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CARBON DIOXIDE EMISSIONS****Publication Classification**(51) **Int. Cl.**
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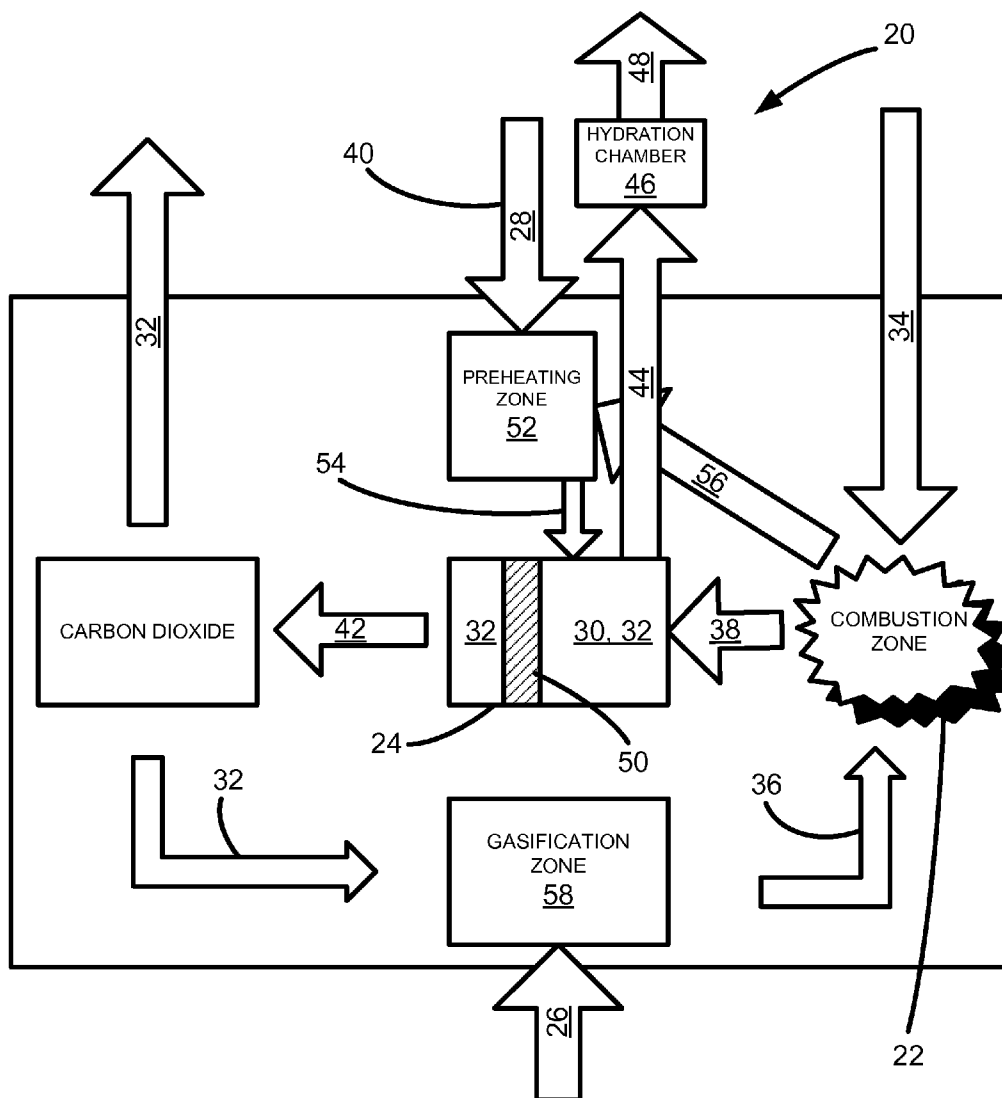
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(52) **U.S. Cl.** 110/216(57) **ABSTRACT**

A reduced emission kiln is described. In some embodiments, the kiln includes a combustion zone for generating heat energy. The combustion zone includes an oxygen inlet and a fuel inlet. In some embodiments, the kiln also includes a calcination zone for converting limestone into lime and carbon dioxide in response to the heat energy from the combustion zone. The calcination zone includes an inlet for limestone, a conduit for directing the carbon dioxide to the combustion zone for use as a flood gas to control the heat energy, an outlet for directing the lime to a hydration chamber, and a carbon dioxide permeable membrane for separating the carbon dioxide in the calcination zone from other materials in the calcination zone and preventing the other materials from entering the conduit for directing the carbon dioxide.

