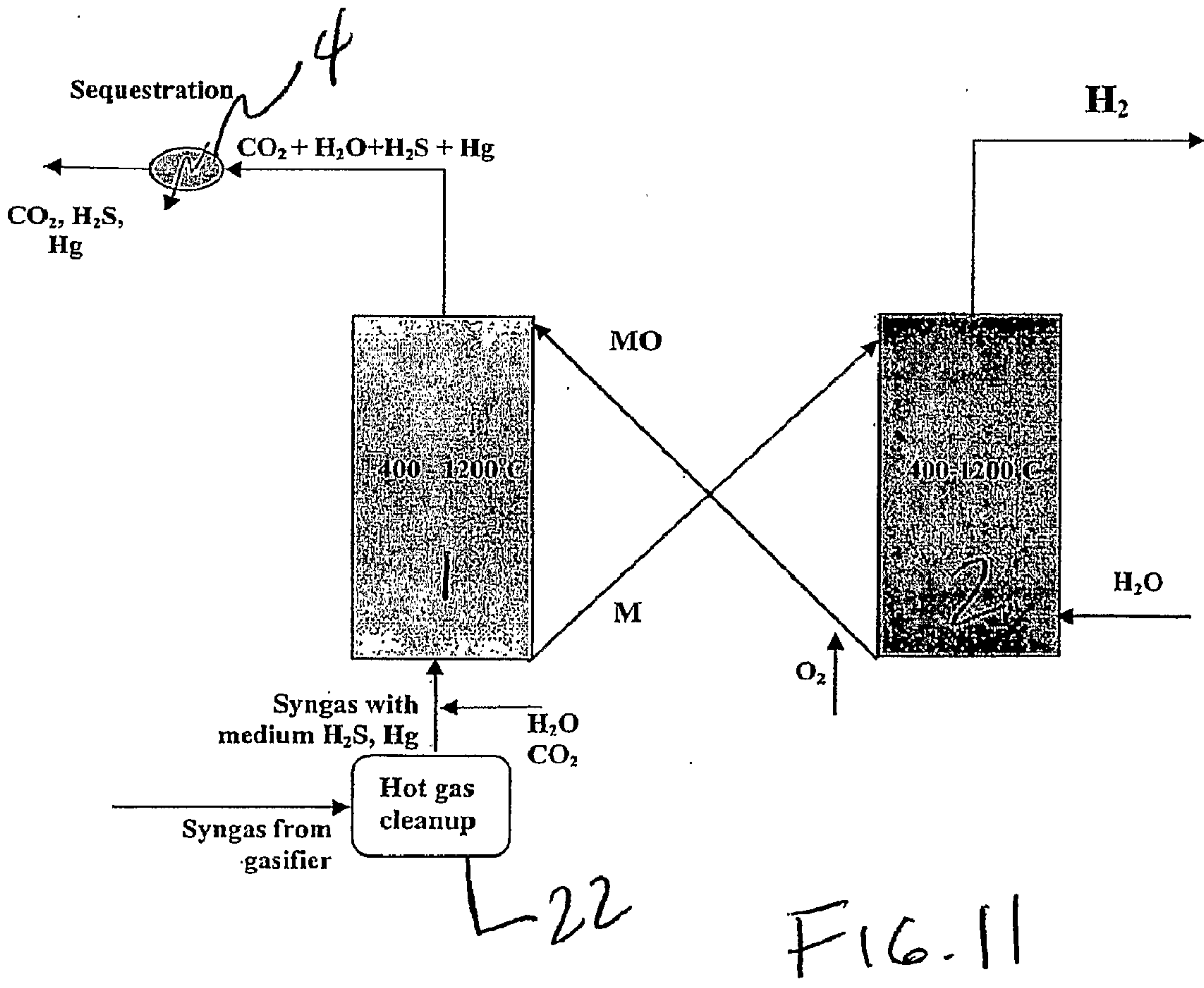
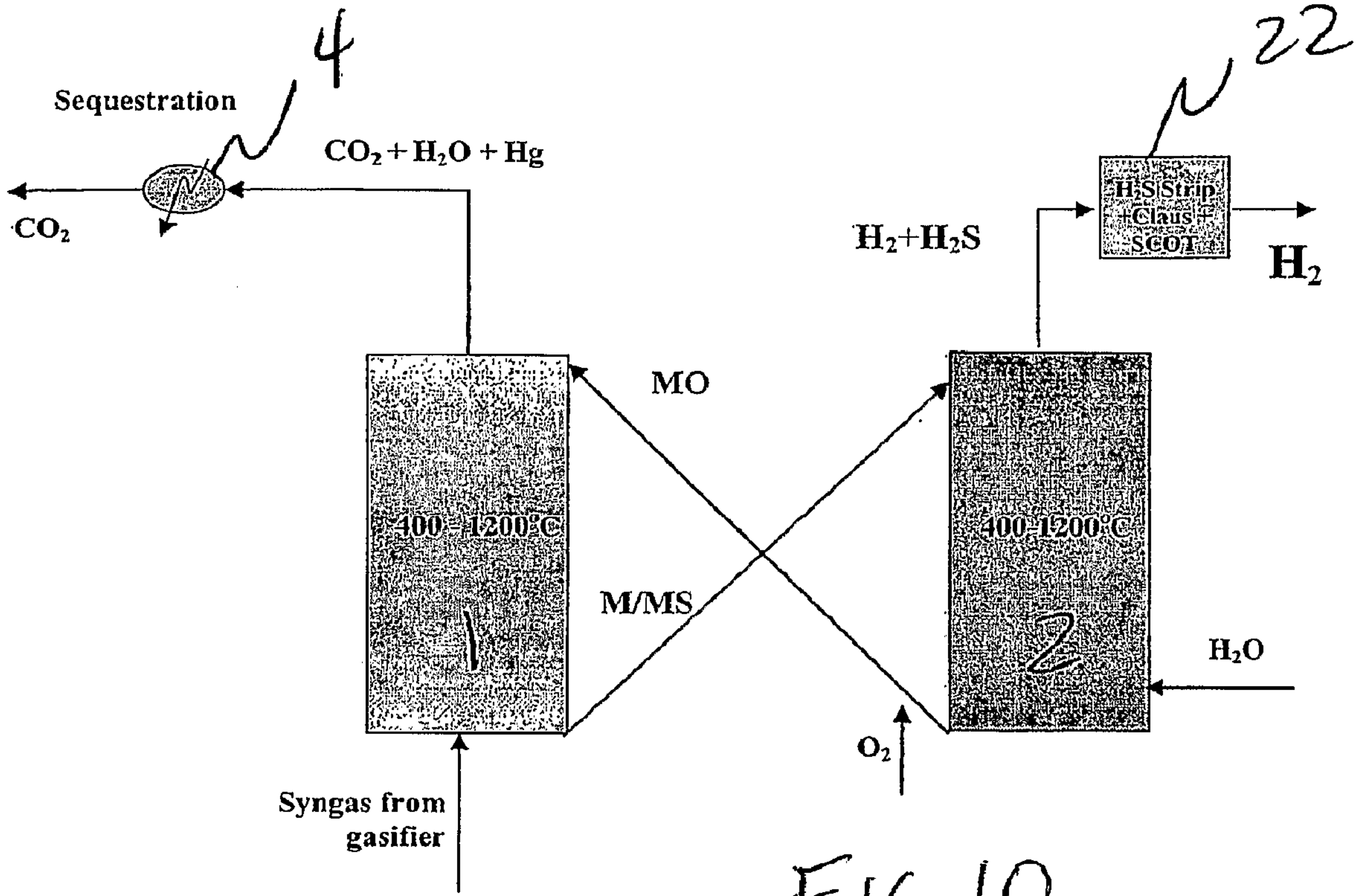


