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(54) Title: SYNTHETIC FUELS AND CHEMICALS PRODUCTION WITH IN-SITU CO_2 CAPTURE

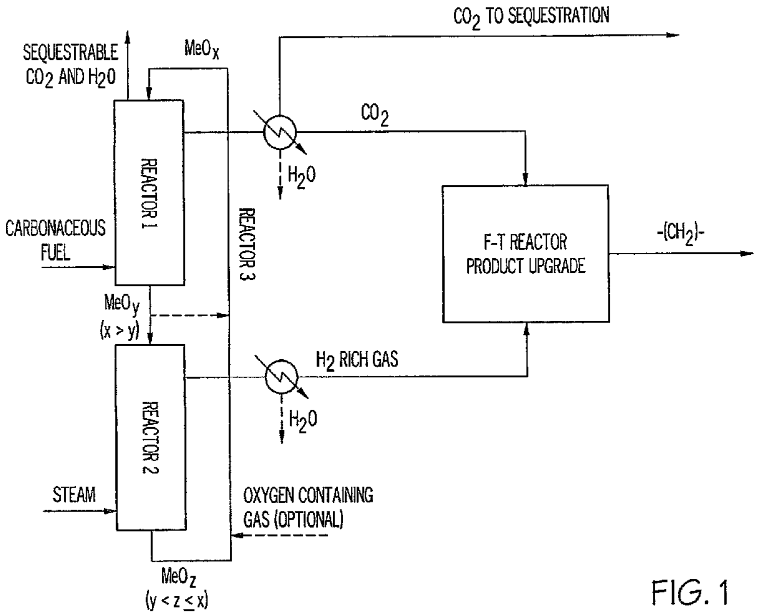

FIG. 1

(57) Abstract: Novel redox based systems for fuel and chemical production with in- situ CO_2 capture are provided. A redox system using one or more chemical intermediates is utilized in conjunction with liquid fuel generation via indirect Fischer-Tropsch synthesis, direct hydro genation, or pyrolysis. The redox system is used to generate a hydrogen rich stream and/or CO_2 and/or heat for liquid fuel and chemical production. A portion of the byproduct fuels and/or steam from liquid fuel and chemical synthesis is used as part of the feedstock for the redox system.

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Synthetic Fuels and Chemicals Production with in-situ CO_2 Capture

The present invention is generally directed to systems and methods for synthetic fuels and chemical products generation with in-situ CO_2 capture. A reduction-oxidation (redox) system using one or more chemical intermediates is generally utilized in conjunction with liquid fuel generation via indirect CO_2 hydrogenation, direct hydrogenation, or pyrolysis.

Fossil fuels including crude oil, natural gas, and coal provide more than 85% of today's energy supply. These fossil fuels are usually transformed to carriers such as electricity and liquid transportation fuels prior to utilization by end consumers. Electricity is mainly produced by relatively abundant energy sources such as coal, natural gas, and nuclear. In contrast, liquid transportation fuel is almost exclusively obtained from crude oil, whose supply is relatively insecure with volatile prices. With an increasing energy demand and concomitant concerns over carbon emissions from fossil fuel usage, affordable synthetic transportation fuels from more abundant resources such as coal, biomass, and oil shale are desirable. To address the environmental concerns, the next generation synthetic fuel production processes need to be able to capture pollutants generated in the process. These pollutants include CO_2, sulfur compounds, and mercury, among others.

Synthetic fuel is generated from gaseous fuels such as natural gas through reforming and the Fischer-Tropsch ("F-T") scheme. Solid fuels such as coal, biomass, and pet coke can be converted to synthetic fuel through indirect liquefaction (gasification – water gas shift – Fischer-Tropsch), direct liquefaction, or pyrolysis. These systems are, however, more capital intensive than oil refining processes. Moreover, their energy conversion efficiencies are relatively low.

Synthetic fuel can also be generated from biomass via biochemical routes. However, a large amount of process water is utilized. Moreover, the biochemical approaches have stringent requirements on the feedstock.

All the aforementioned processes involve CO_2 emissions. CO_2 capture from these processes associates with notable energy losses and hence decreases in process efficiency.

Embodiments of the present invention provide alternatives to produce synthetic fuel from naturally occurring carbonaceous fuel sources with high efficiency and effective CO_2 capture.

Embodiments of the present invention are generally directed to novel redox based systems for fuel and chemical production with in-situ CO_2 capture. A redox system using one or more chemical intermediates is generally utilized in conjunction with liquid fuel generation via indirect Fischer-Tropsch synthesis, direct hydrogenation, or pyrolysis. The redox system is used to generate a hydrogen rich stream and/or CO_2 and/or heat for liquid fuel and chemical production. A portion of the byproduct fuels and/or steam from liquid fuel and chemical synthesis is used as part of the feedstock for the redox system.

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

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:

Figure 1 illustrates a synthetic liquid fuel production embodiment that utilizes a combination of indirect reforming/gasification of carbonaceous feedstock and Fischer-Tropsch synthesis.

Figure 2 is a schematic illustration of another embodiment illustrating the integration of the indirect reforming/gasification and Fischer-Tropsch synthesis.

Figure 3 illustrates another embodiment of the integration of an iron oxide based gaseous fuel indirect reforming/gasification system and Fischer-Tropsch synthesis. Coal and a coal gasification unit are used in this case to produce syngas fuel. Methane and hydrocarbons can also be directly used in this system. Alternatively, a reformer can be installed in place of the gasification unit (gasifier) to convert hydrocarbon fuels.

Figure 4 illustrates another embodiment using the integration of an iron oxide based solid fuel indirect gasification system and Fischer-Tropsch synthesis. Besides biomass and coal, other solid fuels such as pet coke, tar sands, oil shale, and waste derived fuel can also be used in this system.

Figure 5 illustrates another embodiment using the integration of a sorbent enhanced reforming/water gas shift system and Fischer-Tropsch synthesis. Gaseous fuels such as syngas and light hydrocarbons can be used in this system.

Figure 6 is a schematic of another embodiment showing the integration between a direct coal to liquid sub-system and an indirect carbonaceous fuel reforming/gasification sub-system. A sorbent enhanced reforming/water gas shift system can also be used to replace the redox based indirect reforming/gasification sub-system.

Figure 7 shows another embodiment of the integration between a biomass pyrolyzer and an indirect carbonaceous fuel reforming/gasification sub-system for bio-oil synthesis.

Figure 8 is another embodiment illustrating the integration scheme between a biomass pyrolyzer and an indirect carbonaceous fuel reforming/gasification sub-system for bio-oil synthesis.

Figure 9 illustrates additional reducer designs for pulverized coal/biomass conversion in a countercurrent moving bed with coal/biomass powder flowing upwards and metal oxide composites flowing downwards.

Figure 9. (a) illustrates a moving bed reducer design for pulverized coal and biomass conversion; Figure 9 (b) illustrates a potential design for coal injection and conversion.

Embodiment of the present invention are generally directed to systems and methods for converting carbonaceous fuels into synthetic fuels with minimal carbon emission and improved energy conversion efficiency. Such systems and methods generally include an indirect fuel reforming/gasification sub-system and a liquid fuel synthesis sub-system.

Based on the technique through which the synthetic fuel is produced, the various embodiments of the present invention can be generally grouped into three categories, i.e. indirect synthetic fuel generation integrated with an indirect fuel reforming/gasification sub-system, direct synthetic fuel generation integrated with an indirect reforming/gasification sub-system, and direct pyrolysis system integrated with an indirect fuel combustion sub-system. The following specification discusses the three categories respectively.

The indirect synthetic fuel generation system, which is strategically integrated with an indirect fuel reforming/gasification sub-system, is generally represented by Figures 1 – 5.

The indirect conversion of carbonaceous fuels such as coal and natural gas to synthetic liquid fuel through gasification/reforming followed by Fischer-Tropsch synthesis is well established. The processes, however, are inefficient due to the large irreversibility of the gasification/reforming step and the highly exothermic nature of the Fischer-Tropsch synthesis reactions and the inefficiency associated with the heat recovery and utilization. Further, significant energy losses will be incurred if the carbon generated in the process is captured. In addition, the indirect synthetic fuel generation systems are highly capital intensive.

The increasing concerns over energy security and CO_2 emissions have cast serious doubt on both the environmental and economical acceptability of indirect synthetic fuel generation systems. To reduce the cost and carbon footprint of the indirect liquid fuel synthesis systems, drastic improvement in process energy conversion efficiencies coupled with CO_2 capture are highly desirable. Embodiments of the present invention strategically integrate an indirect gasification/reforming sub-system with Fischer-Tropsch sub-system to achieve effects that: 1) reduce the irreversibility of the overall synthetic fuel product system; 2) improve the energy conversion efficiency; and 3) capture the CO_2 generated in the process.

According to one aspect, carbonaceous fuel such as coal, biomass, pet coke, syngas, natural gas, extra heavy oil, wax, and oil shale, are first converted into separate streams of CO_2 and H_2 through the assistance of one or more chemical intermediates.