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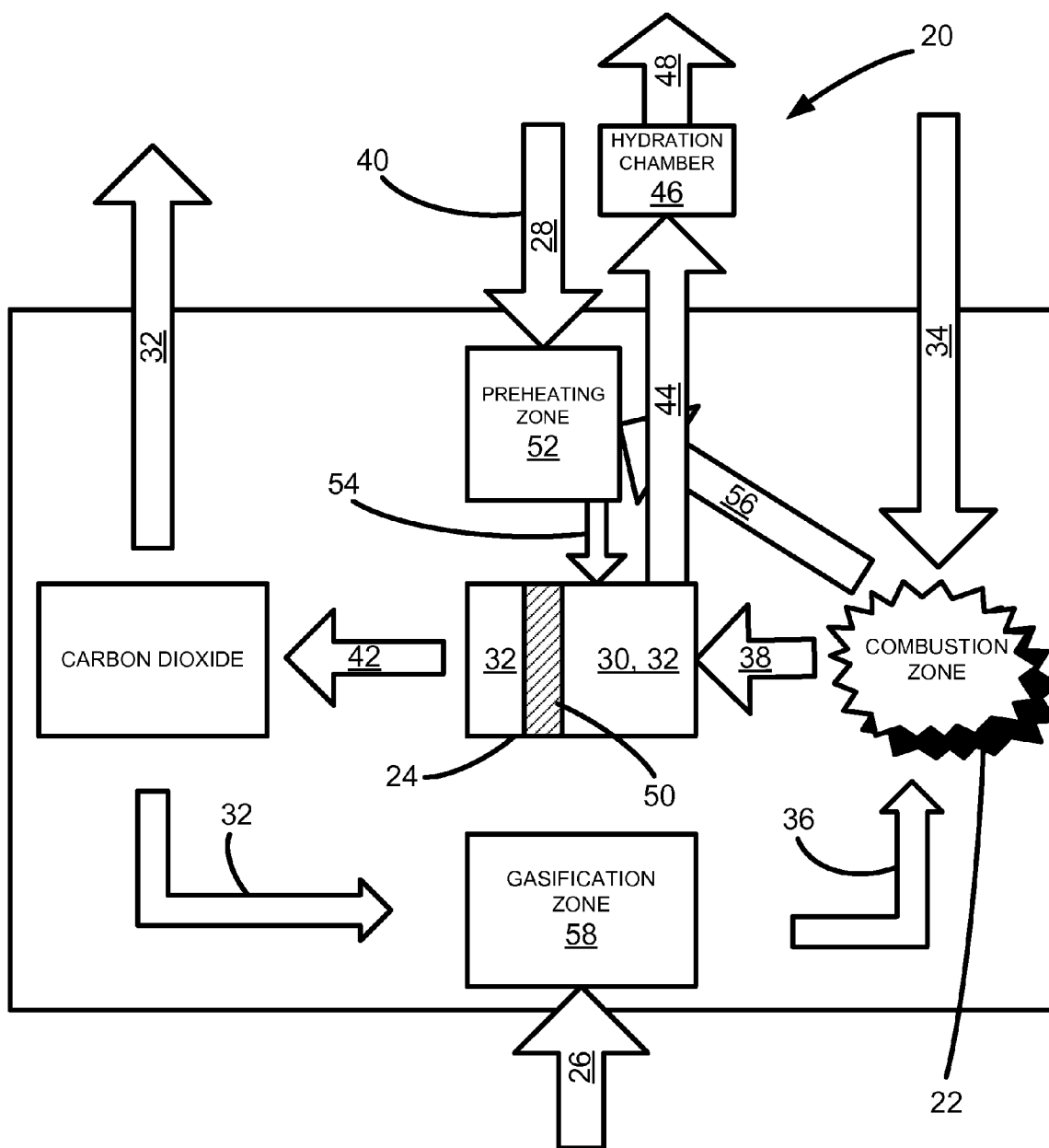