FIG. 9



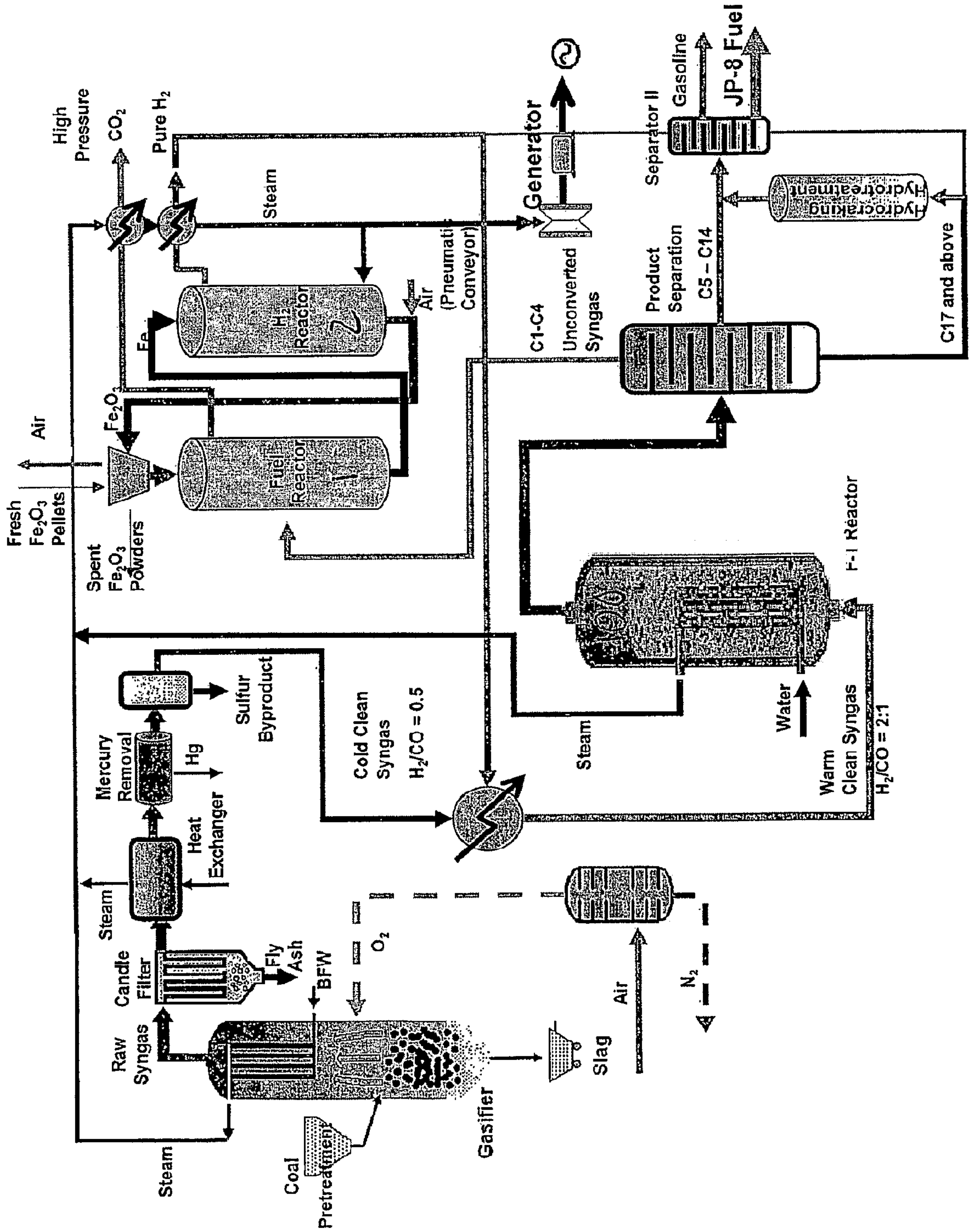


Figure 12

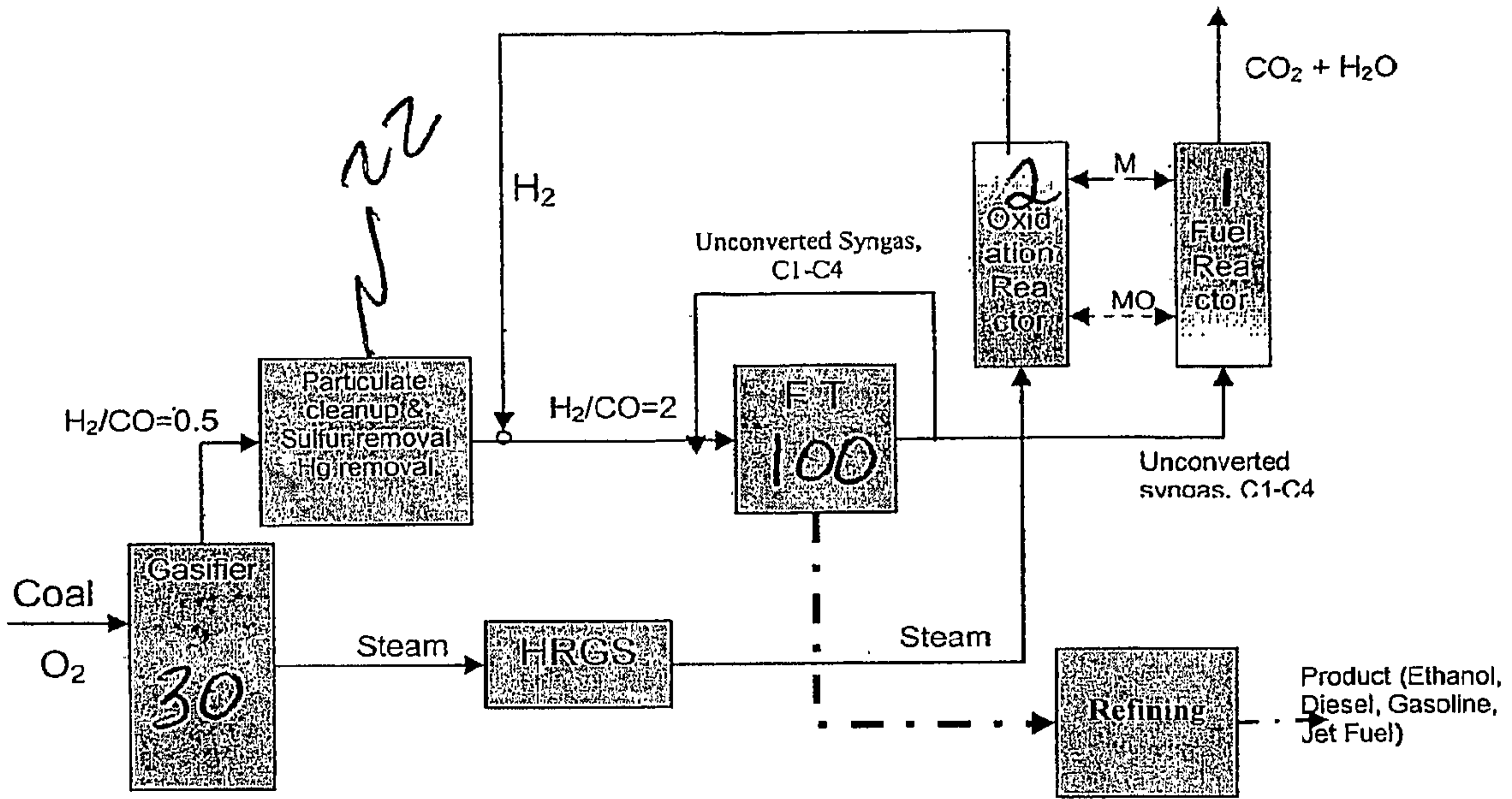


FIG. 13

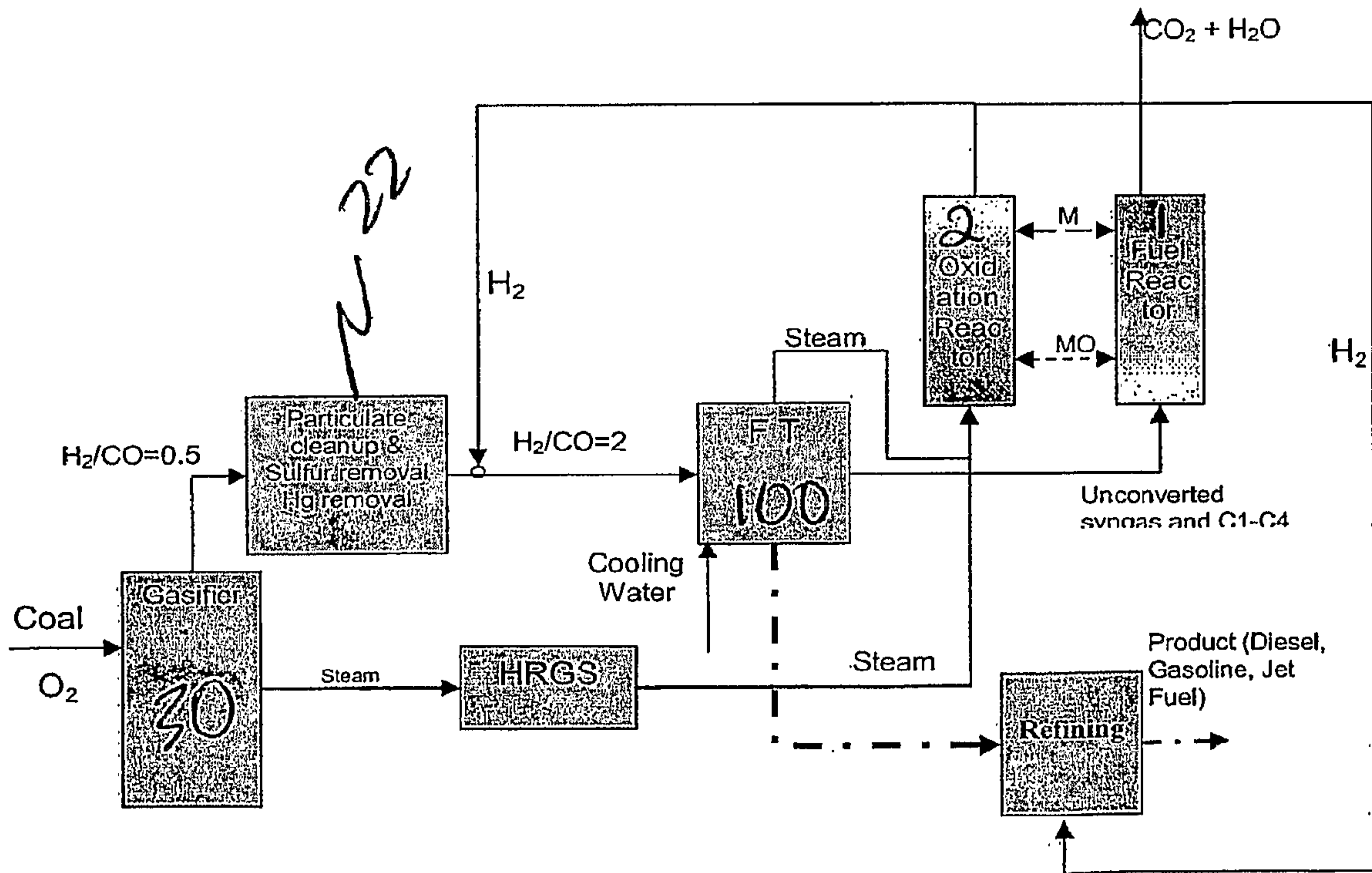


FIG. 14

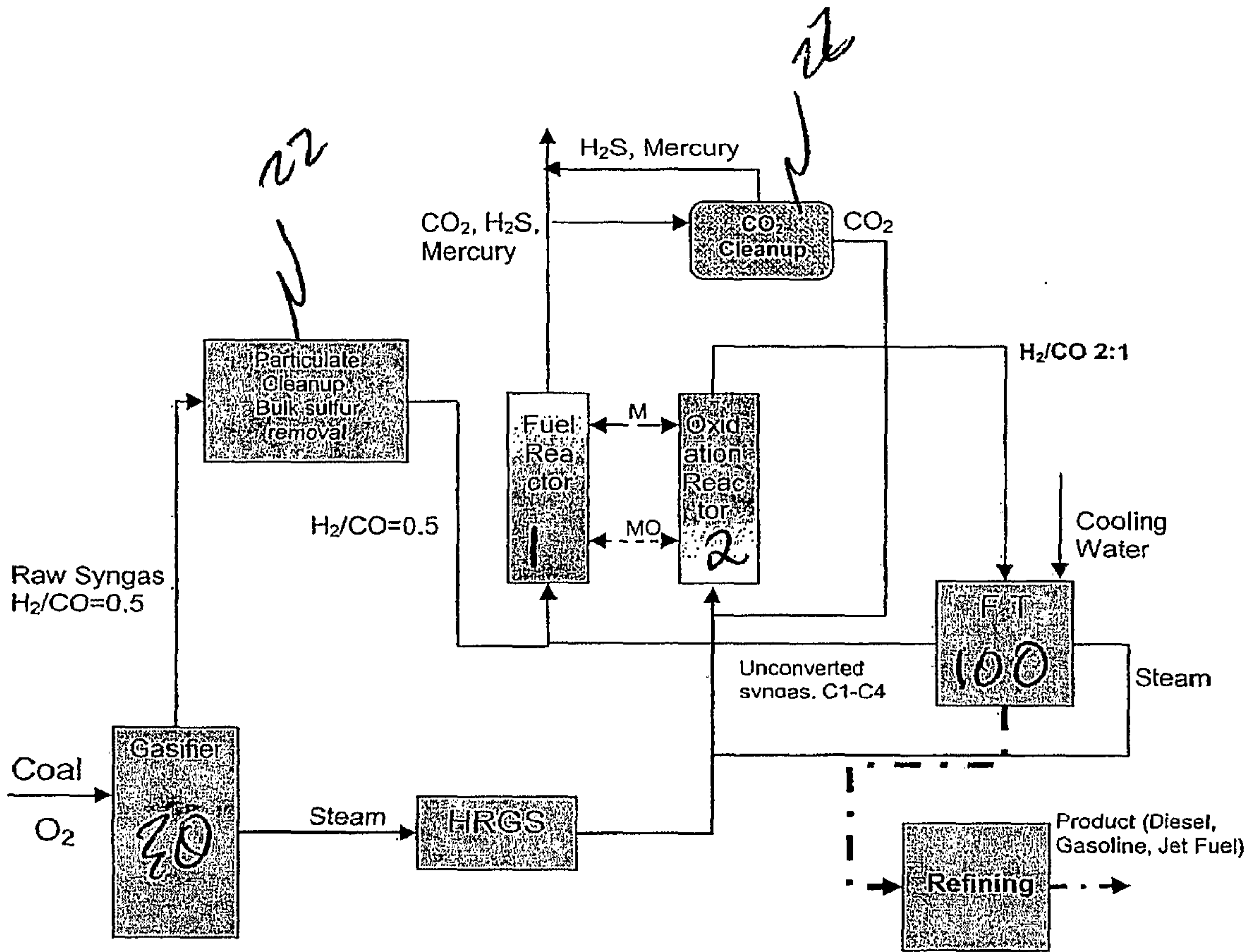


FIG. 15

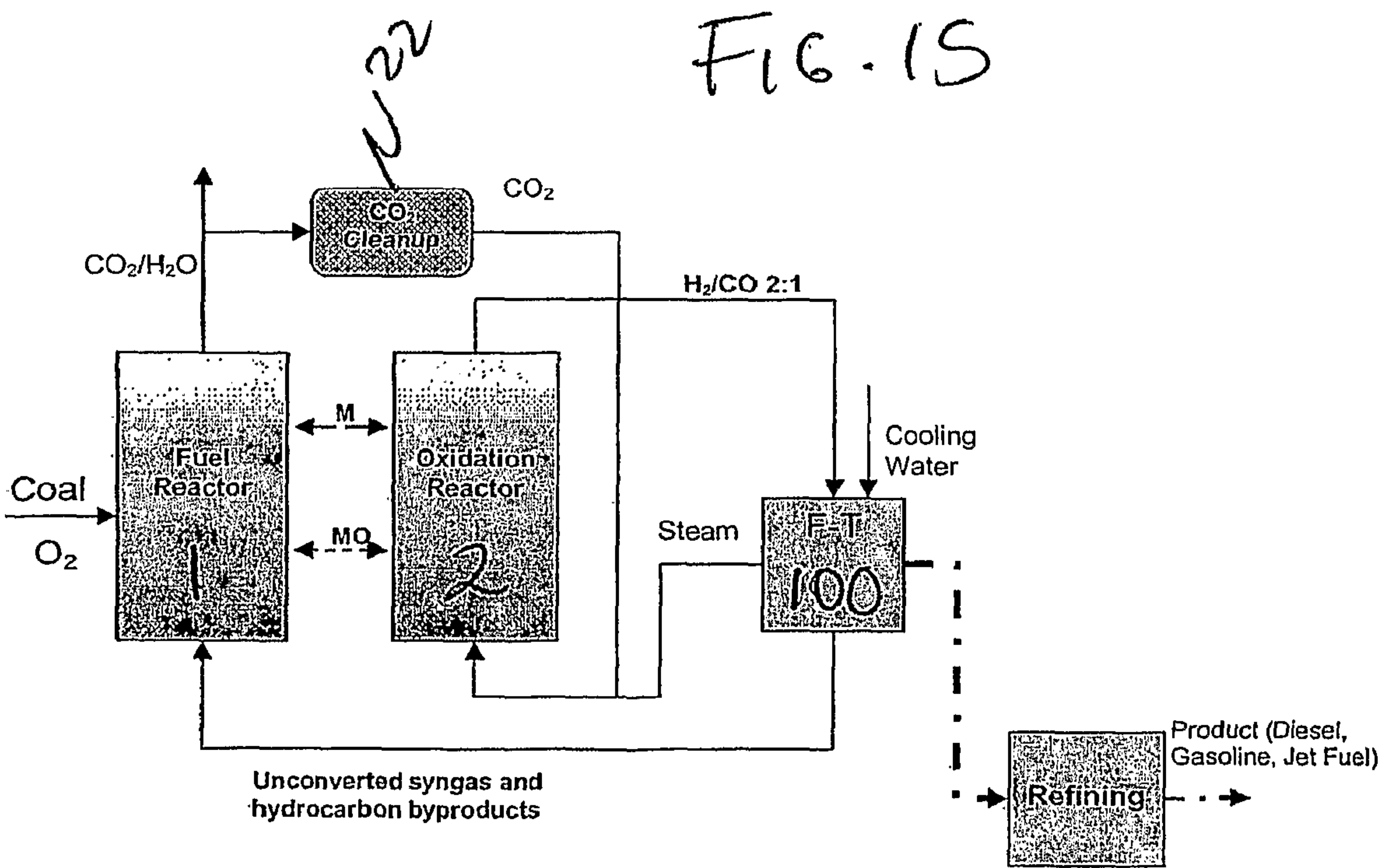