The H_2 and a portion of the CO_2 are then reacted in a Fischer-Tropsch synthesis reactor to produce synthetic fuels and chemicals. The remaining CO_2 is obtained in a concentrated form and can be readily sequestrated. The conversion of CO_2 and H_2, as opposed to CO and H_2, in the Fischer-Tropsch reactor reduces the exothermicity of the F-T reaction. Moreover, this scheme potentially reduces the endothermicity of the gasification/reforming step. As a result, the overall process irreversibility can be reduced. Moreover, the steam produced from the exothermic F-T reactor is readily available for hydrogen generation in the gasification/reforming sub-system. While the use of CO_2 and H_2 for F-T synthesis was studied in the 1990s, the method for CO_2 and H_2 generation from carbonaceous fuels and the unique integration schemes between the CO_2/H_2 generation sub-system described herein are novel.

Figure 1 is generally directed to an integration scheme of a redox based gasification/reforming sub-system and an F-T sub-system. With this configuration, a carbonaceous fuel is indirectly gasified/reformed into two separate streams of CO_2 and H_2. The two streams are then cooled and introduced into the F-T sub-system to produce liquid fuels. The reactions, which are not balanced, in this process include:

$MeO_x + C_xH_yO_z \rightarrow CO_2 + H_2O + MeO_y$ (Reactor 1)

$MeO_y + H_2O \rightarrow MeO_z + H_2$ (Reactor 2, $y<z\leq x$)

$MeO_z + O_2 \rightarrow MeO_x$ (Reactor 3, optional)

$CO_2 + H_2 \rightarrow -(CH_2)- + H_2O$ (CO_2 hydrogenation)

Here $C_xH_yO_z$ refers to a carbonaceous fuel in general. Me is a metal or metal mixture that can be reduced by the carbonaceous fuel and subsequently oxidized by steam and air. Such metals include Fe, Co, In, Mn, Sn, Zn, Cu, W, and combinations thereof.

Reactor 1 is typically operated at 400 – 1200 °C and 1.01×10^5Pa - 8.10×10^6Pa (1 – 80 atm). Reactor 2 is operated at a temperature of 0 – 300 °C lower than Reactor 1. Reactor 3, which is optional depending on the type of metal and the system configuration, is operated at a temperature 0 – 400 °C higher than Reactor 1. In preferred embodiments, Reactor 1 is operated at 600 – 900 °C. The gasification/reforming sub-system is operated at 1.01×10^5Pa - 3.04×10^6Pa (1 – 30 atm).

In certain embodiments, Reactor 1 is endothermic. A portion of the reduced solids from Reactor 1 is directly sent to Reactor 3 for oxidation with oxygen containing gas. The heat released in Reactor 3 is used to compensate for the heat required in Reactor 1. The extra heat generated in Reactor 3 is used for power generation to support the parasitic power usage. A small portion of the hydrogen from Reactor 2 can be used for fuel product upgrading.

As showing in Figure 1, carbonaceous fuel is fed near the bottom of Reactor 1. In one embodiment, the carbonaceous fuel comprises solid particles which are suspended buy the gases in a lower tapered section of Reactor 1 until they are at least to 50% converted before being elutriated towards the tope of Reactor 1. CO_2 rich gas and H_2 rich gas are produced from Reactor 1 and Reactor 2, respectively. These gaseous streams, which may contain steam, can be condensed prior to F-T synthesis. Alternatively, these gaseous streams can be directly used for F-T synthesis.

The F-T sub-system is operated at 200 – 500 °C and 1.01×10^6Pa - 8.10×10^7Pa (10 – 100 atm). In some embodiments, compression of the CO_2 rich gas and H_2 rich gas from the gasification/reforming sub-system are compressed.

Sulfur may present in the carbonaceous fuel, contaminating the CO_2 rich gas and H_2 rich gas streams. One or more sulfur removal units may be used to clean up the product gas streams. In the case where an iron based catalyst is used for F-T synthesis, a high temperature sorbent bed using solid sorbents such as CaO, ZnO, etc. can be used to reduce the sulfur contaminants to levels of 100 ppm or less. When a less sulfur tolerant catalyst such as cobalt based F-T catalyst is used for F-T synthesis, additional sulfur removal steps such as that using MDEA, SELEXOL (trade name), or Rectisol (trade name) may be used. In the case when low sulfur fuel such as low sulfur biomass and sulfur free natural gas or syngas is used, the sulfur removal units are not necessary.

Figure 2 illustrates another process configuration which integrates the redox based gasification/reforming sub-system and the F-T sub-system. In this configuration, the unconverted fuels from the F-T sub-system are recycled back to Reactor 1 along with the carbonaceous fuel feedstock. By doing so, the byproduct from the F-T sub-system is converted to H_2 and CO_2, increasing the liquid fuel yield and selectivity of the process. In addition, the steam generated from the F-T sub-system is redirected to Reactor 2 of the gasification/reforming sub-system, reducing the need for steam generation in the process. The strategic utilization of the products and byproducts of both F-T and gasification/reforming sub-systems and their integration-recirculation schemes reduce the exergy loss of the overall process while increasing the yield of desired product, either chemical or synthetic liquid fuel. Any CO_2 generated in the process is readily sequestrable. As a result, the process is significantly less carbon intensive and more efficient than conventional coal to liquids schemes.

Figure 3 further illustrates a more detailed process configuration, integrating an iron oxide based gasification/reforming sub-system and an F-T sub-system. In this embodiment, the gasification/reforming sub-system comprises a gasification/reforming unit and an iron based redox unit. Solid fuel is first converted into a gaseous fuel mixture. The gaseous fuel is then injected to the reducer of the iron oxide redox system for hydrogen and CO_2 generation. A hot gas cleanup system may be required where the gaseous fuel is contaminated with a high level of sulfur. The three reactor iron oxide based redox system is used to convert the fuel in a manner similar to that disclosed in Thomas US Patent US7,767,191; Fan PCT Application No. WO 2007082089; and Fan PCT Application No. WO 2010037011. The first reactor, the reducer, is configured to oxidize the carbonaceous fuel into CO_2 and steam while reducing a metal oxide based oxygen carrier, such that the average valence of the metal is less than 1. The heat required or generated in the reducer is provided or removed by the oxygen carrier particle. The second reactor, the oxidizer, is configured to (partially) oxidize a portion of the reduced oxygen carrier with steam. The third reactor, the combustor, combusts the partially oxidized oxygen carrier from the oxidizer and the remaining portion of the reduced oxygen carrier from the reducer with air. The reactions in the iron oxide redox system include, without balancing the equations:

Fe_2O_3 + Fuel → Fe/FeO + CO_2 + H_2O (avg. valence of Fe is <1) (Reducer)

Fe/FeO + H_2O → Fe_3O_4 + H_2 (Oxidizer)

Fe_3O_4 + O_2 (Air) → Fe_2O_3 (Combustor)

In one embodiment, all of the hydrogen from the oxidizer and a portion of the CO_2 from the reducer are introduced to the Fischer-Tropsch reactor to generate a mixture of hydrocarbons. The hydrocarbon mixture is then separated and refined. The fraction of the fuel mixture of lower economic value, e.g. unconverted syngas, light hydrocarbons, and naphtha, is sent to either the reducer or the gasifier/reformer to enhance carbon utilization. In essence, most of the carbon in the fuel is either fixed in the final synthetic fuel product or in the concentrated CO_2 stream which is ready for sequestration after moderate compression. Hence, the net life cycle CO_2 emissions of the system are comparable to petroleum based gasoline and diesel when coal is used as the fuel (with CO_2 capture and sequestration). In the case when biomass and natural gas are used as the fuel, the net life cycle CO_2 emission is much lower or even negative. In a carbon constrained scenario, a combination of feedstock such as coal/biomass, coal/natural gas can be used to reduce the CO_2 emissions while taking advantage of abundantly available coal.

The F-T reactor generates a large amount of steam for F-T cooling purposes, and a portion of the steam is used in the oxidizer for hydrogen generation. The rest of the steam, after supplemental firing or superheating with a small portion of byproduct fuel and heat exchanging with high temperature exhaust gas streams in the process, is used for power generation to meet the parasitic energy needs.

The oxygen carrier comprises a plurality of ceramic composite particles having at least one metal oxide disposed on a support. Ceramic composite particles are described in Thomas US Patent US7,767,191; Fan, published PCT Application No. WO 2007082089; and Fan, PCT Application No. WO 2010037011. In addition to the particles and particle formula and synthesis methods described in Thomas, applicants, in a further embodiment, have developed novel methods and supporting materials to improve the performance and strength of the ceramic composite particles used in the present system.

The novel methods include the step of mixing a metal oxide with at least one ceramic support material in slurry form followed by drying, granulation, and pelletization. Ceramic support materials in addition to those described in the prior publications include magnesium oxide, bentonite, olivine, kaoline, and sepiolite. Olivine is also used as a promoter for hydrocarbon conversion.

Figure 4 illustrates an embodiment in which an iron based three reactor redox system directly converts solid fuels into CO_2 and H_2 followed by Fischer-Tropsch synthesis. In this embodiment, an iron oxide based oxygen carrier is reduced by a solid fuel. This is followed by steam regeneration and air combustion in a similar manner as the embodiment shown in Figure 3.