FIG. 1

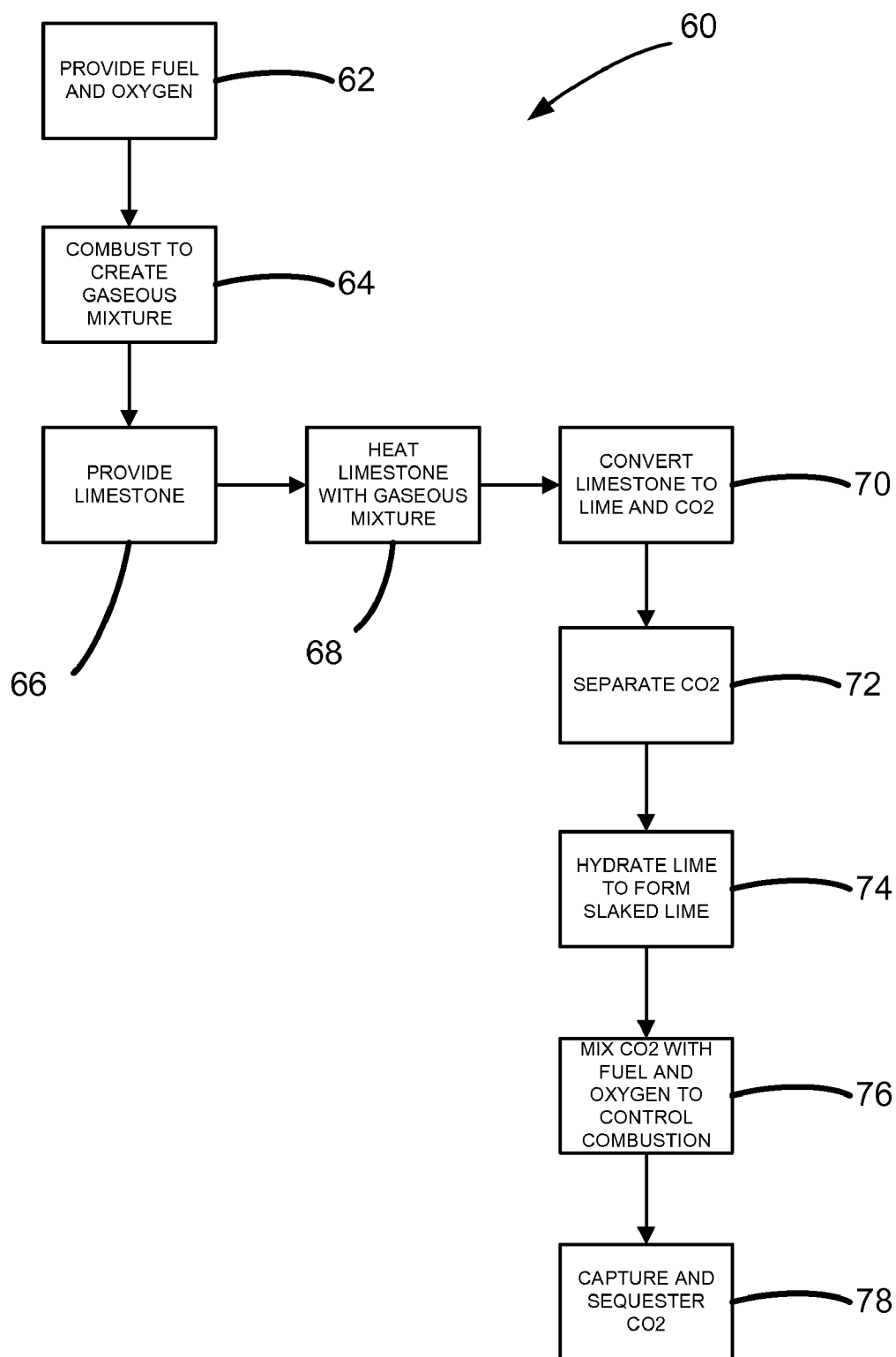
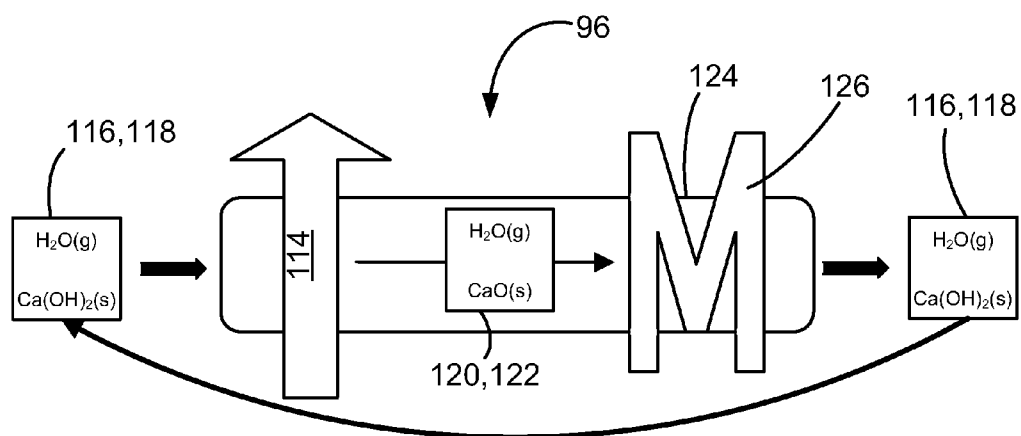
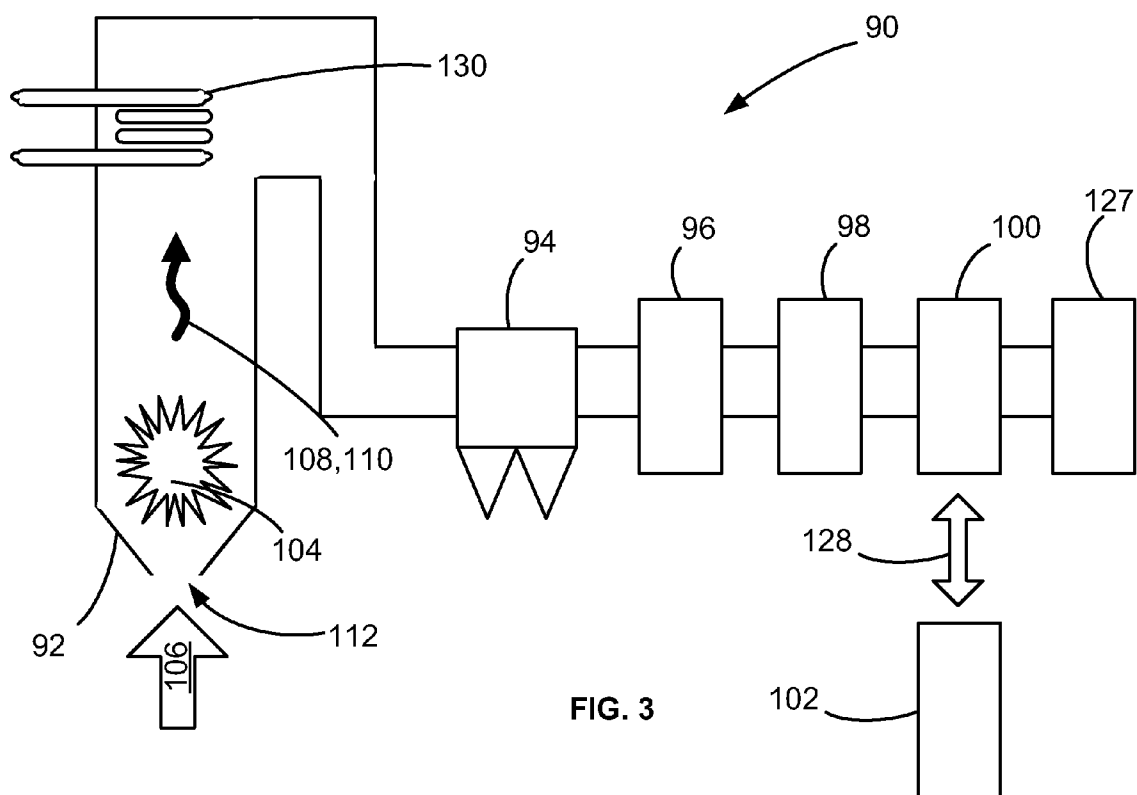