FIG. 16

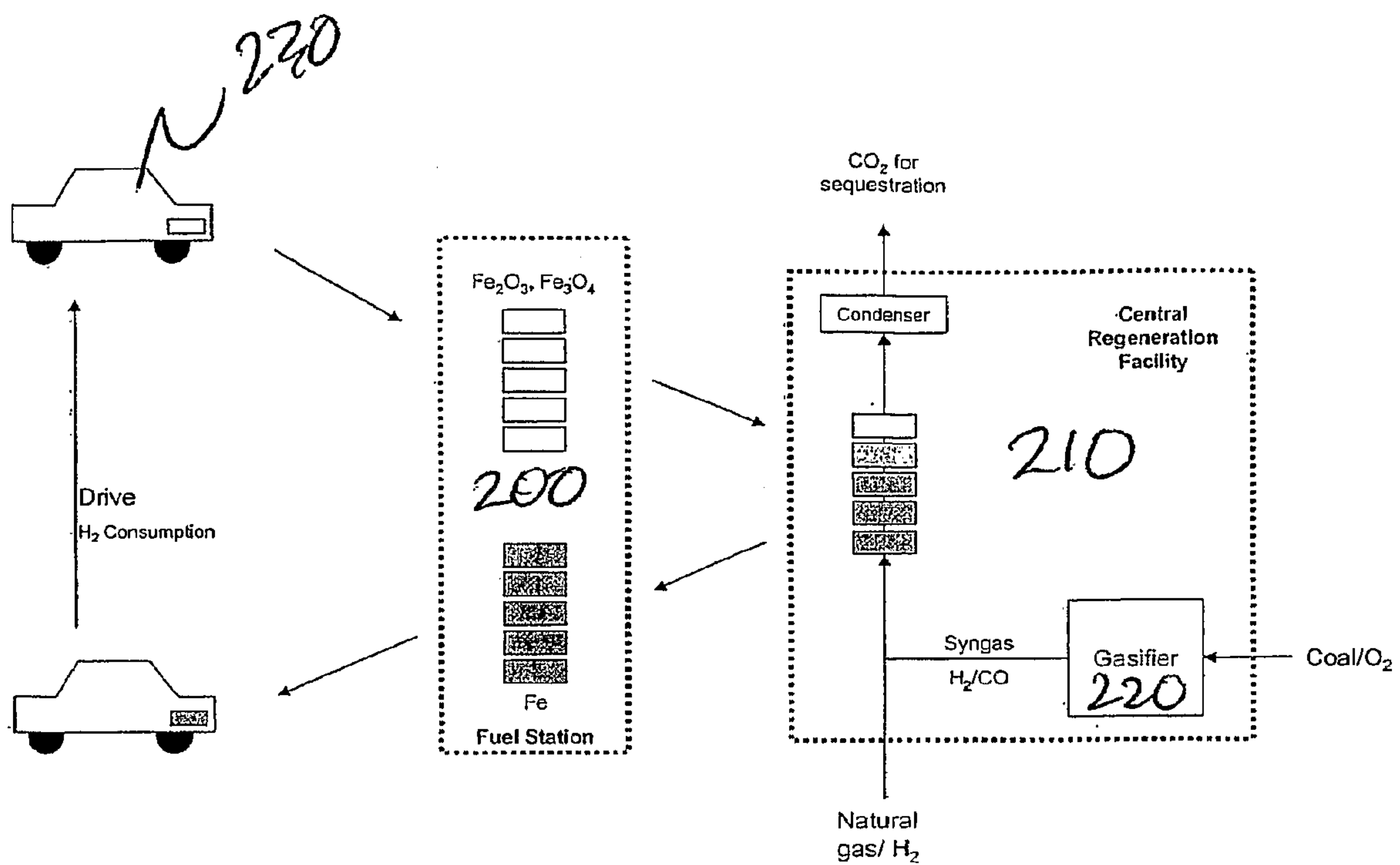


FIG. 17

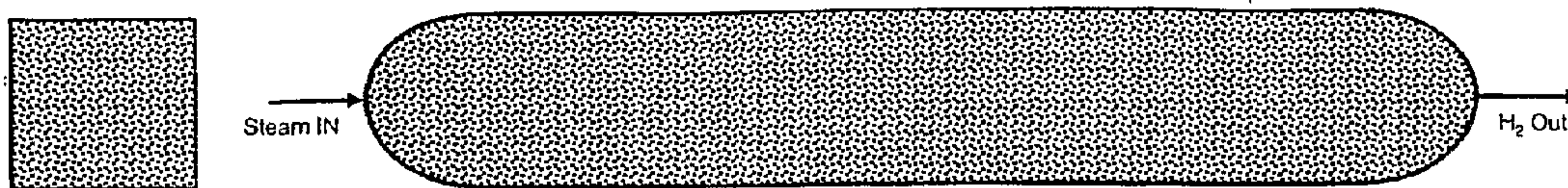


FIG. 18 (a)

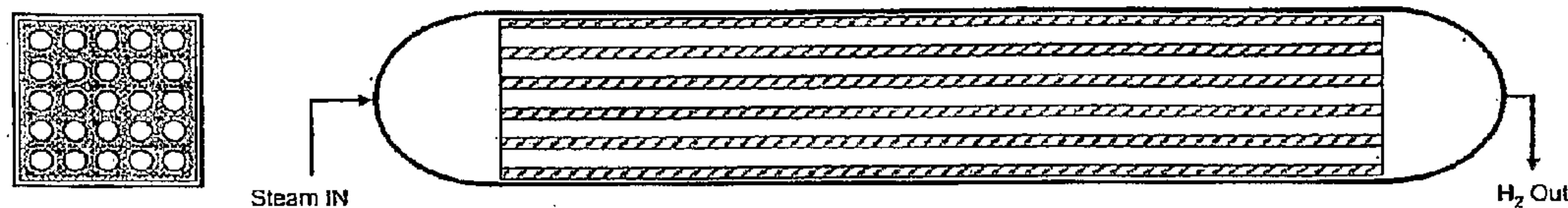


FIG. 18 (b)

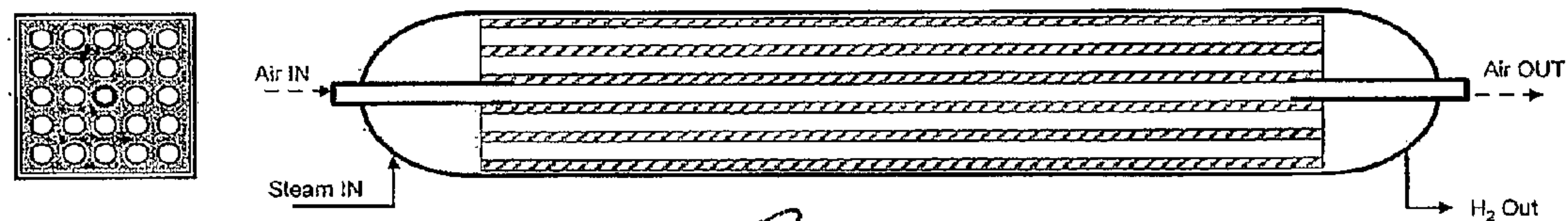


FIG. 18 (c)

