US 20100077947A1

(19) United States

(12) Patent Application Publication

Hack

(10) Pub. No.: US 2010/0077947 A1

(43) Pub. Date: Apr. 1, 2010

(54) METHOD OF COMBUSTING SULFUR-CONTAINING FUEL

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(21) Appl. No.: 12/238,768

(22) Filed: Sep. 26, 2008

Publication Classification

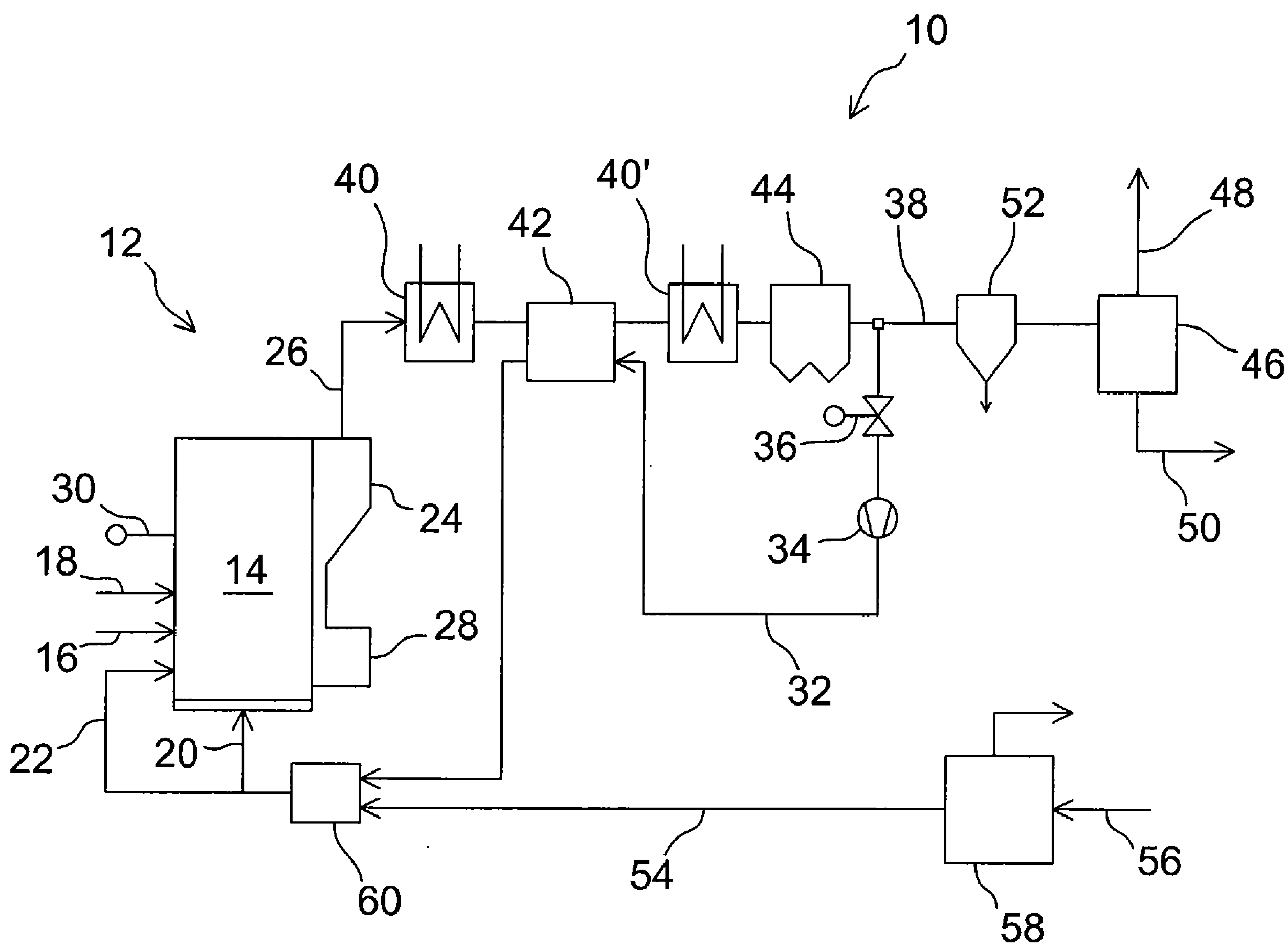
(51) Int. Cl.

F23C 9/00	(2006.01)
F23C 10/00	(2006.01)
F23J 15/02	(2006.01)
F23L 7/00	(2006.01)
F23N 3/00	(2006.01)

(52) U.S. Cl. **110/345**; 110/234; 110/216

(57) ABSTRACT

A method of combusting sulfur-containing fuel in a circulating fluidized bed boiler includes the steps of (a) feeding sulfur-containing fuel into a furnace of the circulating fluidized bed boiler, (b) combusting the fuel with oxidant gas consisting essentially of pure oxygen and circulated exhaust gas, so as to form exhaust gas having carbon dioxide and water as its main components, and (c) feeding calcium carbonate containing material into the furnace so as to capture sulfur dioxide into calcium sulfate in the furnace. The temperature in the furnace is maintained above 870° C.