FIG. 2



METHODS AND SYSTEMS FOR REDUCING CARBON DIOXIDE EMISSIONS

CROSS REFERENCE TO RELATED APPLICATION(S)

[0001] This application claims the benefit of International Application Number PCT/US2006/014495, filed Apr. 18, 2006, which claims the benefit of U.S. Provisional Application No. 60/672,279, filed Apr. 18, 2005, each of which is incorporated by reference as if disclosed herein in its entirety.

BACKGROUND

[0002] Climate change concerns have increased concerns over the level of carbon dioxide emissions from various processes. For example, the lime and cement industries are responsible for approximately 5% of global carbon dioxide emissions. Of these emissions, about 50% arise from the chemical liberation of carbon dioxide bound in carbonates and 40% from fuel consumption with the remainder associated with electricity use and transportation.

[0003] Lime is manufactured from limestone and dolomite by heating these materials in a limekiln. This process results in the evolution of carbon dioxide. The predominant reaction in limekilns, which is commonly referred to as the calcination reaction, is shown in the following equation [1]:



[0004] Combustion of carbonaceous fuel is another process that generates carbon dioxide emissions. Currently, in one method used to reduce carbon dioxide emissions, lime is utilized to convert the carbon dioxide into limestone as shown in the following equation [2]:



[0005] Then, the limestone is fired and converted back into lime as shown Equation [1] and this cycle repeats. However, after repeated cycling, sintering of the lime occurs and its capacity to capture carbon dioxide is greatly reduced.

SUMMARY

[0006] A reduced emission kiln is disclosed. In some embodiments, the reduced emission kiln includes the following: a combustion zone for generating a heat energy, the combustion zone including an oxygen inlet and a fuel inlet; and a calcination zone for converting limestone into lime and carbon dioxide in response to the heat energy from the combustion zone, the calcination zone including an inlet for limestone, a conduit for directing the carbon dioxide to the combustion zone for use as a flood gas to control the heat energy, an outlet for directing the lime to a hydration chamber, and a carbon dioxide permeable membrane for separating the carbon dioxide in the calcination zone from other materials in the calcination zone and preventing the other materials from entering the conduit for directing the carbon dioxide.

[0007] A method of reducing emissions from a kiln is disclosed. In some embodiments, the method includes the following: providing a carbonaceous fuel and oxygen; combusting the carbonaceous fuel and oxygen to form a gaseous mixture including carbon dioxide, the gaseous mixture providing a heat energy; providing limestone; mixing the gaseous mixture with the limestone thereby heating the limestone with the heat energy; converting the limestone to lime and carbon dioxide; separating carbon dioxide from the lime

and from other materials in the gaseous mixture; and mixing at least a portion of the carbon dioxide separated from the lime and from other materials in the gaseous mixture with the carbonaceous fuel and oxygen while combusting the carbonaceous fuel and oxygen thereby controlling the heat energy.