Referring now to the reduction reaction in the first reactor of Figure 4, i.e. the reducer, the reducer utilizes various solid carbonaceous fuels such as biomass, coal, tars, oil shales, oil sands, tar sand, wax, and coke to reduce the iron oxide containing ceramic composite to produce a mixture of reduced metal and/or metal oxide. In addition to the solid carbonaceous fuel, the byproducts and unconverted fuel from the liquid fuel synthesis sub-system are also converted in the reducer. The possible reduction reactions include:

$$FeO_x + \text{Fuel} \rightarrow FeO_y + CO_2 + H_2O$$

$$\text{Fuel} + CO_2 \rightarrow CO + H_2$$

$$\text{Fuel} + H_2O \rightarrow CO + H_2$$

$$FeO_x + CO/H_2 \rightarrow FeO_y + CO_2/H_2O$$

The preferred overall reaction is:

Fe_2O_3 + Fuel → Fe/FeO + CO_2 + H_2O

Specifically, metallic iron (Fe) is formed in the reducer. Simultaneously, an exhaust stream that contains at least 80% CO_2 (dry basis) is produced from the reducer. In preferred embodiments, the CO_2 concentration exceeds 95% and is directly sequestrable.

The preferred designs of the reducer include a moving bed reactor with one or more stages, a multistage fluidized bed reactor, a step reactor, a rotary kiln, or any suitable reactors or vessels known to one of ordinary skill in the art that provide a countercurrent gas-solid contacting pattern. The counter-current flow pattern between solid and gas is used to enhance the gas and solid conversion. The counter-current flow pattern minimizes the back-mixing of both solid and gas. Moreover, this flow pattern keeps the solid outlet of the reactor at a more reductive environment while the gas outlet of the reactor in maintained in a more oxidative environment. As a result, the gas and solid conversion are both enhanced.

Referring back to the oxidation reaction in the second reactor in Figure 4, i.e. the oxidizer, the oxidizer converts a portion of the iron containing oxygen carrier particles from the reducer to higher oxidation state using steam generated from Fischer-Tropsch cooling. The possible reactions include:

Fe + H_2O → FeO + CO/H_2

3FeO + H_2O → Fe_3O_4 + CO/H_2

The preferred designs of the oxidizer also include a moving bed reactor and other reactor designs that provided a countercurrent gas-solid contacting pattern. A countercurrent flow pattern is preferred so that high steam to hydrogen and CO_2 to CO conversion are achieved.

Referring back to the oxidation reaction in the third reactor in Figure 4, i.e. the combustor, air or other oxygen containing gas is used to combust the remaining portion of the reducer solids product and all the oxidizer solids product. The possible reactions in the combustor include:

$$Fe/FeO/Fe_3O_4 + O_2 \rightarrow Fe_2O_3$$

Alternatively, all the reducer oxygen carrier product will be introduced to the oxidizer to react with a sub-stoichiometric amount of steam. Substantially all of the partially regenerated oxygen carrier from the oxidizer will then be introduced to the combustor. By doing this, no by-pass solids stream is needed.

The preferred reactor designs for the combustor include a fast fluidized bed reactor, an entrained bed reactor, a transport bed reactor, or a mechanical conveying system. The functions of the combustor include: oxidation of the oxygen carrier to a higher oxidation state; and re-circulation of the oxygen carrier to the inlet of the reducer for another redox cycle.

The combustor is highly exothermic. The heat generated in the combustor can be used to compensate for the heat required in the reducer. This heat can also be used to preheat the feed streams and to generate power for parasitic energy consumptions. The high pressure gaseous streams discharged from the system can be used to drive expanders for gas compression.

Table 1 illustrates the mass flow of the major streams in a process when Illinois #6 coal and switchgrass are used as the feedstock and synthetic diesel is the product. Table 2 illustrates the energy balance of the system.

Table 1. Mass Balance of the Integrated reforming/gasification – Fischer-Tropsch System for Liquid fuel Synthesis from coal

Coal (feed, kg/s)	CO_2 from Reducer (kmol/s)	H_2 Rich Stream from Oxidizer (kmol/s)	Synthetic Diesel from Fuel Production Sub-System (bbl/day)
36.9	2.2	4.5 (pure H_2 is 2.9)	8700

Table 2. Energy Balance of the Integrated reforming/gasification – Fischer-Tropsch System for Liquid fuel Synthesis from coal

Coal (MW_{th})	Parasitic Power (MWe)	Power Generation(MWe)	Fuel Production (MW_{th})	Process Efficiency (%)
1000	-80	82	620	62.2%

Table 3 illustrates the mass and energy flow of the major streams in a process when switchgrass is used as the feedstock and synthetic diesel is the product.

Table 3. Mass and Energy Balance of the Integrated reforming/gasification – Fischer-Tropsch System for Liquid fuel Synthesis from switchgrass

Switchgrass (Dry feed, kg/s)	Biomass Thermal Input (MW_{th})	Synthetic Diesel from Fuel Production Sub-System (bbl/day)	Process Efficiency (%)
5.3	100	818	55.5

Although the cases exemplified by Tables 1-3 are specific to the type of feedstock, product, reforming/gasification sub-system, and liquid fuel production system, the choices for the aforementioned parameters have a large degree of freedom. For instance, multiple types of solids fuels can be used as the feed and various synthetic fuel products can be produced.

Figure 5 illustrates schematically in an embodiment which the reforming/gasification sub-system is comprised of sorbent enhanced reforming/gasification units. In this embodiment, a calcium based sorbent enhanced reforming process is used as the reforming/water splitting block. The fuel, which can be carbonaceous feed and/or byproduct from the liquid fuel synthesis sub-system, is reformed/shifted to H_2 with the presence of $CaO/Ca(OH)_2$ sorbent and steam generated from the F-T reactor:

$$CaO + Fuel + H_2O \rightarrow CaCO_3 + H_2$$

The spent sorbent is then regenerated at high temperatures using the waste heat from the system in the calciner:

$CaCO_3 \rightarrow CaO + CO_2$

A portion of the byproduct from the liquid fuel synthesis sub-system is combusted to provide the heat for calcination reaction. A hydration step is optionally added to reactivate the sorbent. The concentrated CO_2 from the calciner is then compressed and sequestered.

The hydrogen and a portion of CO_2 produced from the sorbent enhanced reforming scheme are then used to generate synthetic fuel. Compression of the CO_2 stream is required prior to fuel synthesis.

Figure 6 illustrates an embodiment showing the integration between a direct liquefaction sub-system and the reforming/gasification sub-system. The reforming/gasification sub-system is identical to those exemplified in Figures 1 -5, i.e. both metal oxide redox based and sorbent enhanced reforming/gasification sub-systems can be used. The liquid fuel synthesis sub-system comprises a single or two stage direct liquefaction reactor and a refining system. Coal slurry is directly converted to hydrocarbons with the presence of catalyst as well as hydrogen from the reforming/gasification sub-system. The pressure of the direct liquefaction reactor is 5.05×10^6Pa - 1.01×10^7Pa (50 – 100 atm) and the temperature is 400 – 650 °C. The light fraction of the fuel and the byproduct such as heavy residue and char from the refining system are used as the fuel for the reforming/gasification sub-system. Moreover, steam generated in the coal liquefaction unit is also used for hydrogen production in the reforming/gasification sub-system. To generalize, the integrated system uses the byproduct from the liquid fuel synthesis sub-system to generate hydrogen for direct coal liquefaction. Moreover, nearly all the carbon, expect for that in the fuel product, is converted to a CO_2 rich exhaust gas stream from the reforming/gasification sub-system. The CO_2 rich stream is ready to be sequestered.

Figure 7 illustrates an embodiment in which there is integration between a fast pyrolysis process and a redox based fuel combustion process. Biomass can be converted into bio-oil via a fast pyrolysis process. Fast pyrolysis, however, requires effective control of biomass temperature and notable heat input. In this embodiment, a metal oxide based two step redox process is used to provide heat for the pyrolyzer while capturing the carbon byproduct generated in the process.

The metal oxide is used as the carrier for both oxygen and heat. In the first unit, the reducer, high temperature metal oxide (600 – 1400 °C) is reduced by the residue char and light fractions from the pyrolyzer and refining block:

$$MeO_x + \text{unwanted fuel from pyrolyzer and refining block} \rightarrow MeO_y + CO_2$$

This step is mostly endothermic, the hot MeO_y exiting the reducer is at a temperature ranging between 400 – 750 °C.

The MeO_y from the reducer enters into the prolyzer where it provides heat to the biomass feedstock for fast pyrolysis. The MeO_y may become further reduced in the pyrolyzer to MeO_z. The temperature of the MeO_z exiting the pyrolyzer ranges between 300 – 650 °C. The reducer and pyrolyzer can be either a moving bed or a fluidized bed. A fluidized bed is preferred for the pyrolyzer.

The MeO_z from the pyrolyzer is then introduced to the oxidizer, which is similar to the combustor unit described with respect to Figures 1 – 4. In the oxidizer, MeO_z is combusted with oxygen containing gas such as air to regenerate to MeO_x:

$$MeO_z + O_2 \rightarrow MeO_x$$

The outlet temperature of the oxidizer ranges from 600 – 1400 °C. The preferred reactor designs for the oxidizer include a fast fluidized bed reactor, an entrained bed reactor, a transport bed reactor, or a mechanical conveying system. The preferred metal for the redox operation include but are not limited to Co, Fe, Cu, Ni, Mn, and W. The support material and the metal are selected such that the metal oxide composite is not very catalytically active for tar cracking.