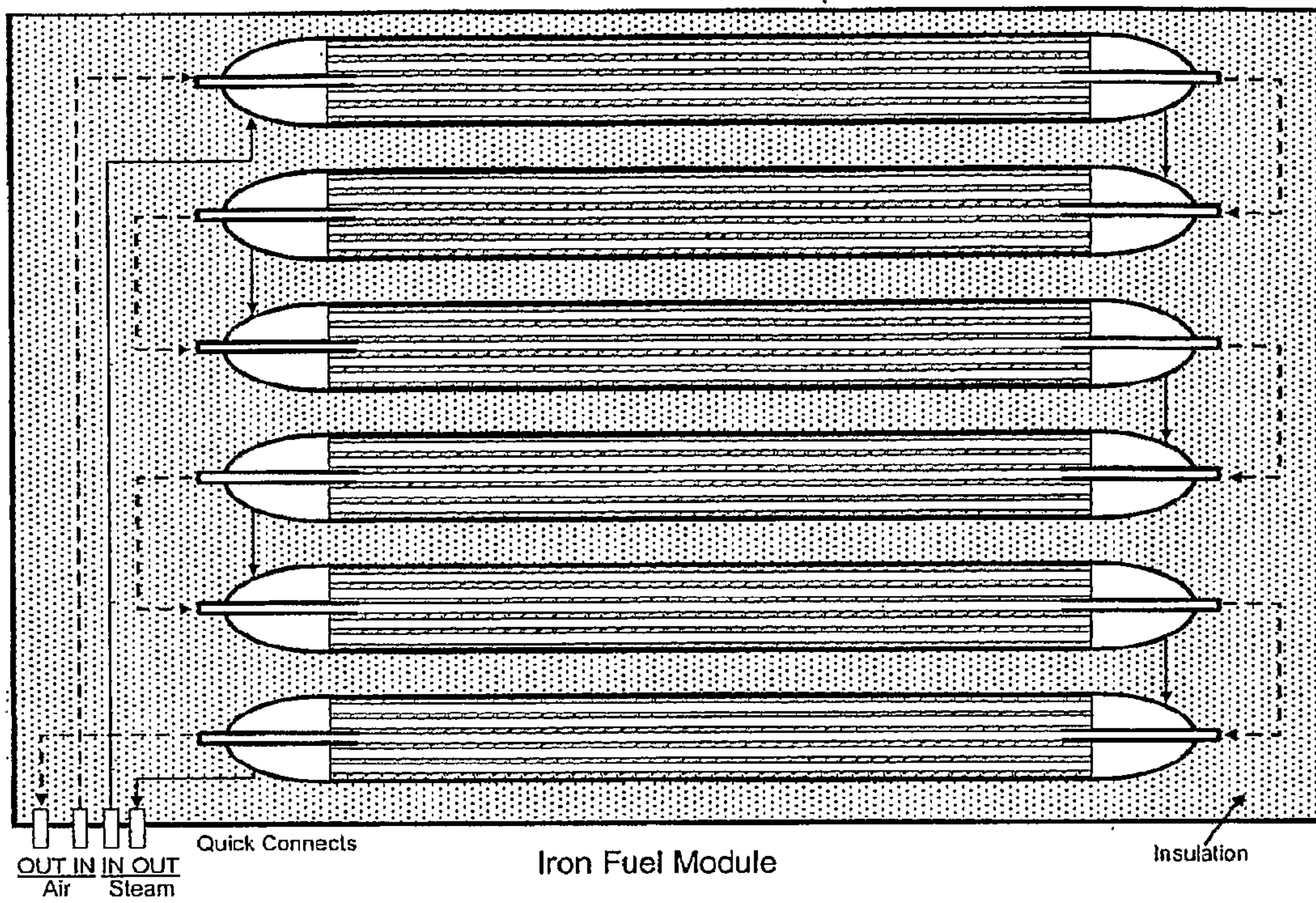


FIG. 19

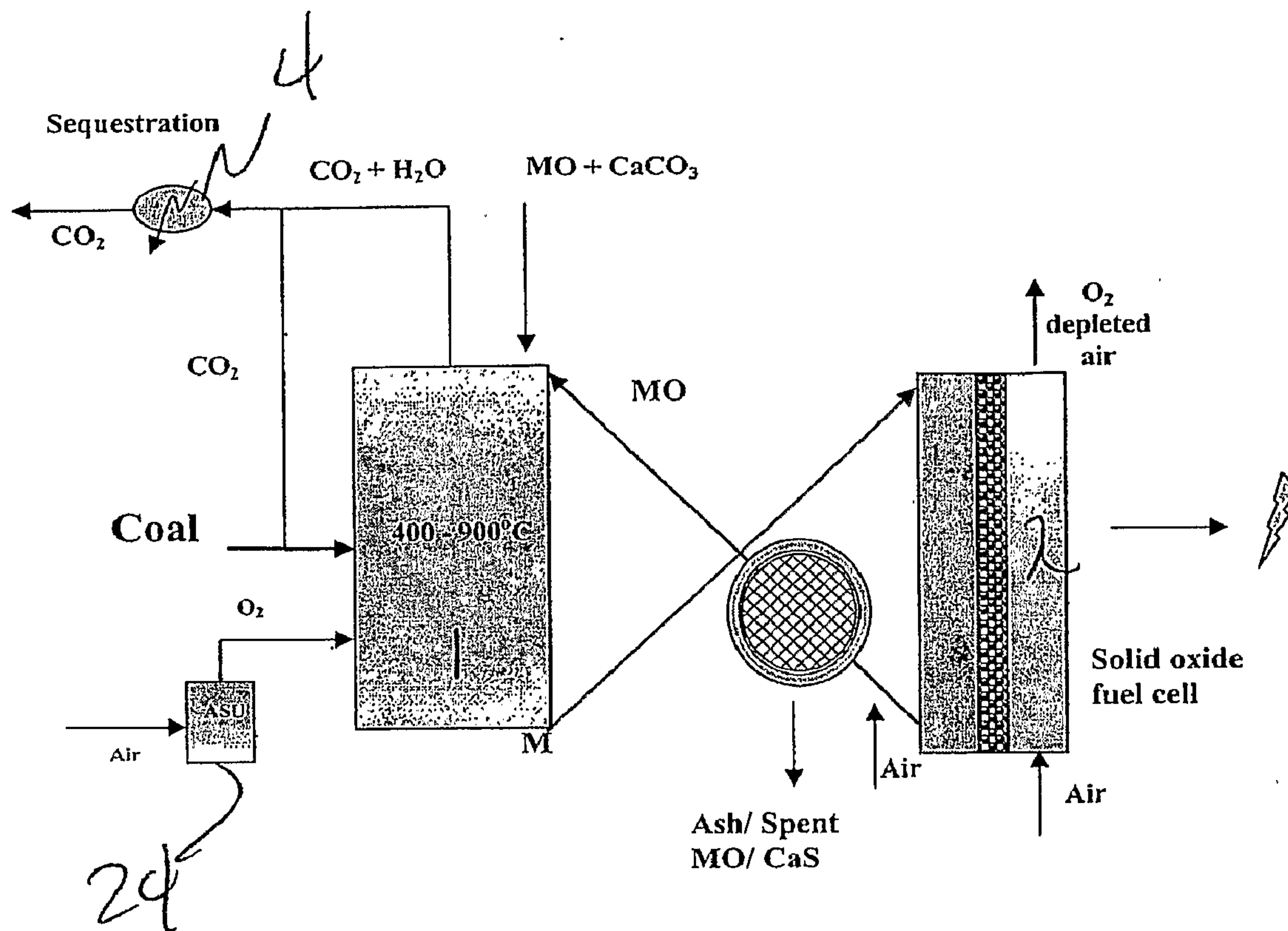


FIG. 20

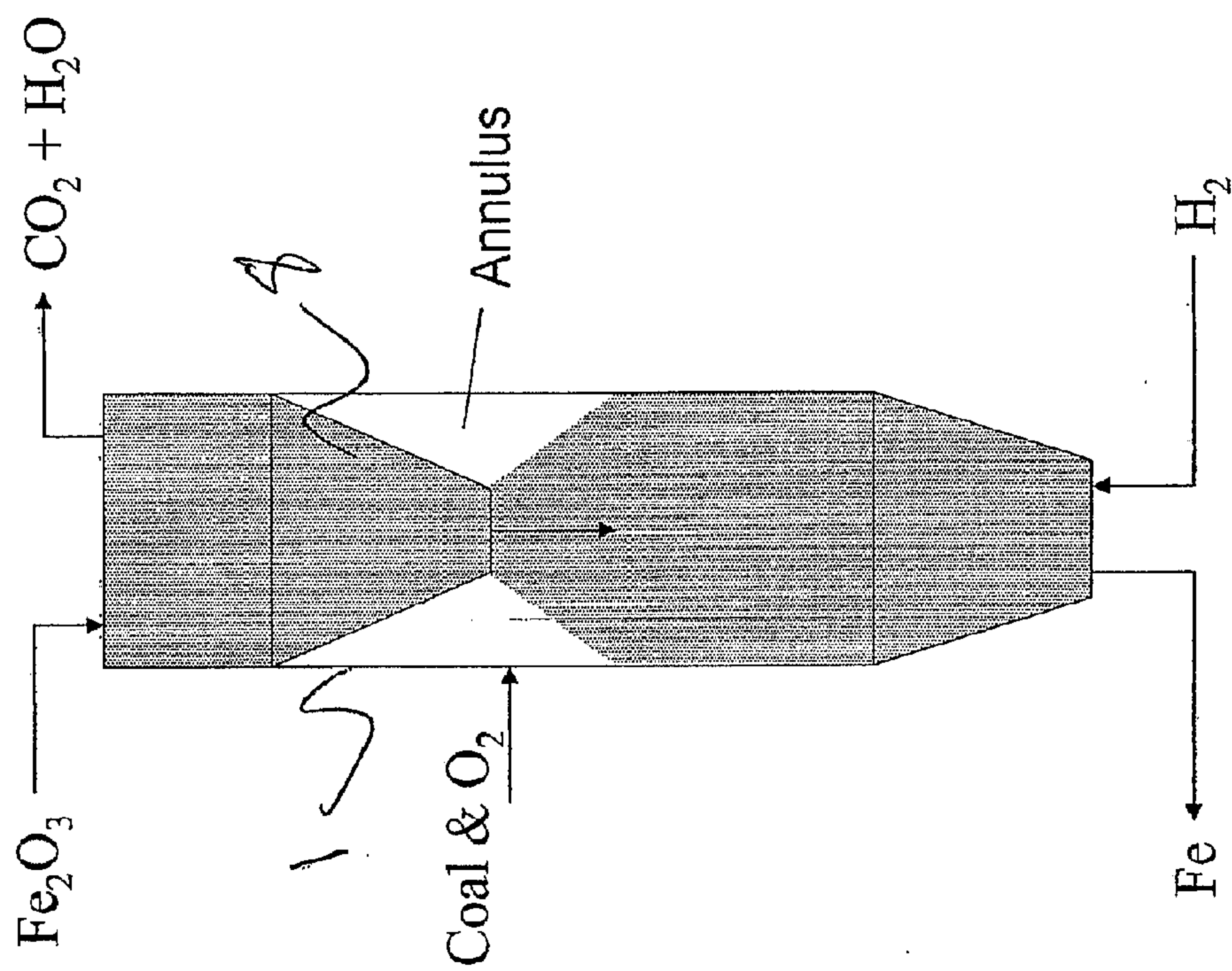


FIG. 21

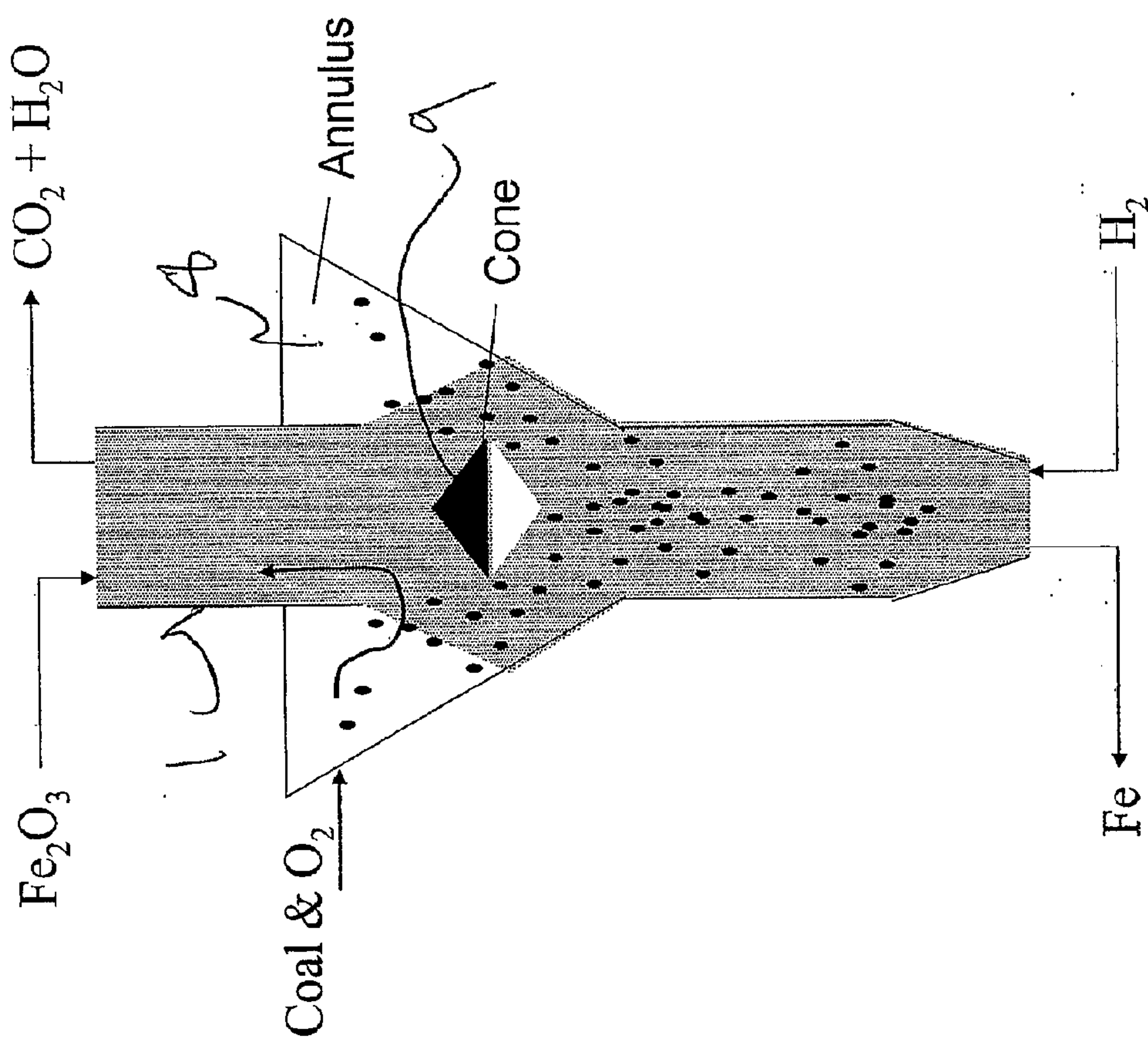


FIG. 22

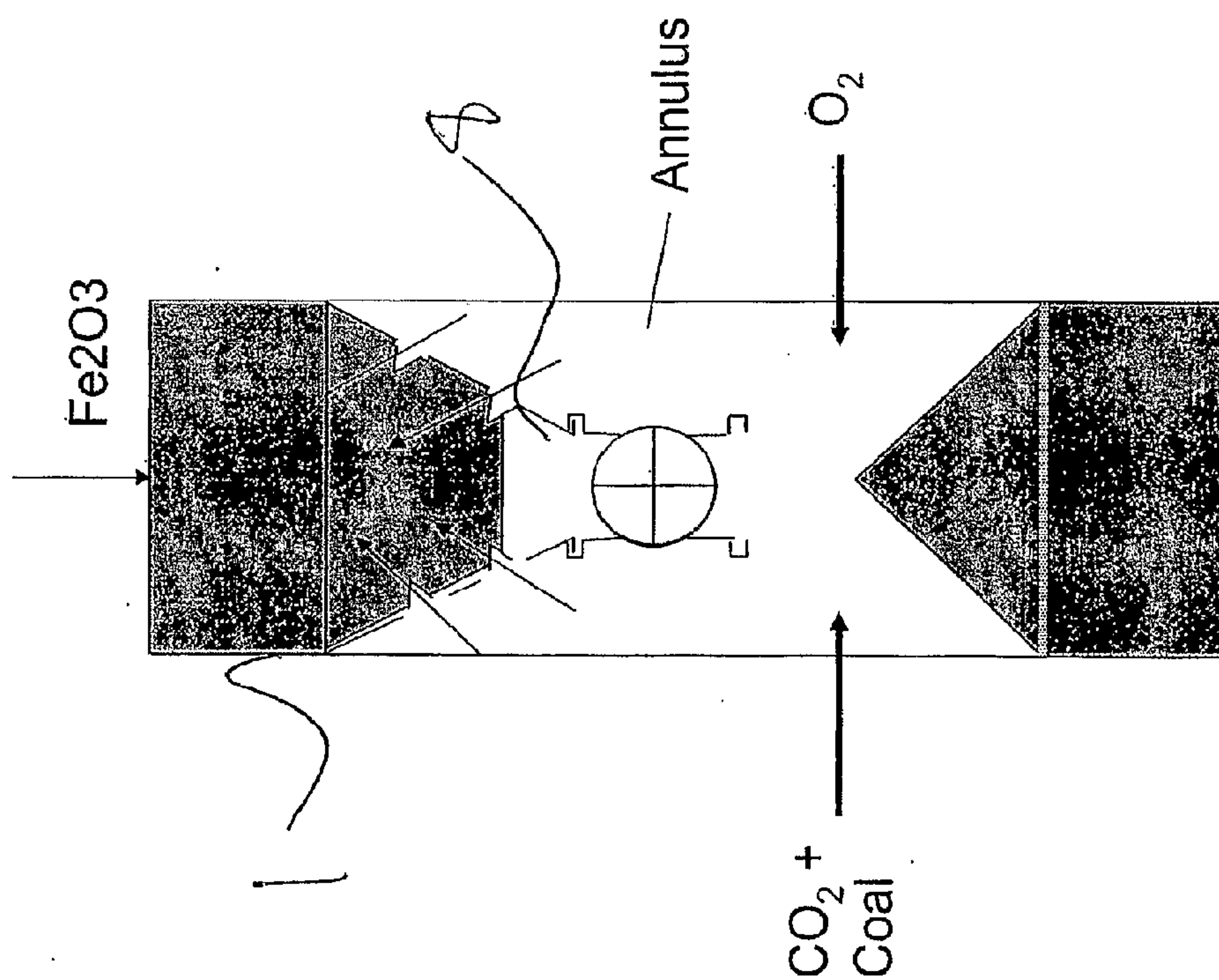


Fig. 18

SYSTEMS AND METHODS OF CONVERTING FUEL

[0001] The present invention is generally directed to systems and methods of converting fuel, and is generally directed to oxidation-reduction reactor systems used in fuel conversion.

[0002] 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. Furthermore, the dependence on fossil fuels is expected to continue in the foreseeable future due to the much lower costs compared to renewable sources. Currently, the conversion of carbonaceous fuels such as coal, natural gas, 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 dioxide to the environment. Sulfur and nitrogen compounds are also generated in this process due to the complex content in coal.

[0003] 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 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.

[0004] 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.

[0005] In one embodiment of the present invention, a system for converting fuel is provided. The system comprises a first reactor comprising a plurality of ceramic composite particles, wherein the ceramic composite particles comprise at least one metal oxide disposed on a support. The first reactor is configured to reduce at least one metal oxide with a fuel to produce a reduced metal or a reduced metal oxide. The system also comprises a second reactor configured to oxidize the reduced metal or reduced metal oxide to produce a metal oxide intermediate, and a third reactor configured to regenerate at least one metal oxide by oxidizing the metal oxide intermediate.

[0006] In another embodiment of the present invention, a method of converting fuel to hydrogen, CO, or syngas is provided. The method comprises the steps of: reducing a metal oxide in a reduction reaction between a fuel and a metal oxide to a reduced metal or a reduced metal oxide; oxidizing the reduced metal or reduced metal oxide with an oxidant to

a metal oxide intermediate, while also producing hydrogen, CO, or syngas; and regenerating the at least one metal oxide by oxidizing the metal oxide intermediate.

[0007] In yet another embodiment, a system comprising a Fischer-Tropsch reactor is provided. The Fischer-Tropsch reactor is configured to produce hydrocarbon fuel from a feed mixture comprising gaseous fuel. The system also comprises a first reactor comprising a plurality of ceramic composite particles, wherein the ceramic composite particles comprise at least one metal oxide disposed on a support. The first reactor is configured to reduce the metal oxides with a gaseous fuel to a reduced metal or a reduced metal oxide, wherein the gaseous fuel comprises at least partially the hydrocarbon fuel produced by the Fischer-Tropsch reactor. The system also comprises a second reactor configured to oxidize the reduced metal or reduced metal oxide with steam to produce metal oxide intermediates.

[0008] In another embodiment, a method of preparing ceramic composite particles is provided. The method comprises reacting a metal oxide with a support material; heat treating the mixture of metal oxide and support material at temperatures of between about 200 to about 1500° C. to produce ceramic composite powders; converting the ceramic composite powders into ceramic composite particles; and reducing and oxidizing the ceramic composite particles prior to use in a reactor.

[0009] Additional features and advantages provided by embodiments of the present invention will be more fully understood in view of the following detailed description.

[0010] The following detailed description of the illustrative embodiments of the present invention can be best understood when read in conjunction with the following drawings, where like structure is indicated with like reference numerals and in which:

[0011] FIG. 1 is a schematic illustration of a system for producing hydrogen from coal according to one or more embodiments of the present invention.

[0012] FIG. 2 is a schematic illustration of another system for producing hydrogen from coal according to one or more embodiments of the present invention;

[0013] FIG. 3 is a schematic illustration of another system for producing hydrogen from coal using direct chemical looping and sieves for ash separation according to one or more embodiments of the present invention;

[0014] FIG. 4 is a schematic illustration of another system for producing hydrogen from coal using direct chemical looping and cyclones for ash separation according to one or more embodiments of the present invention;

[0015] FIG. 5 is a schematic illustration of another system for producing hydrogen from coal, wherein the system utilizes a third reactor for heat recovery according to one or more embodiments of the present invention;

[0016] FIG. 6 is a schematic illustration of another system for producing hydrogen from coal, wherein the system utilizes a sorbent in the first reactor for sulfur removal according to one or more embodiments of the present invention;

[0017] FIG. 7 is a schematic illustration of system for producing hydrogen from syngas according to one or more embodiments of the present invention;