[0008] A reduced emission combustion system is disclosed. In some embodiments, the reduced emission combustion system includes the following: a boiler including a combustion zone for combusting carbonaceous fuels to form a gaseous mixture, the gaseous mixture providing a heat energy; a particle separator for removing fly ash and other particulates from the gaseous mixture; a calcium-based heat exchanger configured to mix and heat steam and slaked lime to form lime and steam, configured to capture the exothermic heat of reaction when the lime reacts to form slaked lime, and configured to recycle the slaked lime to the beginning of the calcium-based heat exchange system, the calcium-based heat exchange system including means for collecting dissolved slaked lime; a dry or wet scrubber for removing contaminants present in the gaseous mixture, the dry or wet scrubber including means for utilizing the dissolved slaked lime from the calcium-based heat exchange system; a carbon dioxide removal chamber for removing carbon dioxide present in the gaseous mixture, the carbon dioxide removal chamber including a mechanism for bringing the gaseous mixture into contact with lime or slaked lime to generate limestone; and a sorbent regenerator for generating lime and carbon dioxide from the limestone generated in the carbon dioxide removal chamber, the sorbent regenerator including means for providing the lime generated to the carbon dioxide removal chamber.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] The drawings show embodiments of the disclosed subject matter for the purpose of illustrating the invention. However, it should be understood that the present application is not limited to the precise arrangements and instrumentalities shown in the drawings, wherein:

[0010] FIG. 1 is a diagram of a reduced emission kiln according to some embodiments of the disclosed subject matter;

[0011] FIG. 2 is a diagram of a method of reducing emissions from a kiln according to some embodiments of the disclosed subject matter;

[0012] FIG. 3 is a diagram of a reduced emission combustion system according to some embodiments of the disclosed subject matter; and

[0013] FIG. 4 is a schematic cross-section of a heat exchanger according to some embodiments of the disclosed subject matter.

DETAILED DESCRIPTION

[0014] Referring now to the drawings and in particular to FIG. 1, one aspect of the disclosed subject matter relates to a reduced emission kiln 20. The term "reduced emission kiln" as used herein can include a kiln having total carbon dioxide emissions to the environment outside of the kiln of less than about 1% or 10,000 parts per million (ppm) of the total gas in the system. In some embodiments, the kiln releases from about 10,000 ppm to about 1 ppm of carbon dioxide into the environment outside of the kiln. In some embodiments, the kiln does not release any carbon dioxide into the environment outside of the kiln.

[0015] In some embodiments, reduced emission kiln 20 includes a combustion zone 22 and a calcination zone 24. A carbonaceous fuel 26 is combusted in combustion zone 22 to heat calcination zone 24. In calcination zone 24, limestone 28 is heated until it converts to lime 30 and heated carbon dioxide (CO_2) 32.

[0016] As used herein, the term “limestone” includes materials predominantly composed of calcium carbonate (CaCO_3), e.g., a material having CaCO_3 and MgCO_3 (dolomite) and the term “lime” as used herein refers to materials predominantly composed of calcium oxide (CaO), e.g., a material having CaO and MgO . The term “carbonaceous fuel” as used herein can include, but is not limited to, carbon, coal, fuel oil, natural gas, petro-coke, waste oil, a gaseous hydrocarbon, such as methane, ethane, propane or butane, tires, and biomass.

[0017] Combustion zone 22 includes an oxygen inlet 34 and a fuel inlet 36. A gas containing substantially oxygen or pure oxygen is fed to combustion zone 22 via oxygen inlet 34 to facilitate combustion of carbonaceous fuel 26. Carbonaceous fuel 26 is introduced to combustion zone via fuel inlet 36. Combustion of carbonaceous fuel 26 generates a heat energy 38 for heating calcination zone 24.

[0018] Calcination zone 24 includes an inlet 40 for limestone 28, a conduit 42 for recycling carbon dioxide 32 to combustion zone 22 for use as a flood gas to temper the combustion reaction taking place in the kiln to control heat energy 38, and an outlet 44 for directing lime 30 to a hydration chamber 46. For example, use of high purity oxygen for combustion may excessively raise the temperature of the kiln and hot carbon dioxide 32 can be utilized as a flood gas to temper the flame temperature. In hydration chamber 46, lime 30 is hydrated to form slaked lime 48. The term “slaked lime” as used herein refers to a material predominantly composed of calcium hydroxide $\text{Ca}(\text{OH})_2$. In some embodiments, calcination zone 24 also includes a carbon dioxide permeable membrane 50 for separating carbon dioxide in the calcination zone from other materials in the calcination zone and preventing the other materials from entering conduit 42. Carbon dioxide permeable membrane 50 is configured so that a substantially pure stream of carbon dioxide, i.e., carbon dioxide 32, flows from calcination zone 24 into conduit 42. In some embodiments, a nearly complete combustion of carbon dioxide will take place in calcination zone 24, thereby producing an effluent from the calcination zone of carbon dioxide and steam. The steam can be condensed and a concentrated stream of carbon dioxide produced and/or captured. In some embodiments, reduced emission kiln 20 includes additional apparatus for capturing and sequestering portions of carbon dioxide 32 not used as a flood gas.

[0019] In some embodiments, calcination zone 24 can be a fluidized bed that avoids mixing air with the carbon dioxide produced in the calcination process. The calciner can be fluidized using a stream of gases, e.g., methane, carbon dioxide, etc., and the heat of combustion can be transferred to the reactive materials. The fluidized bed can operate at temperatures ranging from about room temperature to about 1000 degrees Celsius. The fluidized bed can produce a pure stream of carbon dioxide and a calcined product such as lime.