Figure 8 illustrates another embodiment for the integration of a biomass fast pyrolysis and redox process. In this embodiment, metal oxide composite does not directly contact the biomass feed, i.e. heat is indirectly provided to the fast pyrolyzer. In this embodiment, the fuel for the reducer is again the byproducts and char from fast pyrolysis of biomass. The reducer reduces the hot metal oxide from the oxidizer:

$$MeO_x + \text{unwanted fuel from pyrolyzer and refining block} \rightarrow MeO_y + CO_2$$

This step is often endothermic, the hot MeO_y exiting the reducer at a temperature ranging between 400 – 750 °C.

The reduced MeO_y then enters the oxidizer which is preferably an entrained bed, transport bed, or a fast fluidized bed reactor. The oxidizer is designed similar to a shell and tube heat exchanger with metal oxide composite and air flowing in the shell side. Air oxidizes MeO_y back to MeO_x.

$$MeO_y + O_2 \rightarrow MeO_x$$

Significant heat is generated in this step. Meanwhile, high temperature exhaust air is also generated. The reducer can be either a moving bed or a fluidized bed.

The N_2 rich exhaust air, with a small amount of residual oxygen, can be directly used for biomass feeding and conveying in the fast pyrolyzer to provide the heat. In certain embodiments, an additional combustion step with excess amounts of byproduct fuel from the fast pyrolysis stage can be used to remove the residual oxygen prior to using the high temperature N_2 rich gas for biomass feeding and conveying.

Pulverized biomass is introduced into the pyrolyzer which is installed inside the oxidizer. The pulverized biomass, carried by the high temperature gas, is injected in a tangential direction into the pyrolyzer and is conveyed upwards by the high temperature gas in a swirling manner. The centrifugal force causes the biomass to be close to the pyrolyzer/oxidizer wall through which heat can be transferred to the biomass for pyrolysis. The pyrolyzer is a fast fluidized bed, entrained bed, or a dilute transport bed.

Alternatively, the reducer can be integrated with the pyrolyzer to provide the heat to the pyrolyzer from its outer wall. In both cases, the pyrolyzer is operated at between

300 – 650 °C, the reducer is operated at between 400 – 1300 °C, and the oxidizer is operated at between 450 – 1350 °C.

The performance of the reducer in the redox based reforming/gasification sub-system is important to the success of the integrated embodiments as shown in Figures 1, 2, 3, 4, 6, 7, and 8. In addition to the designs disclosed in Fan, PCT Application No. WO 2007082089; and Fan, PCT Application No. WO 2010037011. improvements have made in the reducer design for conversion of solid fuels.

Figure 9 illustrates an improved design of the reducer. In this design, metal oxide composite particles, which are large (0.5 – 10 mm) and more dense (> 1.5 g/mL), are fed from the top of the reducer. The pulverized biomass or coal or other solid fuels, which are small (< 0.5 mm) and less dense (< 1.5 g/mL) are fed to the bottom section of the reducer. The pulverized coal or biomass is entrained by the conveying gas and flows upwards between the gaps of the composite particles while being converted. The composite particles move downwards and are reduced before exiting the reducer.

CLAIMS

1. A method for producing synthetic liquid fuel from a carbonaceous fuel comprising:

indirectly gasifying the carbonaceous fuel using steam and optionally, an oxygen containing gas and forming separate streams of carbon dioxide and hydrogen rich gases; and

reacting the hydrogen rich gas and a portion of the carbon dioxide in a CO_2 hydrogenation reaction to form a synthetic fuel.

2. A method as claimed in claim 1 in which metal oxide particles are used in the indirect gasification reaction.

3. A method as claimed in claim 1 in which at least a portion of the steam is produced using the heat generated from the CO_2 hydrogenation step.

4. A method as claimed in claim 1 in which the carbonaceous fuel comprises syngas, carbon monoxide, methane rich gas, light hydrocarbons, liquid carbonaceous fuels, coal, biomass, tar sand, oil shale, petroleum coke, heavy liquid hydrocarbons, wax, and mixtures thereof.

5. A method as claimed in claim 1 in which the remaining CO_2 is sequestered after condensing out the moisture.

6. A method as claimed in claim 1 in which at least a portion of the synthetic liquid fuel is used as a feed for the carbonaceous fuel.

7. A method as claimed in claim 2 in which the metal oxide particles comprise iron and/or its oxides.

8. A method as claimed in claim 2 in which the metal oxide particles contain supporting material comprising a ceramic material selected from the group consisting of oxides of Al, Ti, Zr, Y, Si, La, CR, Mg, Mn, Cu, Ca, carbides of Si and Ti, sepiolite, bentonite, and kaolin.

9. A method as claimed in claim 2 in which the metal oxide particles contain Fe_2O_3, and the carbonaceous fuels are indirectly gasified by

reducing the Fe_2O_3 containing particles with the carbonaceous fuel in a first reaction zone comprising a packed moving bed with a countercurrent gas-solids contacting pattern such that the average valence of iron is less than 1;

at least partially oxidizing the reduced iron oxide containing particles with steam to generate a hydrogen rich gas in a second reaction zone comprising countercurrent gas-solids contacting pattern such that the iron oxide is at least partially oxidized to Fe_2O_4; and

oxidizing the iron oxide containing particles with an oxygen containing gas in a third reaction zone and returning the oxidized iron oxide containing particles to said first reaction zone.

10. A method as claimed in claim 9 in which gaseous species selected from CO_2, H_2O, or gaseous fuels from CO_2 hydrogenation, are introduced to the bottom of the said first reaction zone to enhance the conversions of both the iron oxide particles and the carbonaceous fuel.

11. A method as claimed in claim 9 in which the carbonaceous fuel comprises solid carbonaceous fuel particles which are suspended by the gases in a lower section of the first reaction zone until they are at least 50% converted before being elutriated towards the top of the first reaction zone.

12. A method as claimed in claim 1 in which a calcium oxide containing CO_2 sorbent is used to assist in the indirect gasification of the carbonaceous fuels.

13. A method for producing synthetic liquid fuel from carbonaceous fuels comprising:

directly liquefying a solid carbonaceous fuel with a hydrogen rich gas stream; and indirectly gasifying any unconverted solid carbonaceous fuel to form separate streams of hydrogen and CO_2 rich gases.

14. A method for producing synthetic liquid fuel from carbonaceous fuels comprising the steps of:

pyrolyzing a solid carbonaceous fuel directly or indirectly with hot metal oxide containing particles to form a liquid fuel; and

indirectly combusting or gasifying the unconverted solid carbonaceous fuels with metal oxide containing particles to produce heat and a CO_2 rich gas stream.