[0018] FIG. 8 is a schematic illustration of another system for producing hydrogen from coal, wherein carbon dioxide produced in the first reactor is recycled back to the second reactor according to one or more embodiments of the present invention;

[0019] FIG. 9 is a schematic illustration of another system for producing steam from coal according to one or more embodiments of the present invention;

[0020] FIG. 10 is a schematic illustration of yet another system for producing hydrogen from syngas according to one or more embodiments of the present invention;

[0021] Fig. 11 is a schematic illustration of another system for producing hydrogen from syngas, wherein the system comprises pollutant control components according to one or more embodiments of the present invention;

[0022] FIG. 12 is a schematic illustration of a system of chemical looping in conjunction with Fischer-Tropsch (F-T) synthesis according to one or more embodiments of the present invention;

[0023] FIG. 13 is a schematic illustration of another system of chemical looping in conjunction with Fischer-Tropsch synthesis according to one or more embodiments of the present invention;

[0024] FIG. 14 is a schematic illustration of another system of chemical looping in conjunction with Fischer-Tropsch synthesis according to one or more embodiments of the present invention;

[0025] FIG. 15 is a schematic illustration of yet another system of chemical looping in conjunction with Fischer-Tropsch synthesis, wherein the system comprises pollutant control components according to one or more embodiments of the present invention;

[0026] FIG. 16 is a schematic illustration of another system of chemical looping in conjunction with Fischer-Tropsch synthesis, wherein the system operates without the use of a gasifier according to one or more embodiments of the present invention;

[0027] FIG. 17 is a schematic illustration of a system of chemical looping for onboard H₂ storage on a vehicle according to one or more embodiments of the present invention;

[0028] FIG. 18(a) is a schematic illustration of a reactor cassette used in the onboard H₂ storage system of FIG. 17, wherein the reactor cassette comprises Fe containing media and a packed bed of small pellets according to one or more embodiments of the present invention;

[0029] FIG. 18(b) is a schematic illustration of another reactor cassette used in the onboard H₂ storage system of FIG. 17, wherein the reactor cassette comprises Fe containing media and a monolithic bed with straight channels for steam flow according to one or more embodiments of the present invention;

[0030] FIG. 18(c) is a schematic illustration of yet another reactor module used in the onboard H₂ storage system of FIG. 17, wherein the reactor cassette comprises Fe containing media and a monolithic bed with channels for steam and air flow according to one or more embodiments of the present invention;

[0031] FIG. 19 is a schematic illustration of a reactor cassette used in the onboard H₂ storage system of FIG. 17, wherein the reactor cassette utilizes a series of monolithic bed reactors with air injection to provide heat for steam formation according to one or more embodiments of the present invention;

[0032] FIG. 20 is a schematic illustration of a system of chemical looping in conjunction with a solid oxide fuel cell according to one or more embodiments of the present invention;

[0033] FIG. 21 is a schematic illustration of a reactor utilized in the system of the present invention, wherein the

reactor is a moving bed reactor comprising an annular region disposed near a fuel feed location according to one or more embodiments of the present invention;

[0034] FIG. 22 is a schematic illustration of a reactor utilized in the system of the present invention, wherein the reactor is a moving bed comprising an annular region as well as a cone inserted into the moving bed according to one or more embodiments of the present invention; and

[0035] FIG. 23 is a schematic illustration of another reactor utilized in the system of the present invention, wherein the reactor is a moving bed reactor comprising an annular region according to one or more embodiments of the present invention.

[0036] Referring generally to FIG. 1, the present invention is directed to systems and methods for converting fuel by redox reactions of ceramic composite particles. As shown in FIG. 1, the system comprises two primary reactors, as well as additional reactors and components, which will be described in detail below. The first reactor 1, which is configured to conduct a reduction reaction, comprises a plurality of ceramic composite particles having at least one metal oxide disposed on a support. As would be familiar to one of ordinary skill in the art, the ceramic composite particles may be fed to the reactor via any suitable solids delivery device/mechanism. These solids delivery devices may include, but are not limited to, pneumatic devices, conveyors, lock hoppers, or the like. Ceramic composite particles are described in Thomas et al. U.S. Published App. No. 2005/0175533 A1, which is incorporated herein in its entirety by reference. In addition to the particles and particle synthesis methods disclosed in Thomas, the Applicants, in a further embodiment, have developed alternative methods of making the ceramic composite, which may improve the efficacy and activity of the ceramic composite particles in the present system. Two of these alternative methods are co-precipitation and spray drying.