[0020] In some embodiments, reduced emission kiln 20 includes a preheating zone 52 for preheating limestone 28 before it enters calcination zone 24. Preheating zone 52 includes a conduit 54 for directing preheated limestone 28 to calcination zone 24. In some embodiments, reduced emission

kiln 20 includes a conduit 56 for directing heat energy 38 from combustion zone 22 to preheating zone 52. In some embodiments, an auxiliary heating source (not shown) is used to heat preheating zone 52.

[0021] In some embodiments, reduced emission kiln 20 includes a gasification zone 58 to convert various non-gaseous fuels to a gas prior to burning. For example, carbon dioxide 32, which is produced in calcination zone 24, can be utilized to gasify carbonaceous fuel 26, e.g., coal, in gasification zone 58 according to the Boudouard reaction prior to combusting in combustion zone 22. In some embodiments, an oxygen supply (not shown) and conduit (not shown) for providing oxygen to gasification zone 58 is included. Oxygen provided to gasification zone 58 can be utilized to gasify carbonaceous fuel 26 in the gasification zone prior to combusting in combustion zone 22.

[0022] Referring now to FIG. 2, some embodiments include a method 60 of reducing emissions from a kiln. At 62, carbonaceous fuel and oxygen are provided. At 64, the carbonaceous fuel and oxygen are combusted to form a heated gaseous mixture including carbon dioxide. In some embodiments, the carbonaceous fuel is gasified prior to combusting. The heated gaseous mixture provides heat energy. At 66, limestone is provided. At 68, the heated gaseous mixture is mixed with the limestone thereby heating the limestone with the heat energy. At 70, the limestone is converted to lime and carbon dioxide. In some embodiments, the limestone is preheated prior to converting. In some embodiments, heat energy generated at 64 is used to preheat the limestone. At 72, the carbon dioxide is separated from the lime and from other materials in the gaseous mixture. At 74, the lime is hydrated to form slaked lime. Slaking the lime helps maintain its reactivity for future use as a carbon dioxide sorbent. At 76, a portion of the carbon dioxide separated from the lime and from other materials in the gaseous mixture is used as a flood gas to control the heat energy generated during combustion of the carbonaceous fuel and oxygen. At 78, a portion of the carbon dioxide separated from the lime and from other materials in the gaseous mixture is captured and sequestered.

[0023] Referring now to FIGS. 3 and 4, some embodiments include a reduced emission combustion system 90. System 90 includes a boiler 92, a particle separator 94, a calcium-based heat exchanger 96, a dry or wet scrubber 98, a carbon dioxide removal chamber 100, and a sorbent regenerator 102.

[0024] Boiler 92 includes a combustion zone 104 for combusting carbonaceous fuels 106 to form a heated gaseous mixture 108. In some embodiments, boiler 92 is operated at temperatures of at least about 1000 degrees. Gaseous mixture 108 provides a heat energy 110 to be used elsewhere in system 90. As carbonaceous fuel 106 burns, solid ash can be created and removed from a point 112 adjacent the bottom of combustion zone 104. Gaseous mixture 108 can contain carbon dioxide, fly ash, and other contaminants, e.g., sulfur dioxide (SO_2) gas. Particle separator 94 includes known mechanisms for removing fly ash and other particulates from a flue gas, i.e., from gaseous mixture 108. For example, particle separator 94 can be an electrostatic precipitator or filters.

[0025] As best illustrated in FIG. 4, calcium-based heat exchanger 96 includes a heat absorption zone 114, e.g., made of tubes, that contains a steam 116 and a slaked lime 118. A heat source such as heat energy 110 is applied to heat absorption zone 114 to heat steam 116 and slaked lime 118 until it converts to a lime 120 and a steam 122. The initial temperature of gaseous mixture 108 and resulting heat energy 110 can

be above from 500 degrees Celsius to about 900 degrees Celsius. In some embodiments, the temperature of the heated lime 120 and or steam 122 can be above about 100 degrees Celsius to 900 degrees Celsius. In some embodiments, heat absorption zone 114 can absorb up to about 100% of the heat from gaseous mixture 108. Calcium-based heat exchanger 96 also includes a heat release zone 124. When lime 120 combines with steam 122 to re-form slaked lime 118, the exothermic heat of reaction generated is captured by heat exchange tubes 126 or similar mechanisms in heat release zone 124 and used elsewhere in system 90. Slaked lime 118 is recycled to heat absorption zone 114. In some embodiments, calcium-based heat exchanger 96 includes a mechanism (not shown), e.g., filter, drain, conduit, etc., for collecting any slaked lime that is dissolved in water in the heat exchanger. The dissolved slaked lime (not shown) can be used in dry or wet scrubber 98 to remove other contaminants from gaseous mixture 108.