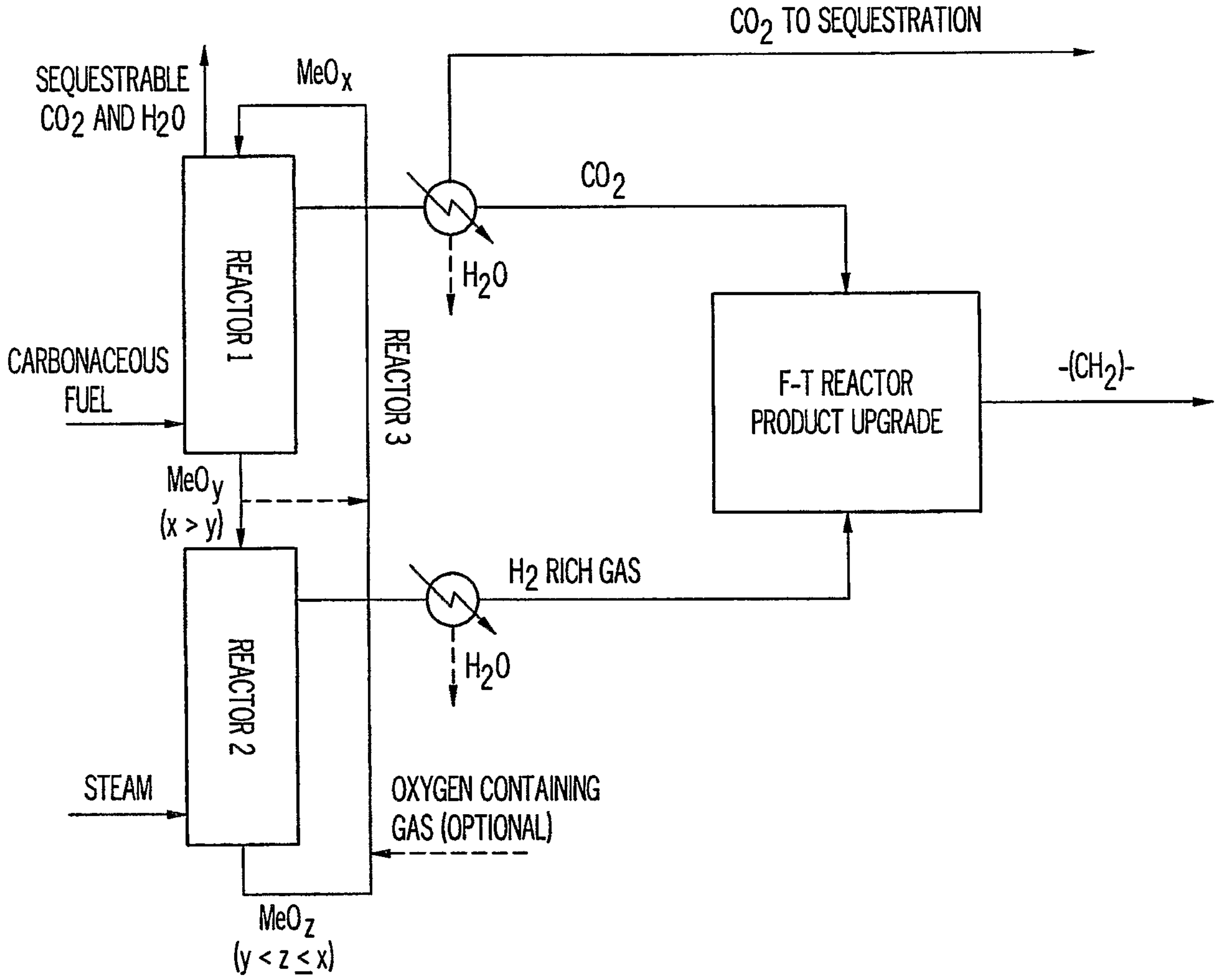

SEQUESTRABLE CO2 AND H2O
MeOx
CO2 TO SEQUESTRATION
CO2
REACTOR 1
H2O
REACTOR 3
CARBONACEOUS FUEL
F-T REACTOR PRODUCT UPGRADE
-(CH2)-
MeOy (x > y)
H2 RICH GAS
REACTOR 2
H2O
STEAM
OXYGEN CONTAINING GAS (OPTIONAL)
MeOz (y < z ≤ x)

FIG. 1

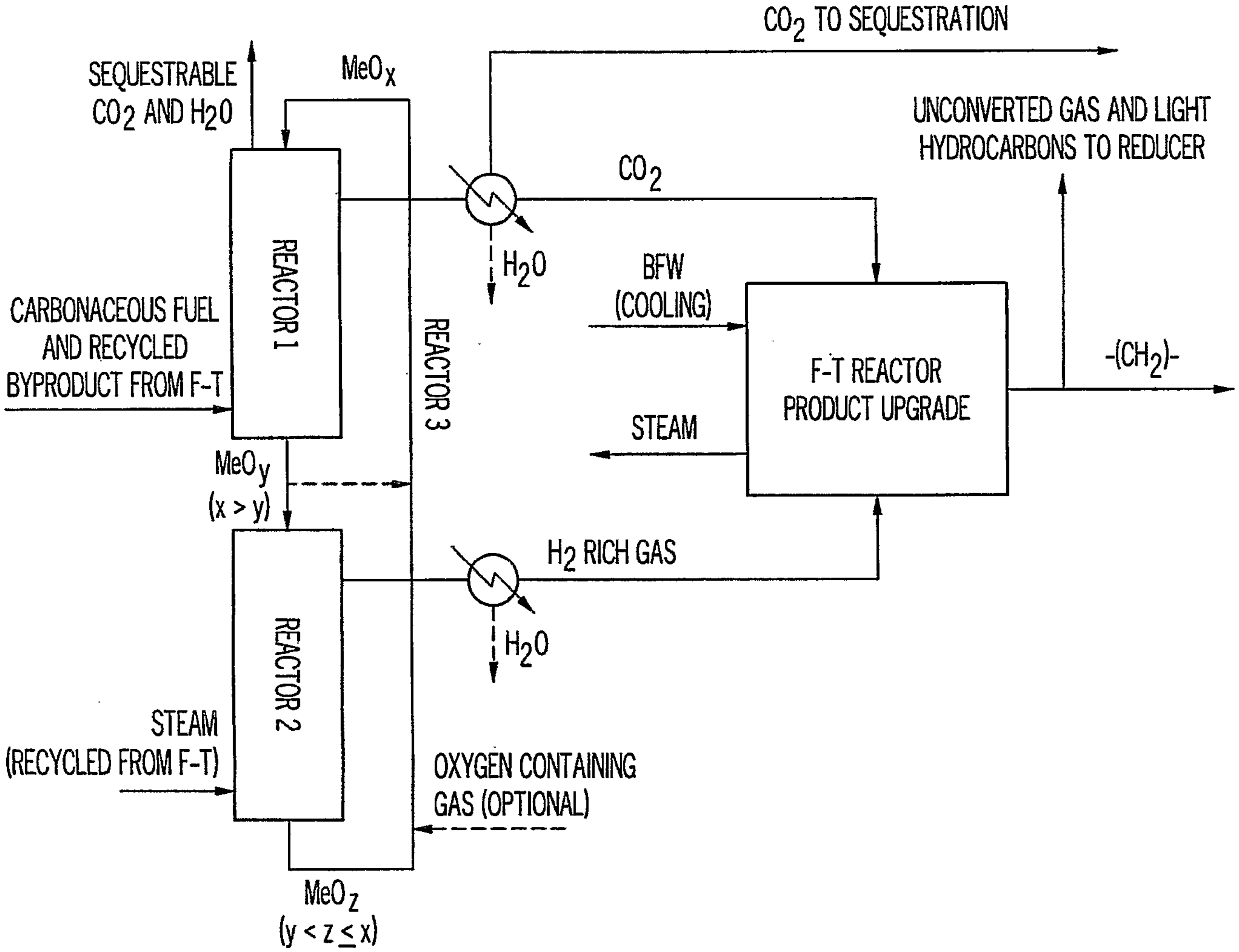

SEQUESTRABLE
CO_2 AND H_2O
MeO_x
CO_2 TO SEQUESTRATION
UNCONVERTED GAS AND LIGHT
HYDROCARBONS TO REDUCER
REACTOR 1
CO_2
H_2O
BFW
(COOLING)
CARBONACEOUS FUEL
AND RECYCLED
BYPRODUCT FROM F-T
REACTOR 3
F-T REACTOR
PRODUCT UPGRADE
-(CH_2)-
STEAM
MeO_y
$(x > y)$
H_2 RICH GAS
REACTOR 2
H_2O
STEAM
(RECYCLED FROM F-T)
OXYGEN CONTAINING
GAS (OPTIONAL)
MeO_z
$(y < z \leq x)$