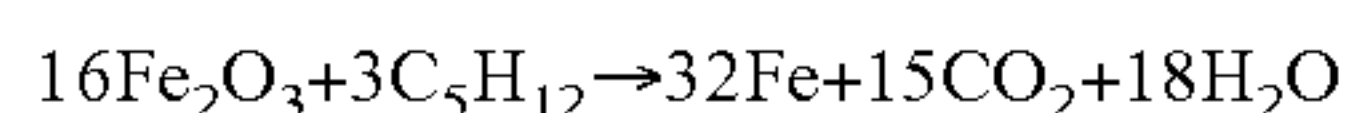
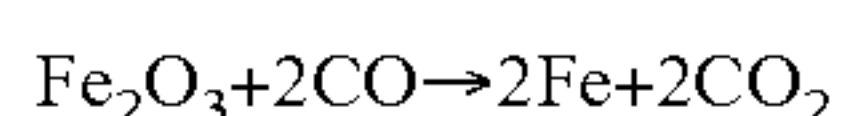
[0037] The third alternative method includes the step of physically mixing a metal oxide with a ceramic support material. Optionally, a promoter material may be added to the mixture of metal oxides and support material. After mixing, the mixture is heat treated at temperatures of between about 200 to about 1500° C. to produce ceramic composite powders. Heat treating may occur in the presence of inert gas, steam, oxygen, air, H₂, and combinations thereof at a pressure of between vacuum pressure and about 10 atm. The method may also include a chemical treatment step, wherein the mixture of metal oxides and support material are treated with an acid, base, or both to activate the ceramic composite powder. After powder production, the ceramic composite powders may be converted into ceramic composite particles by methods known to one of ordinary skill in the art. These methods may include, but are not limited to, extrusion, granulation, and, pressurization methods such as pelletization. The particle may comprise various shapes and forms, for example, pellets, monoliths, or blocks.

[0038] The method then includes the step of reducing and oxidizing the ceramic composite particles prior to use in a reactor. This cycle is important for the ceramic composite particles because this mixing process may produce a particle with increased activity, strength and stability. This cycle is important for the ceramic composite particles to increase their activity, strength and stability. This treatment also leads to a reduced porosity (0.1-50 m²/g) as well as crystal structure changes that make the particle readily reducible and oxidizable without losing its activity for multiple such reaction

cycles. The porosity in Thomas patent is not reported but it is stated that the particle was porous and had mesopores. Although the description of particle synthesis in this application is limited to spray dry, co-precipitation, and direct mixing approach, ceramic composite particles produced by other techniques such as sol-gel, wet impregnation, and other methods known to one of ordinary skill in the art are also operable in the reactors of the present system.

[0039] The metal oxide of the ceramic composite comprises a metal selected from the group consisting of Fe, Cu, Ni, Sn, Co, Mn, and combinations thereof. Although various compositions are contemplated herein, the ceramic composite typically comprises at least 40% by weight of the metal oxide. The support material comprises at least one component selected from the group consisting of SiC, oxides of Al, Zr, Ti, Y, Si, La, Sr, Ba, and combinations thereof. The ceramic composite comprises at least 5% by weight of the support material. In further embodiments, the particle comprises a promoter material. The promoter comprises a pure metal, a metal oxide, a metal sulfide, or combinations thereof. These metal based compounds comprise one or more elements from the group consisting of Fe, Ni, Sn, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, B, P, V, Cr, Mn, Co, Cu, Zn, Ga, Mo, Rh, Pt, Pd, Ag, and Ru. The ceramic composite comprises up to 40% by weight of the promoter material. In an exemplary embodiment of the ceramic composite, the metal oxide comprises Fe₂O₃ supported on a TiO₂ support, and specifically a support comprising a mixture of TiO₂ and Al₂O₃. In another exemplary embodiment, the ceramic composite may also comprise Fe₂O₃ supported on an YSZ (Yttria stabilized Zirconia) support.

[0040] Referring back to the reduction reaction of the first reactor **1**, the first reactor **1** receives a fuel, which is utilized to reduce the at least one metal oxide of the ceramic composite 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:



[0041] In this example, the metal oxide of the ceramic composite, Fe₂O₃, is reduced by a fuel, for example, CO, to produce a reduced metal oxide, Fe. Although Fe is the predominant reduced composition produced in the reduction reaction of the first reactor **1**, FeO or other reduced metal oxides with a higher oxidation state are also contemplated herein.

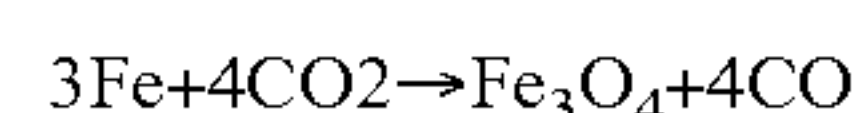
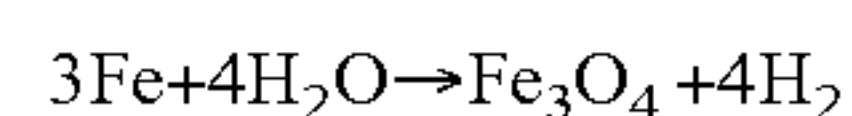
[0042] The first reactor **1** and second reactor **2** may include various suitable reactors to allow an overall countercurrent contacting between gas and solids. Such may be achieved using a moving bed reactor, a series of fluidized bed reactors, a rotatory kiln, a fixed bed reactor, combinations thereof, or others known to one of ordinary skill in the art.

[0043] As shown in FIGS. **21-23**, the first reactor **1** may comprise a moving bed reactor with an annular region **8** created around the moving bed. Although various orientations for the annulus **8** are possible, the annulus **8** is typically

located at a region where a reducing fuel is being introduced. As shown in FIG. **22**, the moving bed reactor may also include a mixing device, e.g. a cone **9**, inserted in the moving bed to radially distribute the ceramic composite particles and mix unconverted fuel with the ceramic composite particles. Although FIG. **22** illustrates the cone **9** in conjunction with the annulus **8**, it is contemplated that the moving bed reactor may incorporate a cone **8**, but not an annulus in some embodiments. The annular region **8** allows the first reactor **1** to introduce solid and liquid fuels into the middle of a moving bed of solids ceramic composites. In one embodiment, the fuel may be introduced pneumatically and then partially combusted in the annulus **8**. The unburnt fuel drops down onto the heap of ceramic composites in the annulus **8** and is mixed with them for further reactions. FIGS. **21**, **22** and **23** show some of the different methods to form the annular region **8**. FIG. **21** uses an internal hopper to create the annular region. FIG. **23** uses an internal hopper along with a rotary valve to create an even larger annular region with better control over the flow of ceramic composite particles. FIG. **22** creates an external annular region for the flow of the moving bed and uses a mixing device, e.g. a cone **9** to disperse the solids axially so that unconverted fuel may be distributed uniformly over the entire cross section of the moving bed.

[0044] The first reactor **1** may be constructed with various durable materials suitable to withstand temperatures of up at least 1200° C. The reactor 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. Other interconnects as can be determined easily by a person skilled in the art may also be used.

[0045] After reduction in the first reactor **1**, the reduced metal or reduced metal oxide particles are then delivered to the second reactor **2** to undergo an oxidation reaction. The second reactor **2**, which may comprise the same reactor type or a different reactor type than the first reactor **1**, is 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 ceramic composite. For example, and not by way of limitation, the following equation illustrates possible oxidation reactions:



[0046] In this example which centers on ceramic composites that utilize Fe₂O₃ as the metal oxide, oxidation in the second reactor using steam will produce a resultant mixture that includes metal oxide intermediates comprising predominantly Fe₃O₄. Fe₂O₃ and FeO may also present. Furthermore, although H₂O, specifically steam, is the oxidant in this example, numerous other oxidants are contemplated, for example, CO, O₂, air, and other compositions familiar to one of ordinary skill in the art.

[0047] Referring to the solid fuel conversion embodiment of FIG. **1**, the system comprises two moving bed reactors **1**

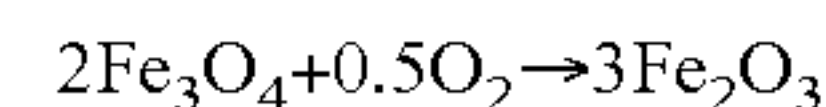
and 2. The first reactor 1, which defines a moving bed, operates by having the solids (Fe_2O_3 and coal) moving downwards in a densely packed mode, while the gases, for example, H_2 , steam, CO , CO_2 , or combinations thereof move upwards. This movement of solids and gases is defined as a countercurrent contacting pattern. The Fe_2O_3 containing ceramic composite particles are introduced from the top via a gravitational feeder while solid fuel, e.g. coal is introduced at a region of the first reactor 1 lower than the feed location of the ceramic composite particles. Typically, the reactors operate at a temperature in the range of about 400 to about 1200° C. and a pressure in the range of about 1 to about 150 atm; however, one of ordinary skill in the art would realize that temperatures and pressures outside these ranges may be desirable depending on the reaction mechanism and the components of the reaction mechanism. In the embodiment of FIG. 1, coal is introduced in pulverized form by pneumatically conveying with oxygen or carbon dioxide or steam. After the coal is delivered to the first reactor 1, coal will devolatilize and form char. The volatiles may also react with Fe_2O_3 to form CO_2 and water. The outlet gas composition of the first reactor 1 may contain predominantly CO_2 and steam. Subsequently, the CO_2 and steam may be fed to a condenser 4 to separate the steam and the CO_2 . The CO_2 obtained after condensation of water will be relatively pure and may be sequestered under the ocean or in geological formations or enhanced oil recovery without emitting to the atmosphere and contributing to green house warming of the earth.

[0048] The char formed on devolatilization of coal will then react with partially reduced iron oxide as it flows downwardly in the first reactor 1. To enhance the char reaction with iron oxide, a small amount of hydrogen is introduced at the bottom of the moving bed to result in the formation of H_2O on its reaction with partially reduced iron oxide. The H_2O produced will react with downwardly flowing char leading to its gasification into H_2 and CO . The hydrogen formed will then react with the partially reduced iron oxide in order to further reduce the reduced iron oxide, thereby enhancing the char-iron oxide reaction rates. The hydrogen introduced at the bottom of the reactor will also ensure that the iron oxide particles are greatly reduced to Fe as they exit the first reactor 1. In some cases, some carbon is intentionally left unconverted in the particle to generate CO using steam in the second reactor. In yet some other cases, an excess of ceramic composite particles comprising Fe_2O_3 may be inserted into the first reactor 1 in order to enhance reaction rates.

[0049] The exiting reduced Fe containing particles may then be introduced into the second reactor 1. Like in the first reactor 1, the second reactor 2 may also comprise a moving bed with a countercurrent contacting pattern of gas and solids. Steam is introduced at the bottom of the reactor and it oxidizes the reduced Fe containing particles as the particles move downwardly inside the second reactor 2. In this embodiment, the product formed is hydrogen, which is subsequently discharged from the top of the second reactor 2. 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 second reactor 2, the solid product from this reactor is expected to be mainly metal oxide intermediate, Fe_3O_4 . The amount of Fe_2O_3 produced in the second reactor 2 depends on the oxidant used, as well as the amount of oxidant fed to the second reactor 2. The steam present in the hydrogen product of reactor 2 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 first reactor 1 as described above. In addition to utilizing the same reactor type as the first reactor 1, the second reactor 2 may similarly operate at a temperature between about 400 to about 1200° C. and pressure of about 1 to about 150 atm.

[0050] To regenerate the metal oxide of the ceramic composite, the system utilizes a third reactor 3, which is configured to oxidize the metal oxide intermediate to the metal oxide of the composite. Referring to the embodiment FIG. 1, the third reactor 3 may comprise an air filled line or tube used to oxidize the metal oxide intermediate. Referring to the FIG. 5 embodiment, the oxidation of the metal oxide intermediate may be conducted a heat recovery unit 3. The following equation lists one possible mechanism for the oxidation in the third reactor 3:



[0051] Referring to the embodiment of FIG. 1, the Fe_3O_4 product may be oxidized to Fe_2O_3 in solid conveying system 6. Different mechanisms can be used for solid transportation. FIG. 1 shows it as a transport system using pneumatic conveyor driven by air. Belt conveyors, bucket elevators, screw conveyors, moving beds and fluidized bed reactors may also be used to transport the solids. The resultant depleted air stream is separated from the particles and its high-grade-heat content recovered for steam production. After regeneration, the ceramic composite particle is not degraded and maintains full particle functionality and activity. In further embodiment, the particle may undergo numerous regeneration cycles, for example, 10 or more regeneration cycles, and even greater than 100 regeneration cycles, without losing its functionality. This system can be used with existing systems involving minimal design change, thus making it economical.