[0026] In some embodiments, calcium-based heat exchanger 96 can be integrally incorporated within combustion system 90. For example, gaseous mixture 108 can pass over heat absorption zone 114 and heat generated by the exothermic heat of reaction and captured by heat exchange tubes 126 can be utilized to dry solids entering combustion system 90. As discussed further below, the heat generated by the exothermic heat of reaction and captured by heat exchange tubes 126 can also be utilized to heat feed water and drive one or more turbines for generating electricity.

[0027] In some embodiments, heat absorption zone 114, heat release zone 124, and heat exchange tubes 126 are not necessarily limited as a component of combustion system 90 and can be embodied as a separate component that can be used in any suitable systems or processes. For example, any heat containing substance can be contacted or passed over heat absorption zone 114 and the heat generated by the exothermic heat of reaction from the re-formation of slaked lime 118 can be utilized in any desired process, e.g., to heat feed water for another process. For example, calcium-based heat exchanger 96 can be used to improve the efficiency of a Fischer-Tropsch process.

[0028] Dry or wet scrubber 98 can be a conventional scrubber for removing other contaminants, e.g., sulfur dioxide, etc., present in gaseous mixture 108. In some embodiments, dry or wet scrubber 98 is connected with calcium-based heat exchanger 96, which provides dissolved calcium hydroxide for use in the scrubber. For example, dry sorbent scrubbing or lime spraying can be utilized in scrubber 98.

[0029] In dry sorbent scrubbing, limestone pellets can be introduced to the top of a tank where the surface of the limestone pellets reacts with contaminants, e.g., sulfur dioxide, contained in gaseous mixture 108. The reacted pellets can fall down into a hopper and then be fed into a device that scrapes the reacted outside layer of the limestone pellets. The regenerated limestone pellet can be fed back to the top of the tank and the scrubbing repeated.

[0030] In lime spraying, powdered lime, either in a dry state or mixed with water to form a paste, can be used. The lime can be sprayed into gaseous mixture 108 inside a reaction chamber where it reacts with the contaminants. For example, if sulfur dioxide is the predominant contaminant to be removed, lime may turn into gypsum, which can be captured for use in other processes. As used herein, "gypsum" refers to compounds including calcium sulfate dehydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

[0031] Carbon dioxide capture chamber 100 can be a conventional apparatus for removing carbon dioxide by bringing

a mixture containing carbon dioxide, e.g., gaseous mixture 108, into contact with lime or slaked lime to generate limestone. For example, carbon dioxide capture chamber 100 can include a chamber, a tube, a container, or the like having holes that allow passage of carbon dioxide into and out of the chamber, tube, container, or the like. Carbon dioxide capture chamber 100 can also include a fluidized bed or circulating fluidized bed wherein lime or slaked lime are suspended on an upward blowing stream of carbon dioxide. In some embodiments, a bubbling fluidized bed can be utilized. Carbon dioxide capture chamber 100 can also include cyclones (not shown) that separate the solids and residual exhaust or flue gas before discharging any exhaust to the atmosphere via a stack 127. As further discussed below, the lime or slaked lime used in carbon dioxide capture chamber 100 can be generated in sorbent regenerator 102.

[0032] Sorbent regenerator 102 is used to generate lime and carbon dioxide from the limestone generated in carbon dioxide capture chamber 100. In some embodiments, sorbent regenerator 102 includes a conduit 128 for providing lime generated to carbon dioxide capture chamber 100. In some embodiments, sorbent regenerator 102 includes a conduit (not shown) for providing any excess lime generated to boiler 92 and combustion zone 104 for combustion. In some embodiments, sorbent regenerator 102 is a low emission kiln such as reduced emission kiln 20, which is described above.

[0033] In some embodiments, system 90 includes additional heat exchangers (not shown) for capturing heat generated in sorbent regenerator 102. For example, where reduced emission kiln 20 is included in system 90, heat exchangers for capturing heat from calcination zone 24 and combustion zones 22, 104 can be included.

[0034] In some embodiments, system 90 is used to heat steam and drive turbines to generate electricity. Heated gaseous mixture 108 can indirectly heat pipes 130 containing, for example, steam, which can then drive one or more turbines (not shown) to generate power, such as electricity.

[0035] With minor variations for particular applications, e.g., variations in feed materials and operation temperatures, uses for an oxygen-blown reduced emission kiln according to the disclosed subject matter include, but are not limited to the following: the production of lime, clinker, and cement with reduced carbon dioxide emissions; reducing the emissions from power plants that run on coal or one or more fossil fuels; reducing carbon dioxide emissions from iron and steel blast furnaces; reducing emissions for paper production processes; for performing Fischer-Tropsch processes with reduced carbon dioxide emissions; and reducing carbon dioxide emissions in a system used for the heat treatment of solids or the volatilization of pollutants, such as a soil remediation method in which soil is burned to oxidize pollutants. For example, an oxygen-blown reduced emission kiln according to the disclosed subject matter can be utilized to capture the carbon dioxide gases contained in the exhaust gas of one or more of the processes described above.

[0036] Although the disclosed subject matter has been described and illustrated with respect to embodiments thereof, it should be understood by those skilled in the art that features of the disclosed embodiments can be combined, rearranged, etc., to produce additional embodiments within the scope of the invention, and that various other changes, omissions, and additions may be made therein and thereto, without parting from the spirit and scope of the present application.