FIG. 2

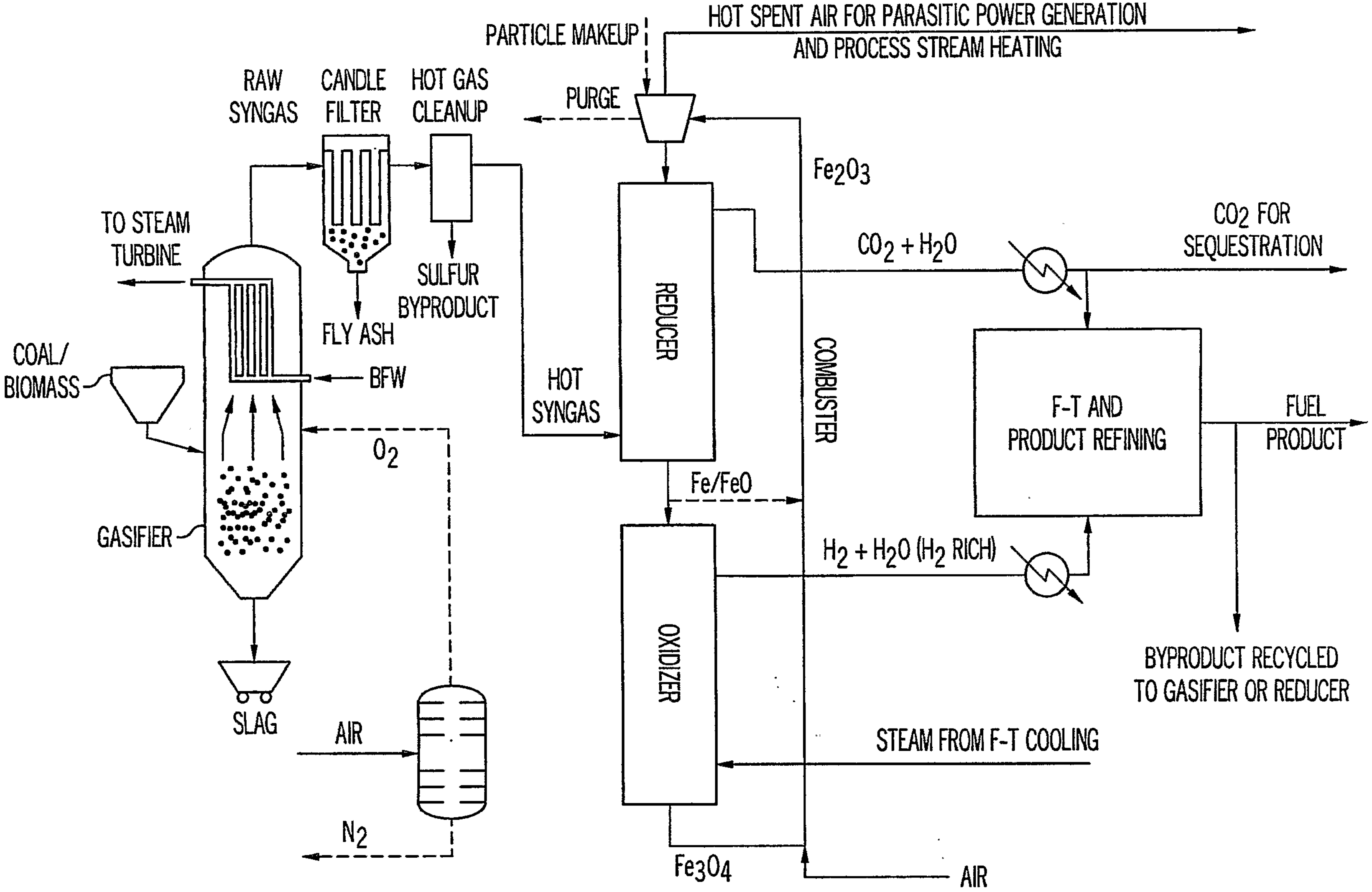

PARTICLE MAKEUP
HOT SPENT AIR FOR PARASITIC POWER GENERATION AND PROCESS STREAM HEATING
RAW SYNGAS
CANDLE FILTER
HOT GAS CLEANUP
PURGE
Fe_2O_3
TO STEAM TURBINE
SULFUR BYPRODUCT
FLY ASH
REDUCER
$CO_2 + H_2O$
CO_2 FOR SEQUESTRATION
COAL/ BIOMASS
BFW
COMBUSTER
HOT SYNGAS
F-T AND PRODUCT REFINING
FUEL PRODUCT
O_2
Fe/FeO
GASIFIER
$H_2 + H_2O$ (H_2 RICH)
OXIDIZER
BYPRODUCT RECYCLED TO GASIFIER OR REDUCER
SLAG
AIR
STEAM FROM F-T COOLING
N_2
Fe_3O_4
AIR

FIG. 3

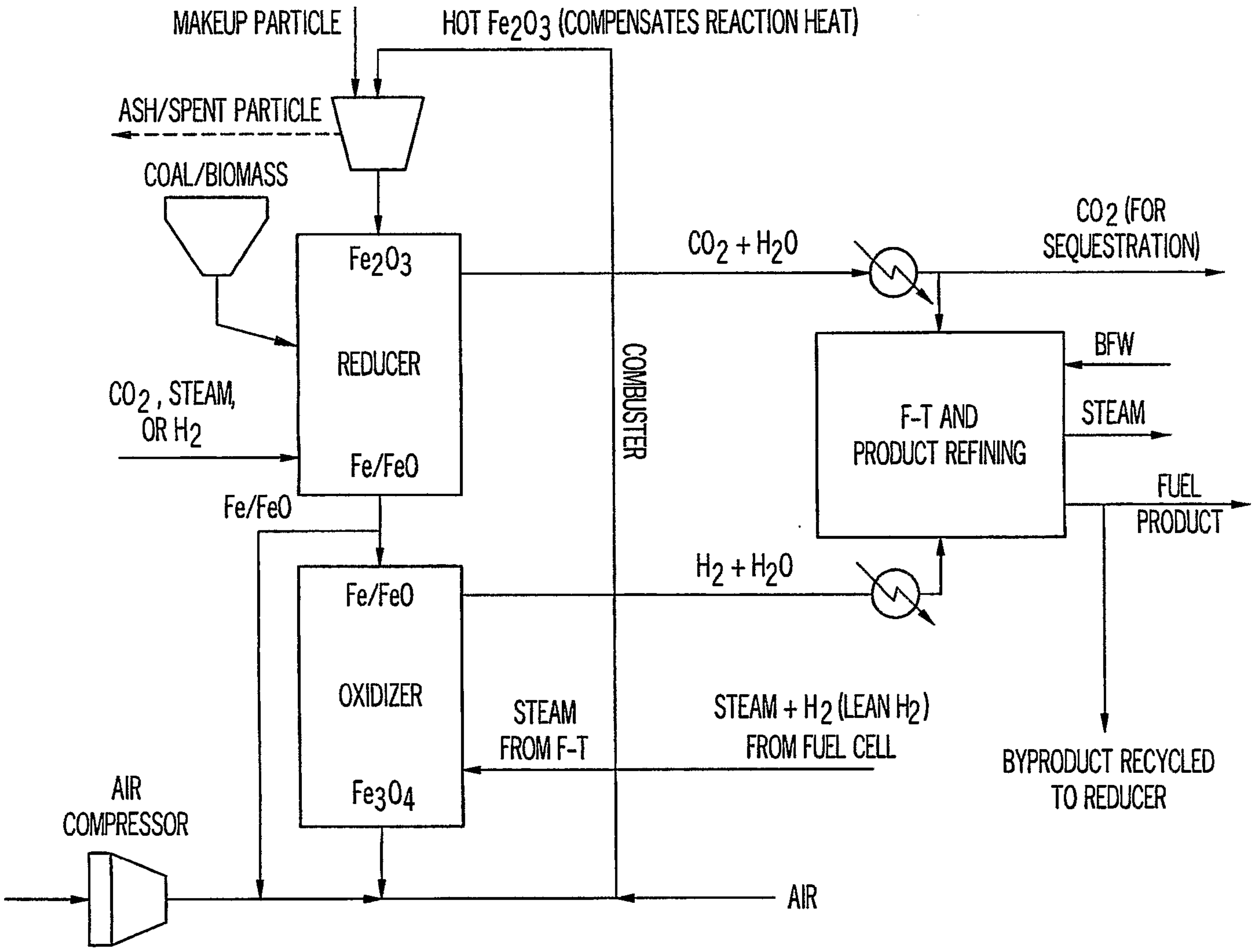

MAKEUP PARTICLE
HOT Fe_2O_3 (COMPENSATES REACTION HEAT)
ASH/SPENT PARTICLE
COAL/BIOMASS
Fe_2O_3
REDUCER
Fe/FeO
CO_2, STEAM, OR H_2
Fe/FeO
Fe/FeO
OXIDIZER
Fe_3O_4
COMBUSTER
$CO_2 + H_2O$
CO_2 (FOR SEQUESTRATION)
BFW
F-T AND PRODUCT REFINING
STEAM
FUEL PRODUCT
$H_2 + H_2O$
STEAM FROM F-T
STEAM + H_2 (LEAN H_2) FROM FUEL CELL
BYPRODUCT RECYCLED TO REDUCER
AIR COMPRESSOR
AIR

FIG. 4

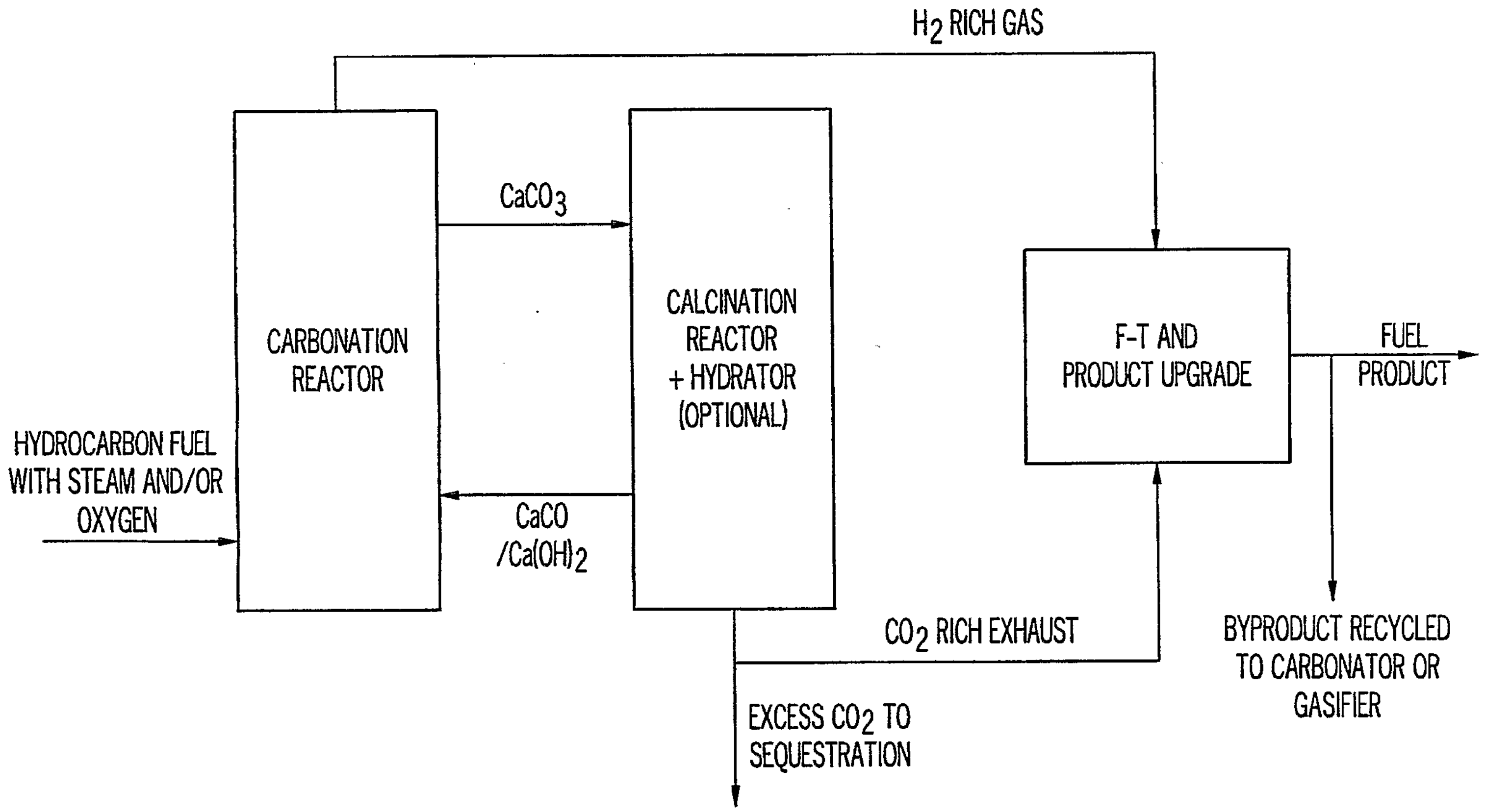

H_2 RICH GAS
CARBONATION REACTOR
$CaCO_3$
CALCINATION REACTOR + HYDRATOR (OPTIONAL)
F-T AND PRODUCT UPGRADE
FUEL PRODUCT
HYDROCARBON FUEL WITH STEAM AND/OR OXYGEN
CaCO /$Ca(OH)_2$
CO_2 RICH EXHAUST
BYPRODUCT RECYCLED TO CARBONATOR OR GASIFIER
EXCESS CO_2 TO SEQUESTRATION