[0052] The iron particles exiting the first reactor 1 may also contain ash and other unwanted byproducts. If the ash is not removed after the first 1 or second reactor 2 stages, the ash may keep building up in the system. Numerous devices and mechanisms for ash removal would be familiar to one of ordinary skill in the art. For example, ash may be removed based on the size of ash with respect to the iron oxide particles from any of the solid streams in the system. If pulverized coal is used as the fuel source, it will yield fine ash particles, typically lower than 100 μm in size. The size of the ceramic composite particles may vary based on the metal components used and the oxidation-reduction reaction in which the ceramic composite is utilized. In one embodiment, the particle comprises a size between about 0.5 to about 50 mm. As a result, simple sieving, for example, simple sieving at high temperatures, may result in removal of ash. Simple sieving uses the size and density differences between the wanted and unwanted solid particles in the separation process. Other methods, for example, mechanical methods, and methods based on weight, or magnetic properties, may be used to separate ash and unwanted materials. Separation devices, such as cyclones, will be further discussed in later embodiments.

[0053] Heat integration and heat recovery within the system and all system components is highly desirable. Heat integration in the system is specifically focused on generating the steam for the steam requirements of the second reactor 2. This steam can easily be generated using the high grade heat available in the hydrogen, CO_2 and depleted air streams exiting reactors 1, 2, 3, respectively. In the process described

above, there is also a desire to generate pure oxygen. To generate this pure oxygen, at least part of the hydrogen may be utilized.

[0054] The residence time in each reactor is dependent upon the size and composition of individual ceramic composite particles, as would be familiar to one of ordinary skill in the art. For example, the residence time for a reactor comprising Fe based metal oxides may range from about 0.1 to about 20 hours.

[0055] As stated above, additional unwanted elements may be present in addition to ash. Trace elements like Hg, As, Se are not expected to react with Fe_2O_3 at the high temperatures of the process. As a result they are expected to be present in the CO_2 stream produced. If CO_2 is to be used as a marketable product, these trace elements must 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 CO_2 stream is let out into the atmosphere, depending upon the rules and regulations existing at that time. If it is decided to sequester the CO_2 for long term benign storage, e.g. in a deep geological formation, there may not be a need to remove these unwanted elements. Moreover, CO_2 may be sequestered via mineral sequestration, which may be more desirable than geological storage, because it is safer and more manageable. Additionally sequestering CO_2 has an economic advantage for global CO_2 credit trading, which may be highly lucrative.

[0056] Furthermore, sulfur may constitute another 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. This will be liberated on reaction with steam in reactor 2 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 would include the introduction of sorbents, for example, CaO, MgO, etc. Additionally, as shown in the embodiment of FIG. 6, sorbents may be introduced into the first reactor 1 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.

[0057] Although the 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 reactor 1 to 2 and contaminate the hydrogen stream. Depending upon the purity of the hydrogen required, it may be necessary 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 first reactor 1 along with coal, in solid fuel conversion embodiments, in order to improve the efficiency of hydrogen production in the system.

[0058] Referring to FIG. 2, the hydrogen produced in the second reactor 2 may provide additional benefits to the system. For instance, the hydrogen may be fed a power generation section 10 configured to produce electricity from a hydrogen product of the second reactor 2. As would be familiar to one of ordinary skill in the art, the power generation section 10 may comprise air compressors 12, gas turbines 14, steam turbines, electric generators 16, fuel cells, etc. In

another embodiment, unconverted H_2 from fuel cell can be recycled to the middle region of reactor 2, this helps to increase fuel cell efficiencies while reducing the fuel cell size. Thus improve the overall system efficiency.

[0059] Referring to FIG. 3, another coal conversion system similar to FIG. 1 is provided. Part of the CO_2 is recycled back as carrier gas for the injection of coal. Both of the reactors operate under 400-1200° C. and the reduced metal particles would be transported to the second reactor 2 by an inert gas such as N_2 from the air separation unit. The hydrogen produced in second reactor 2 may also be used for transportation of reduced metal oxide particles. The reduced metal will be separated out from the nitrogen gas and fed into the second reactor 2 to react with steam to generate H_2 . The H_2 generated would contain H_2S due to the sulfur inside the coal, and would attach to the particle to form MeS. As shown, a traditional sulfur scrubbing unit 22 may be used to remove H_2S and generate pure H_2 . The oxidized particles from the outlet of the second reactor 2 would go through an ash separation system using a sieve. In this embodiment, most of the ash and metal oxide particles, as a result of attrition, would be separated out for regeneration, while the rest of the metal oxide particles would be introduced back into the inlet of the first reactor 1 using a feed device, for example, a pneumatic conveyor by air, where the makeup ceramic composite would also be fed. As used herein, makeup ceramic composite particles refer to fresh particle used to replace the fines or ceramic composite particles rendered too small or ineffective due to attrition and deactivation. The typical makeup ceramic composite rate would be less than 2% of the particle flow rate in the system.

[0060] Referring to FIG. 4, a different solid conveying system, as well as a different ash separation unit, may be used for coal direct reactor system. Here, the reduced metal particles are transferred to the second reactor 2 using a bucket elevator in an N_2 environment. After being oxidized in the second reactor 2 to metal oxide intermediates, the metal oxide intermediates are sent to a cyclone 3 using a pneumatic conveyor with air so that the particle is already oxidized by the time it reaches the cyclone. The fines due to attrition and the coal ash may be removed along with air while the particles will be separated out with the cyclone and fed into the first reactor along with the makeup metal oxide particles. The makeup rate is again less than 2% of the particle flow rate in the system. Other devices like a particle classifier or other devices commonly known to one of ordinary skill in the art may also be used for ash separation.

[0061] Referring to the FIG. 5 embodiment, a third reactor 3 in form of a fluidized bed is utilized to recover the heat for further oxidation of the particles exiting the second reactor i.e. the metal oxide intermediates, such as Fe_3O_4 . In other embodiments and figures this reactor was shown as the transport line from the second reactor 2 to first reactor 1 where air or oxygen is introduced. It will be a transport reactor, a fast fluidized bed, a fluidized bed, a riser or pneumatic conveying system. Here, the metal oxide intermediates, e.g. Fe_3O_4 , from the outlet of the second reactor 2 are injected into a heat recovery unit 3 where oxygen or air is introduced to oxidize the particles back into their highest oxidation state i.e. the metal oxide of the ceramic composite, e.g. Fe_2O_3 . In addition to the oxidation conversion, heat is generated in this process, and the particles' temperature may also increase drastically. The particles with significantly higher temperature may be introduced back into the first reactor 2 and the heat stored in the particle would provide, at least in part, the heat required

for reduction reactions. For particles with high heat capacity, it may be desirable, in one exemplary embodiment, to utilize a support such as SiC, which has high thermal conductivity.

[0062] As shown in the embodiment of FIG. 6, sorbent materials, such as modified calcium carbonate or calcium oxide or calcium hydroxide, may be injected into the first reactor 1 to remove the sulfur from the coal. The CaCO_3 injection rate will range from about 1% to about 15% of the metal oxide flow rate in the system; however, the injection rate varies depending on the composition of the coal used. Magnesium oxide may also be used as a sorbent. Generally, the size of the sorbent particle is smaller than the ceramic composite particles, and may in some exemplary embodiment, comprise a particle size ranging from about 100 μm to about 1 mm depending on the size of the ceramic composite particle in the system. The spent sorbent, after sulfur capture, would be separated out with ash and regenerated afterwards for further use in the first reactor 1. In this embodiment, pure H_2 may be produced without the need of a scrubber.

[0063] Referring generally to FIGS. 7-9, system embodiments for converting gaseous fuels are provided. As shown in FIG. 9, part of the CO_2 produced in the first reactor 1 may be split and introduced into second reactor 2 along with steam. By controlling the feed rates of steam and CO_2 , syngas having a different H_2 and CO ratio can be obtained. The syngas can be introduced to a gas turbine to generate electricity or it can be used for chemical/liquid fuel synthesis. In order to generate syngas with an H_2/CO ratio of about 2:1 for Fischer-Tropsch synthesis to produce liquid fuel, a typical steam and CO_2 feed rate ratio should be around 2:1. The present system in conjunction with Fischer-Tropsch synthesis will be discussed in greater detail below. The output ratio of H_2/CO may also be varied by recycling part of the output after condensation of water to a middle section of the second reactor 2. This will allow more water gas shift reaction to convert unconverted CO_2 into CO.

[0064] As shown in the FIG. 9 embodiment of syngas conversion, reduced metal particles are burnt with air in the second reactor 2. The heat generated may be extracted using water to generate high temperature steam. The steam can then be either used for electricity generation or it can be used to extract heavy oil from oil shale. In the embodiment of FIG. 10, the system must account for the fact that H_2S in raw syngas would react with metal to form metal sulfide. Reduced metal and metal sulfide would be introduced to the second reactor 2 to react with steam. The product stream in this system would contain H_2 and H_2S . H_2S may be taken out using traditional scrubber technology and a H_2 rich stream would be achieved. By using gaseous fuel, e.g. syngas, instead of solid fuel, the ash separation process may be avoided.

[0065] Referring to the FIG. 11 embodiment, a hot gas sulfur removal unit using sorbents such as CaO is utilized to remove bulk quantities of H_2S in raw syngas to below 100 ppm. The pretreated syngas is then mixed with steam and CO_2 of appropriate quantity, typically <15% and introduced to the bottom of the first reactor 1. Due to the equilibrium between H_2S and steam/ CO_2 , H_2S as well as Hg will not react with the particles inside the first reactor 1. As a result, the pollutant will come out of the first reactor 1 along with CO_2 and can be sequestered together. Only pure metal particles will enter the second reactor 2 and therefore, H_2 rich streams may be generated without using low temperature sulfur and mercury removal units. Additionally, ceramic composite particles with

degraded activity or size, which are no longer effective in the processes of the first and second reactor, may be used instead of CaO to remove the H_2S , for example, to a level below 30 ppm.

[0066] Referring generally to FIG. 13, the chemical looping system, as a hydrogen generator, may be coupled with Fischer-Tropsch (F-T) synthesis system, directed to producing chemicals or liquid fuels. Syngas from modern gasifiers usually fail to provide enough H_2 concentration to meet the requirements of F-T synthesis ($\text{H}_2/\text{CO}=2:1$). The feedstock for the first reactor 1 is part of the byproduct from the F-T reactor 100 and unconverted syngas. In a further embodiment, the feedstock may include part of the product from the refining system. The rest of the byproduct and unconverted syngas is recycled to the F-T reactor 100 to enhance the conversion, or, it can also be recycled to the gasifier to make more syngas. Moreover, steam for the second reactor can be obtained from both the gasifier and the F-T reactor 100, as F-T reactions are usually highly exothermic. The H_2 product of the second reactor 1, which may contain some CO and which is generated from chemical looping reactors is recycled back to adjust the H_2/CO ratio of the F-T feed to about 2:1. This adjustment may occur, in some embodiments, after the clean syngas exits the gasifier 30 and is delivered to gas cleanup units 22. In this case, a stoichiometric amount of byproducts and unconverted syngas are used to generate H_2 for gas tune up i.e., adjustment of the ratio to about 2:1, while the rest of the gas stream is recycled back into the F-T reactor 100. By converting the C1-C4 byproducts and unconverted syngas into H_2 , which is the feedstock of F-T reactor 100, system efficiency and product selectivity can be greatly improved. The operating pressure for the chemical looping system would be similar to the F-T process, for example, around 20 atm for medium pressure synthesis.

[0067] The embodiments of FIG. 12 and 14 are similar to the one described in FIG. 13; with one major difference being that all the byproducts are used to generate H_2 . The excessive amount of H_2 can be used for hydrocracking of the wax product from the F-T reactor 100. If an excessive amount of H_2 remains after hydrocracking, a combustion turbine or a fuel cell can be utilized to generate electricity for plant use or for the energy market in general.

[0068] In the F-T embodiment of FIG. 15, hot gas cleanup is used before the first reactor 1 and the rest of the pollutants would come out from the first reactor 1 without attachment to the particles. Here, part of the CO_2 generated from the first reactor 1 is introduced to a product cleanup unit or a CO_2 separation unit to extract substantially pure CO_2 from the exhaust gas stream of the first reactor 1. The substantially pure CO_2 is then introduced into second reactor 2 along with steam to form clean syngas with a H_2/CO ratio of about 2:1. The syngas is then used in F-T reactor 100 to produce liquid fuels or chemicals. The byproduct stream from the F-T reactor 100 would also be recycled back to first reactor to further increase the syngas production rate of the chemical looping system. Referring to FIG. 16, the F-T system may be combined with a coal converting system instead of syngas. In this embodiment, sorbents may be fed into the system to take out sulfur. Byproducts of F-T synthesis may also be fed into the first reactor 1 to make more syngas. In this solid fuel conversion embodiment, a gasifier is not needed; consequently, the system may comprise less equipment, thereby lowering costs and capital investment while improving system efficiency.