What is claimed is:

1. A reduced emission kiln, said kiln comprising:
 - a combustion zone for generating a heat energy, said combustion zone including an oxygen inlet and a fuel inlet; and
 - a calcination zone for converting limestone into lime and carbon dioxide in response to said heat energy from said combustion zone, said calcination zone including an inlet for limestone, a conduit for directing the carbon dioxide to said combustion zone for use as a flood gas to control said heat energy, an outlet for directing the lime to a hydration chamber, and a carbon dioxide permeable membrane for separating the carbon dioxide in said calcination zone from other materials in said calcination zone and preventing the other materials from entering said conduit for directing the carbon dioxide.
2. The kiln according to claim 1, further comprising a hydration chamber for hydrating the lime received from said outlet for directing the lime, wherein the lime is converted to slaked lime in said hydration chamber.
3. The kiln according to claim 1, further comprising means for capturing the carbon dioxide present in said calcination zone.
4. The kiln according to claim 1, further comprising a gasification zone for gasifying fuels to be combusted in said combustion zone, said gasification zone including a fuel inlet and a conduit for directing the gasified fuels to said combustion zone.
5. The kiln according to claim 1, further comprising a preheating zone for preheating limestone, said preheating zone including a conduit for directing preheated limestone to said calcination zone.
6. The kiln according to claim 5, further comprising a conduit for directing said heat energy from said combustion zone to said preheating zone.
7. The kiln according to claim 1, wherein a carbonaceous fuel is combusted in said combustion zone.
8. A method of reducing emissions from a kiln, said method comprising:
 - providing a carbonaceous fuel and oxygen;
 - combusting said carbonaceous fuel and oxygen to form a gaseous mixture including carbon dioxide, said gaseous mixture providing a heat energy;
 - providing limestone;
 - mixing said gaseous mixture with said limestone thereby heating said limestone with said heat energy;
 - converting said limestone to lime and carbon dioxide;
 - separating carbon dioxide from said lime and from other materials in said gaseous mixture; and
 - mixing at least a portion of the carbon dioxide separated from said lime and from other materials in said gaseous mixture with said carbonaceous fuel and oxygen while combusting said carbonaceous fuel and oxygen thereby controlling said heat energy.
9. The method according to claim 8, further comprising: hydrating said lime.
10. The method according to claim 8, further comprising: capturing at least a portion of said carbon dioxide separated from said lime and from other materials in said gaseous mixture.
11. The method according to claim 8, further comprising: gasifying said carbonaceous fuel prior to combusting.
12. The method according to claim 8, further comprising: preheating limestone prior to converting.
13. The method according to claim 12, further comprising: preheating limestone with said heat energy.
14. A reduced emission combustion system, said system comprising:
 - a boiler including a combustion zone for combusting carbonaceous fuels to form a gaseous mixture, said gaseous mixture providing a heat energy;
 - a particle separator for removing fly ash and other particulates from said gaseous mixture;
 - a calcium-based heat exchanger configured to mix and heat steam and slaked lime to form lime and steam, configured to capture the exothermic heat of reaction when the lime reacts to form slaked lime, and configured to recycle the slaked lime to the beginning of said calcium-based heat exchange system, said calcium-based heat exchange system including means for collecting dissolved slaked lime;
 - a dry or wet scrubber for removing contaminants present in said gaseous mixture, said dry or wet scrubber including means for utilizing said dissolved slaked lime from said calcium-based heat exchange system;
 - a carbon dioxide removal chamber for removing carbon dioxide present in said gaseous mixture, said carbon dioxide removal chamber including means for bringing said gaseous mixture into contact with lime or slaked lime to generate limestone; and
 - a sorbent regenerator for generating lime and carbon dioxide from said limestone generated in said carbon dioxide removal chamber, said sorbent regenerator including means for providing said lime generated to said carbon dioxide removal chamber.
15. The system according to claim 14, wherein said sorbent regenerator is a low emission kiln comprising:
 - a combustion zone for generating a heat energy, said combustion zone including an oxygen inlet and a fuel inlet; and
 - a calcination zone for converting limestone into lime and carbon dioxide in response to said heat energy from said combustion zone, said calcination zone including an inlet for limestone, a conduit for directing the carbon dioxide to said combustion zone for use as a flood gas to control said heat energy, an outlet for directing the lime to a hydration chamber, and a carbon dioxide permeable membrane for separating the carbon dioxide in said calcination zone from other materials in said calcination zone and preventing the other materials from entering said conduit for directing the carbon dioxide.
16. The system according to claim 15, further comprising: a heat exchanger for capturing heat from said calcination zone.
17. The system according to claim 15, further comprising: a heat exchanger for capturing heat from said combustion zone.
18. The system according to claim 15, further comprising: means for feeding lime generated in said calcination zone to said combustion zone.
19. The system according to claim 14, further comprising means for generating electricity.
20. The system according to claim 19, wherein said means for generating electricity include a turbine system.