FIG. 5

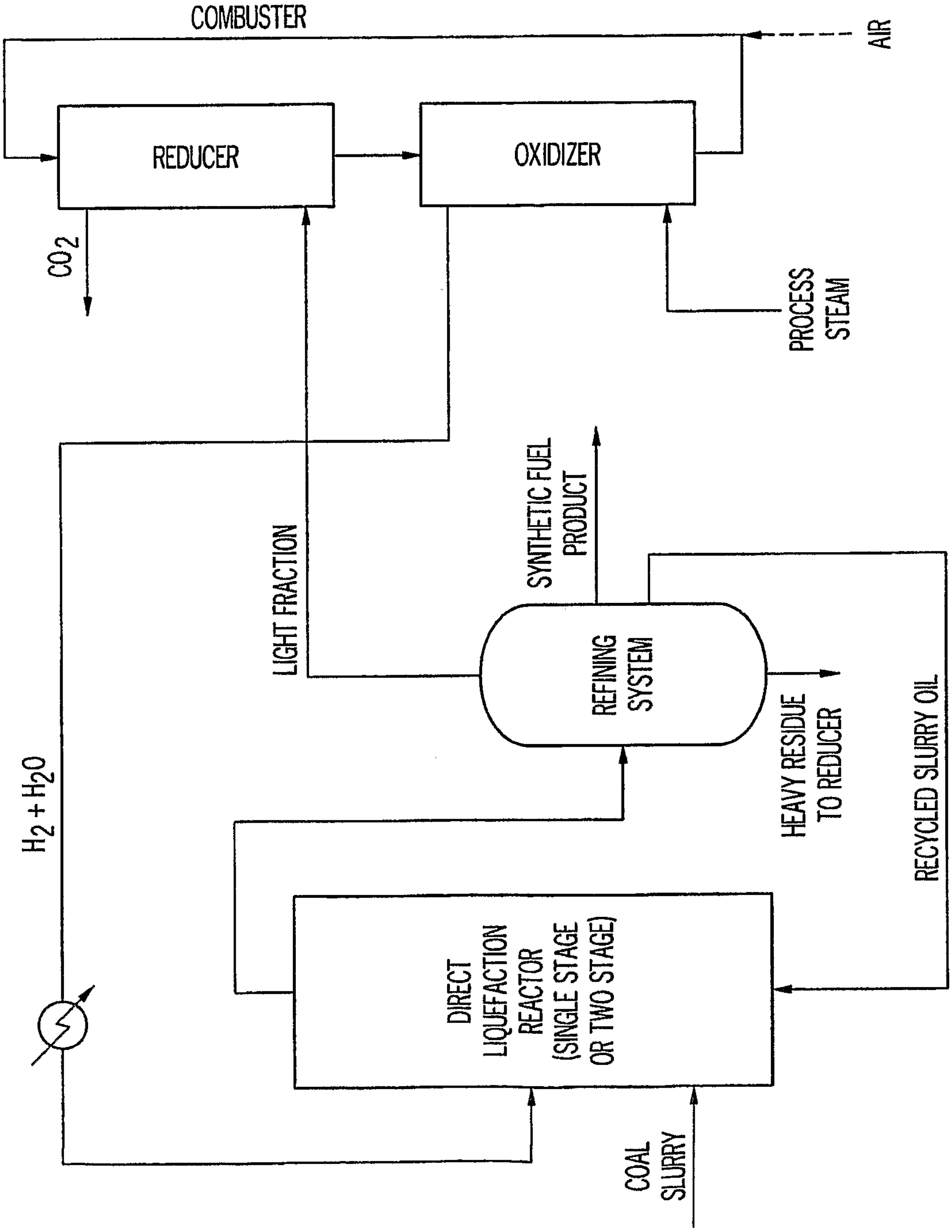

COMBUSTER
AIR
REDUCER
OXIDIZER
CO_2
PROCESS STEAM
$H_2 + H_2O$
LIGHT FRACTION
SYNTHETIC FUEL PRODUCT
REFINING SYSTEM
HEAVY RESIDUE TO REDUCER
RECYCLED SLURRY OIL
DIRECT LIQUEFACTION REACTOR (SINGLE STAGE OR TWO STAGE)
COAL SLURRY

FIG. 6

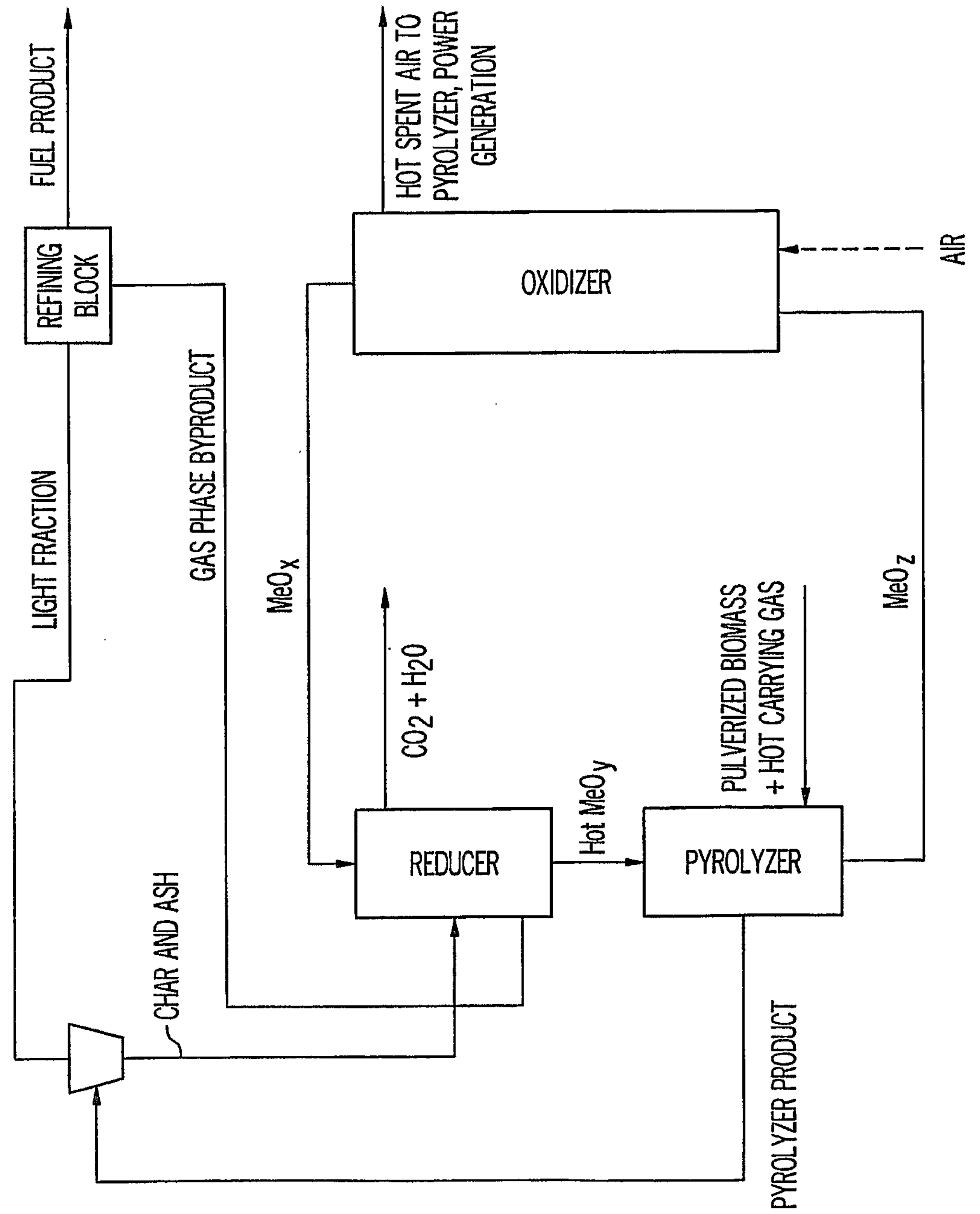

FUEL PRODUCT
REFINING BLOCK
LIGHT FRACTION
GAS PHASE BYPRODUCT
HOT SPENT AIR TO PYROLYZER, POWER GENERATION
OXIDIZER
AIR
MeO_x
$CO_2 + H_2O$
PULVERIZED BIOMASS + HOT CARRYING GAS
MeO_z
CHAR AND ASH
REDUCER
Hot MeO_y
PYROLYZER
PYROLYZER PRODUCT