[0069] In all the F-T embodiments, part of the steam generated in the F-T reactor may be superheated by high temperature streams from the chemical looping system of the present invention or gasifiers. The superheated steam may comprise various uses, for example, driving a steam turbine for parasitic energy or as a feed stock in reactor 2.

[0070] In the embodiment of FIG. 17, an additional use for the present system is provided. In this example, metal oxide particles such as Fe_2O_3 are processed into a packed bed or monolith in a module or cartridge for onboard H_2 storage in a vehicle 230. Here, the modules are processed in a central facility 210 to get reduced to its metal form using carbonaceous fuel such as syngas. The reduced modules are then distributed to fuel stations 200 and installed into a car 230 to replace the spent modules. Steam would be obtained from the PEM fuel cell or Hydrogen Internal Combustion Engine and would be introduced into the model to react with the reduced particles to generate H_2 to drive the car. The typical temperature for the reaction would be around 250-700° C., as the reaction is exothermic. The temperature in the module can either be maintained by well designed insulations or the heat recovery in other areas of the system. The modules would consist of different individual enclosures and each enclosure can either be a packed bed of pellets or it can be monolith. In one exemplary embodiment, the monolith may comprises small channels with diameter of 0.5-10 mm while the thickness of the wall that is made of particles are kept below 10 mm. FIGS. 18(a)-(c), and FIGS. 18 illustrates some examples of the modules, i.e. reactors with Fe containing media having: (a) a packed bed of small pellets; (b) a monolithic bed with straight channels for steam; and (c) a monolithic bed with channels for steam and air.

[0071] FIGS. 18c and FIG. 18b show that air will flow through some of the channels while steam flows through the rest of the channels. By this kind of flow arrangement, the channels with air going through would generate heat for the adjacent channels keeping them at desirable temperature (250-700° C.) for hydrogen production. FIG. 19 shows one possible arrangement using the enclosure design shown in FIG. 18(c). Here, different enclosures are packed into a module and connected with one another to consistently generate H_2 for a fuel cell or an internal combustion engine in the car 230. The air and steam channels may be strictly separated from one another using the special monolith design and connection scheme.

[0072] Referring to FIG. 20, the present system may also be utilized in fuel cell technologies. In this exemplary embodiment of FIG. 20, reduced metal particles are directly fed into a solid oxide fuel cell that can process solid fuels directly. In effect, the solid oxide fuel cell acts the second reactor 2 in the oxidation reduction system. Particles are reduced in the fuel reactor and then introduced to the fuel cell to react with oxygen or air under 500-1000° C. to produce electricity. The oxidized particle is recycled back to the fuel reactor to be reduced again. Because of the applicability of the present system, it is contemplated that the present invention may be incorporated in numerous other industrial processes.

[0073] It is noted that terms like “preferably,” “generally,” “commonly,” and “typically” are not utilized herein to limit the scope of the claimed invention or to imply that certain features are critical, essential, or even important to the structure or function of the claimed invention. Rather, these terms

are merely intended to highlight alternative or additional features that may or may not be utilized in a particular embodiment of the present invention.

[0074] 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, 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.

[0075] Having described the invention in detail and by reference to specific embodiments thereof, it will be apparent that modifications and variations are possible without departing from the scope of the invention defined in the appended claims. More specifically, although some aspects of the present invention are identified herein as preferred or particularly advantageous, it is contemplated that the present invention is not necessarily limited to these preferred aspects of the invention.

1. A system for converting fuel comprising:
 - a first reactor comprising a plurality of ceramic composite particles, the ceramic composite particles comprising at least one metal oxide dispersed on a support, wherein the first reactor is configured to reduce the at least one metal oxide with a fuel to produce a reduced metal or a reduced metal oxide, and is further configured to produce carbon dioxide, steam, or combinations thereof;
 - a second reactor configured to oxidize at least a portion of the reduced metal or reduced metal oxide from the first reactor to produce a metal oxide intermediate, and is further configured to produce hydrogen, carbon monoxide, syngas, heat or combinations thereof wherein the oxidant utilized in the oxidizing steps comprises steam, carbon dioxide, air, oxygen, or combinations thereof, wherein the oxidants being configured to produce the syngas in the second reactor; and
 - a third reactor in communication with the first reactor, the second reactor or both that is configured to regenerate the at least one metal oxide by oxidizing the metal oxide intermediate of the second reactor, and is further configured to produce heat in the third reactor.
2. A system according to claim 1 wherein the second reactor is also configured to produce H_2 , CO, heat, or combinations thereof.
3. A system according to claim 1 wherein the H_2 /CO ratio of the syngas is controlled by recycling part of the second reactor product, or controlling the amount of CO_2 and steam oxidants inputted into the second reactor.
4. A system according to claim 1 wherein the ceramic composite particles comprise a promoter.
5. A system according to claim 1 wherein the fuel comprises a solid fuel, a liquid fuel, a gaseous fuel, or combinations thereof.
6. A system according to claim 1 further comprising a separation unit configured to remove ash, char, or unwanted materials from a product stream of the second reactor, the third reactor, or both.
7. A system according to claim 8 wherein the ash separator comprises a cyclone, a sieve, a particle classifier, or combinations thereof.

8. A system according to claim 1 wherein the first and second reactors are configured to operate at a pressure of between about 1 atm to about 150 atm.

9. A system according to claim 1 wherein the first and second reactors are configured to operate at a temperature of between about 400 to about 1200 C.

10. A system according to claim 1 wherein the metal oxide comprises a metal selected from the group consisting of Fe, Cu, Ni, Sn, Co, Mn, and combinations thereof, and the support material comprises at least one component selected from the group consisting of SiC, oxides of Al, Zr, Ti, Y, Si, La, Sr, Ba, and combination thereof.

11. A system according to claim 1 further comprising a power generation section configured to produce electricity from a product of the second reactor.

12. A system according to claim 1 further comprising at least one heat exchanger configured to heat a feed comprising water, steam and combinations thereof.

13. A system according to claim 1 wherein the first reactor and the second reactor comprise at least one moving bed reactor, a series of fluidized bed reactors, a rotatory kiln, a fixed bed reactor, or combinations thereof.

14. A system according to claim 13 wherein the first reactor and the second reactor defines a countercurrent contacting pattern between gas and solids.

15. A system according to claim 1 wherein the first reactor is a moving bed reactor comprising a mixing device inserted in the moving bed to radially distribute the ceramic composite particles and mix unconverted fuel with the ceramic composite particles.

16. A system according to claim 1 wherein the first reactor is a moving bed reactor defines an annular region created around the moving bed, the annular region being location where a fuel is introduced.

17. A system according to claim 1 further comprising a conveyor or pneumatic feeding device configured to deliver the solid fuel to the first reactor.

18. A system according to claim 1 further comprising a solid fuel gasifier, a candle filter, a mercury removal unit, a gas cleanup component, a pressure swing absorption unit, a water gas shift reactor, or combinations thereof.

19. A system according to claim 1 wherein the first reactor comprises metal carbonates, metal oxides, or metal hydroxides configured to capture pollutants, heavy metals, or combinations thereof.

20. A system according to claim 1 wherein the first reactor is operable to receive a recycled H₂ stream at a bottom portion of the reactor.

21. A system according to claim 1 wherein the first reactor is operable to receive the fuel at a first reactor region below a feed region of the ceramic composite particles.

22. A system according to claim 1 wherein the first reactor is operable to receive feeds including oxygen, CO₂, air, steam, and combinations thereof at a location adjacent the middle region in which the fuel is fed.

23. A system according to claim 1 wherein the system is coupled to a solid oxide fuel cell.

24. A system according to claim 1 wherein the system is in fluid communication with a Fischer-Tropsch reactor.

25. A system according to claim 24 further comprising a refining section.

26. A system according to claim 1 wherein the first and second reactors comprise packed beds in the form of portable

cassettes, wherein the portable cassettes are configured to generate and store hydrogen in a vehicle.

27. A system comprising:

a Fischer-Tropsch reactor configured to produce hydrocarbon fuel from a feed mixture comprising fuel;

a first reactor comprising a plurality of ceramic composite particles, the ceramic composite particles comprising at least one metal oxide disposed on a support, wherein the first reactor is configured to reduce the at least one metal oxide with fuel to a reduced metal or a reduced metal oxide, the fuel being comprised at least partially of the hydrocarbon product of the Fischer-Tropsch reactor; and

a second reactor configured to oxidize the reduced metal or reduced metal oxide with steam to produce metal oxide intermediates,

wherein the second reactor is also configured to produce syngas.

28. A system according to claim 27 further comprising:

a gaseous fuel feed source;

a refining system to treat the hydrocarbon products generated in the system.

29. A system according to claim 27, wherein the oxidant is steam, CO, air, O₂, or combinations thereof.

30. A system according to claim 27, wherein the steam utilized in the second reactor comprises at least partially steam generated in a Fischer-Tropsch reactor or a gasifier.

31. A system according to claim 27 further comprising a third reactor in communication with the first reactor and configured to regenerate the at least one metal oxide by oxidizing the metal oxide intermediates.

32. A system according to claim 27 wherein the second reactor is also configured to produce hydrogen.

33. A system according to claim 27 wherein the fuel fed to the first reactor comprises at least partially syngas produced by gasification of a hydrocarbon fuel.

34. A system according to claim 27 wherein byproducts of the Fischer-Tropsch reactor are recycled to the first reactor.

35. A system according to claim 27 further comprising a steam turbine configured to produce electricity from steam generated in the system.

36. A system according to claim 27 further a gaseous fuel mixing location, wherein a gaseous fuel feed and a hydrogen containing product from the second reactor are operable to mix to produce a gaseous fuel having a molar ratio of hydrogen to carbon monoxide equal to about 2 to 1, the gaseous fuel being used in the feed mixture of the Fischer-Tropsch reactor.

37. A method of preparing ceramic composite particles comprising the steps of reacting a metal oxide with a support material;

heat treating the mixture of metal oxide and support material at temperatures of between about 200 to about 1500° C. to produce ceramic composite powders;

converting the ceramic composite powders into ceramic composite particles;

reducing and oxidizing the ceramic composite particles prior to use in a reactor.

38. A method according to claim 37 further comprising adding a promoter material to the mixture of metal oxide and support material.

39. A method according to claim 37 wherein heat treating occurs in the presence of inert gas, steam, oxygen, air, H₂, and combinations thereof at a pressure of between vacuum pressure and about 10 atm.

40. A method according to claim **37** further comprising chemically treating the mixture of metal oxide and promoter to activate a ceramic composite powder.

41. A method according to claim **37** wherein the reacting step occurs via spray drying, direct mixing, co-impregnation, or combinations thereof.

42. A method according to claim **37** wherein the conversion of ceramic composite powders occurs via extrusion, granulation, pelletization, and combinations thereof.

43. A particle produced by the method of claim **37**.

44. A particle according to claim **43** wherein the metal oxide comprises a metal selected from the group consisting of Fe, Cu, Ni, Sn, Co, Mn, and combinations thereof.

45. A particle according to claim **43** wherein the ceramic composite comprises at least 40% by weight of the metal oxide.

46. A particle according to claim **43** wherein the support material comprises at least one component selected from the group consisting of SiC, oxides of Al, Zr, Ti, Y, Si, La, Sr, Ba, and combination thereof.

47. A particle according to claim **43** wherein the ceramic composite comprises at least 5% by weight of the support material.

48. A particle according to claim **43** wherein the particle comprises a promoter comprising a pure metal, a metal oxide, a metal sulfide, or combinations thereof, wherein the metal comprises one or more from the group consisting of Fe, Ni, Sn, Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, B, P, V, Cr, Mn, Co, Cu, Zn, Ga, Mo, Rh, Pt, Pd, Ag, and Ru.

49. A particle according to claim **48** wherein the ceramic composite comprises up to 40% by weight of the promoter material.

50. A method according to claim **37** wherein the ceramic composite particles are in the form of pellets, monoliths, blocks, or combinations thereof.

51. A method according to claim **37** wherein the particle is operable to maintain activity after 10 or more regeneration cycles.

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