FIG. 7

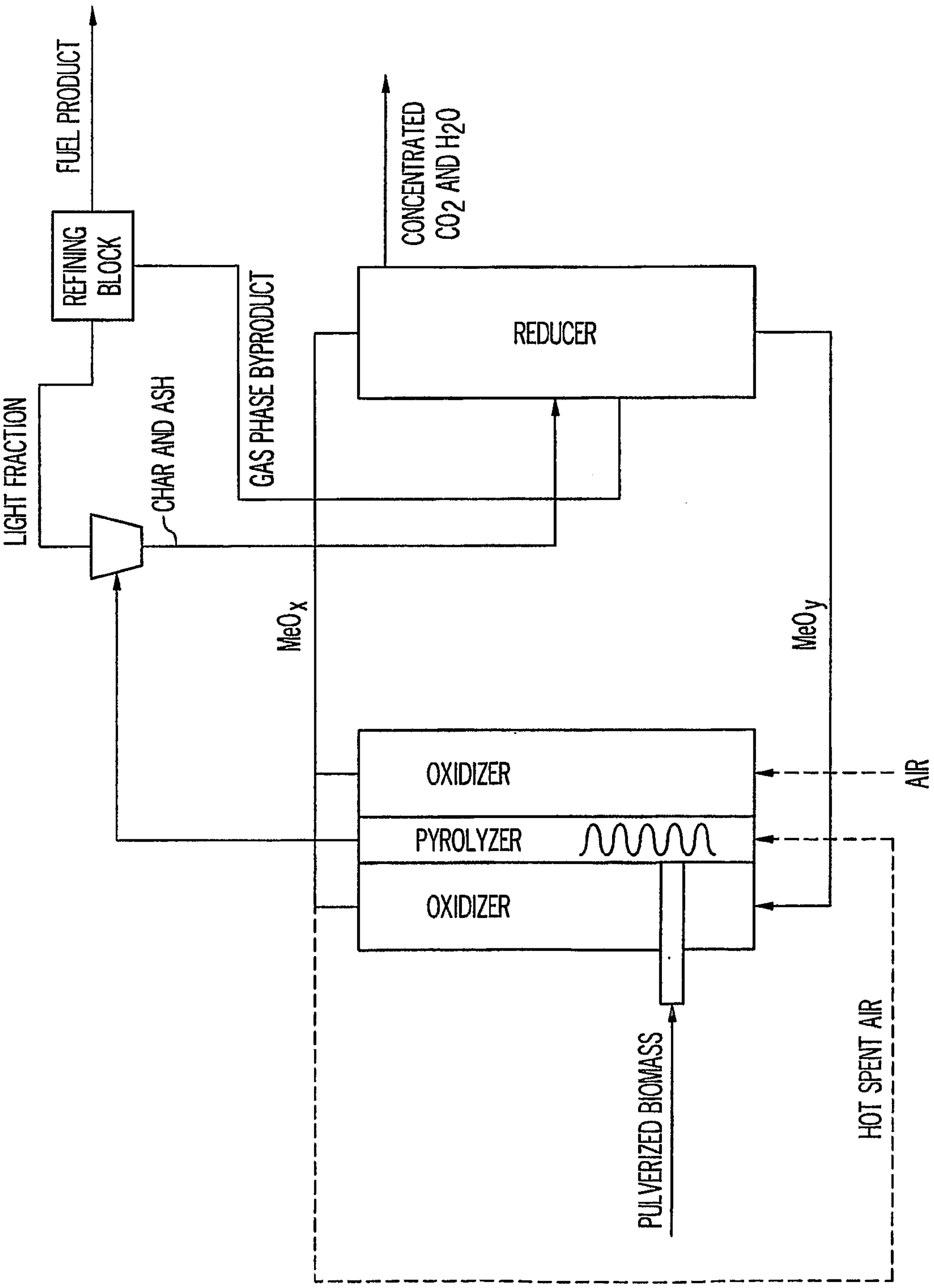
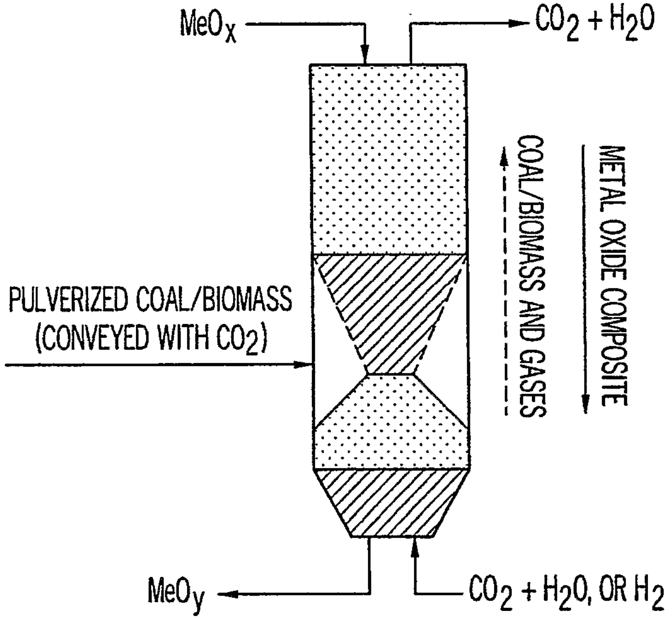

FUEL PRODUCT
REFINING BLOCK
CONCENTRATED CO_2 AND H_2O
GAS PHASE BYPRODUCT
REDUCER
LIGHT FRACTION
CHAR AND ASH
MeO_x
MeO_y
OXIDIZER
PYROLYZER
OXIDIZER
AIR
PULVERIZED BIOMASS
HOT SPENT AIR

FIG. 8



REACTIONS :

$CH_4 + 4Fe_2O \rightarrow CO_2 + 2H_2O + 8FeO$

COAL/BIOMASS $\rightarrow C + CH_4$

$CO + FeO \rightarrow Fe + CO_2$

$C + CO_2 \rightarrow 2CO$

$C + H_2O \rightarrow CO + H_2$

$CO + FeO \rightarrow Fe + CO_2$

$H_2 + FeO \rightarrow Fe + H_2O$

FIG. 9A

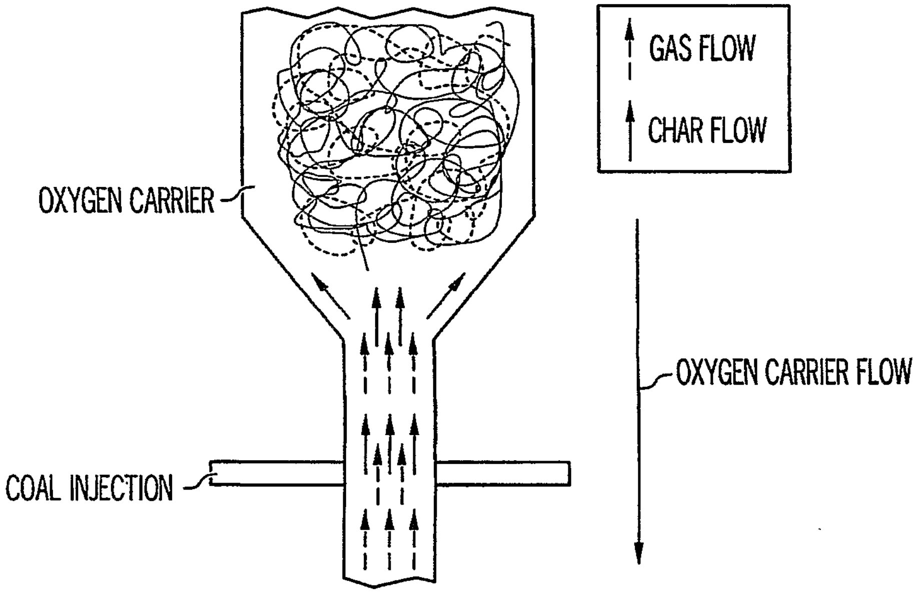

GAS FLOW
CHAR FLOW
OXYGEN CARRIER
OXYGEN CARRIER FLOW
COAL INJECTION

FIG. 9B

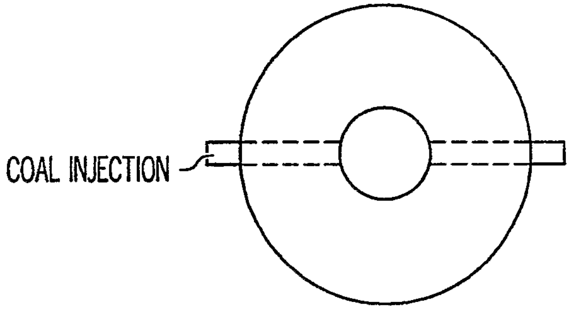

COAL INJECTION

FIG. 9C