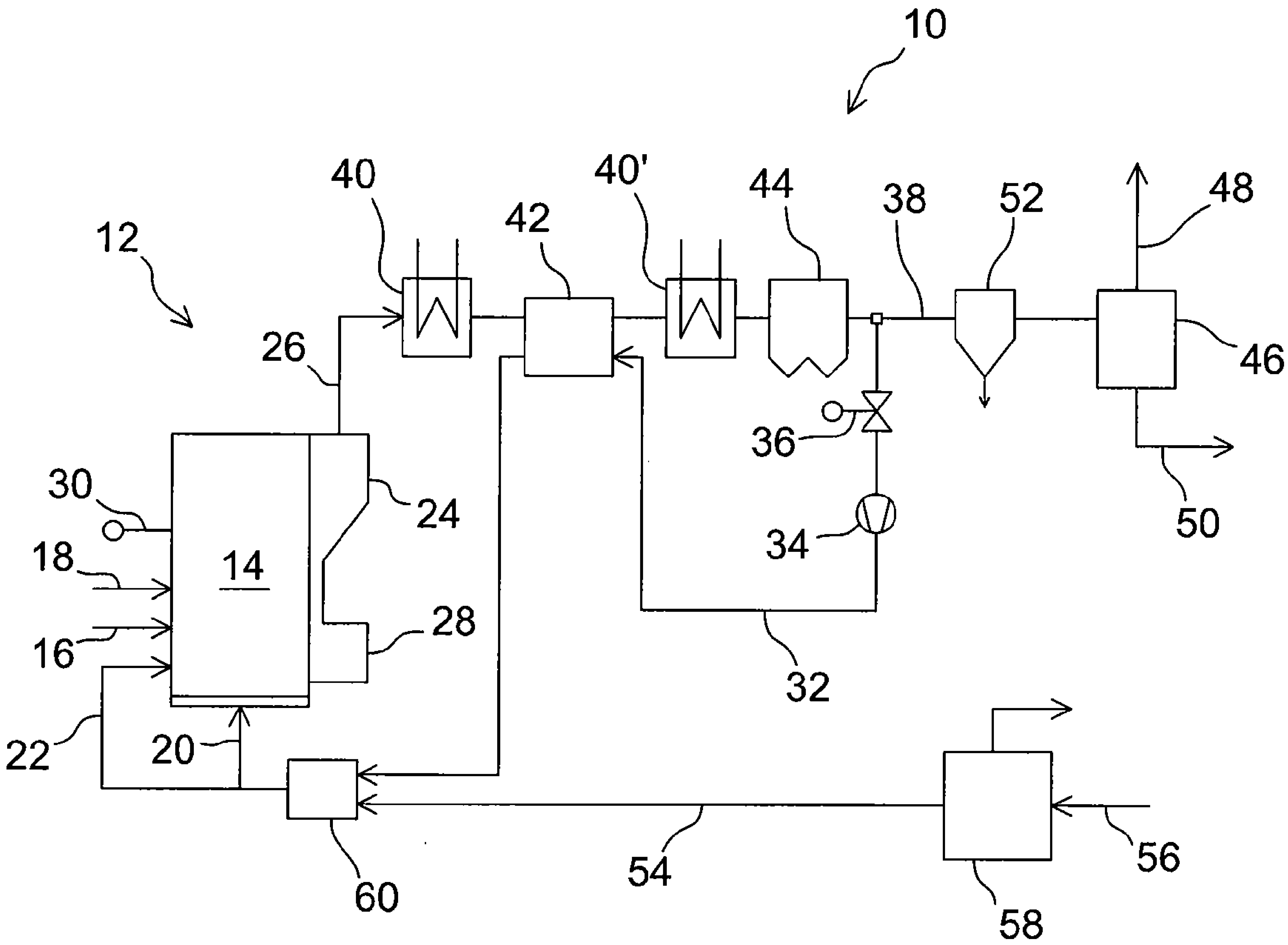

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Fig. 1

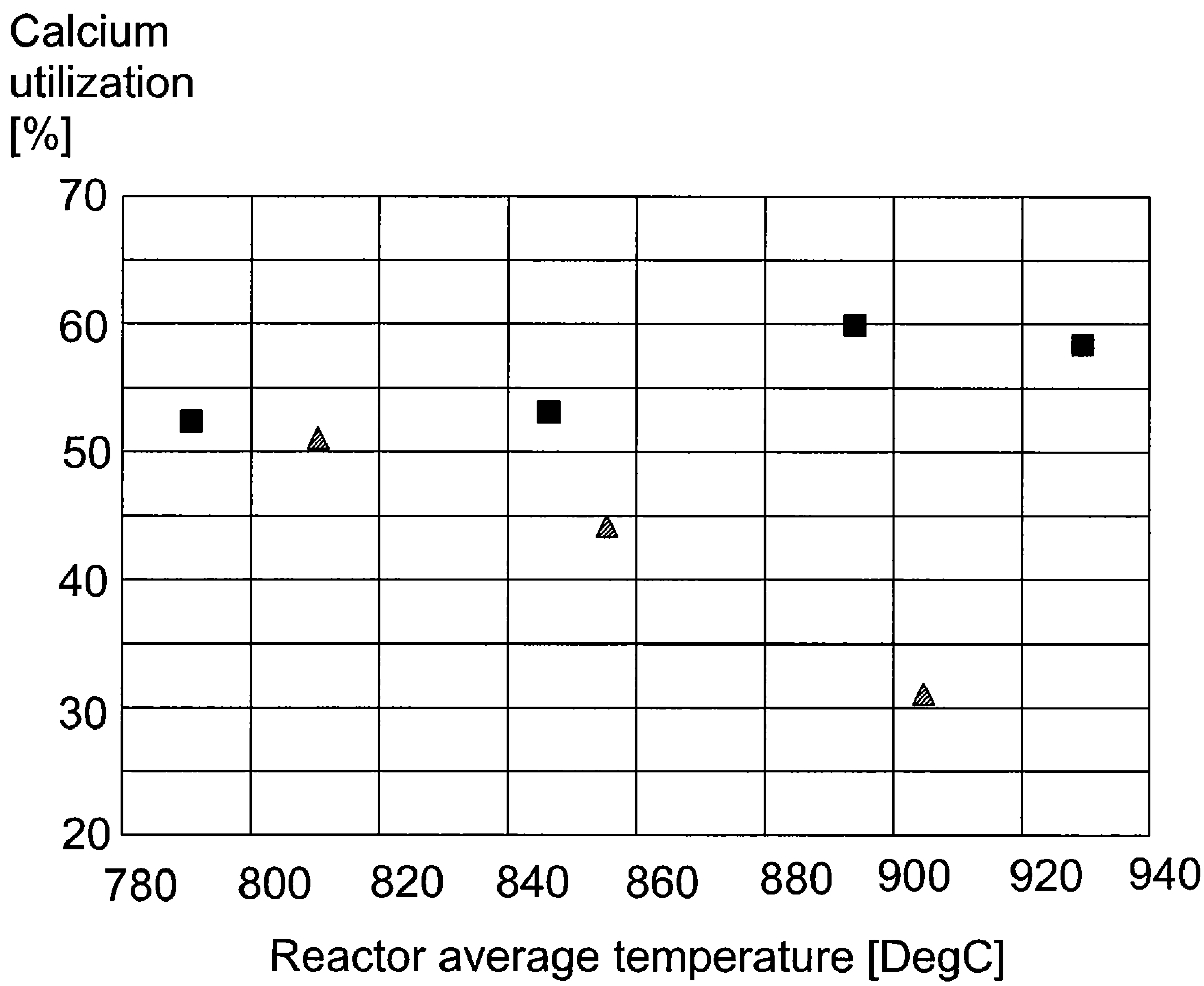
Calcium utilization [%]
70
60
50
40
30
20
780
800
820
840
860
880
900
920
940
Reactor average temperature [DegC]

Fig. 2

METHOD OF COMBUSTING SULFUR-CONTAINING FUEL

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates to a method of efficiently combusting sulfur-containing fuel in a circulating fluidized bed boiler by using oxyfuel combustion, i.e., the fuel is combusted by using pure oxygen or a mixture of a substantially pure oxidant and circulated fluidizing gas as the oxidant gas. The invention especially relates to oxyfuel combustion, in which the fuel is combusted with an oxidant gas having an oxygen content of about the same as that or higher than that of air.

[0003] 2. Description of the Related Art

[0004] Combustion of sulfur-containing fuels, such as coal, generates sulfur dioxide, SO_2, which is an acid rain creating pollutant, if released to the atmosphere. In order to minimize pollution of the environment, today's combustion systems often comprise special equipment, such as an exhaust gas scrubber, arranged in the exhaust gas channel to remove sulfur dioxide from the exhaust gas. Such special equipment is usually expensive to build and to operate.

[0005] When combusting fuel in a circulating fluidized bed boiler, most of released sulfur dioxide is usually already captured in the furnace, by feeding calcium carbonate ($CaCO_3$) containing material, typically, limestone, into the furnace. The calcium carbonate, $CaCO_3$, is calcined in the furnace to calcium oxide, CaO, which captures sulfur dioxide into calcium sulfate, according to the reactions:

$$CaCO_3\text{->}CaO+CO_2 \quad \text{(i)}$$

$$CaO+SO_2+\tfrac{1}{2}O_2\text{->}CaSO_4. \quad \text{(ii)}$$

The formed calcium sulfate can then be removed from the furnace together with the ashes. Thus, a combustion process using a circulating fluidized bed boiler does not need additional sulfur capturing equipment in the exhaust gas channel, or the efficiency of such equipment can be relatively low.

[0006] The reactivity of calcium carbonate to capture sulfur dioxide in a conventional circulating fluidized bed boiler increases with temperature, reaching an optimum value, typically, around 850° C. The optimum temperature may vary depending on the type of the fuel and the sorbent, and other parameters of the process. The efficiency of the capturing of sulfur dioxide drops quite rapidly at temperatures above the optimum. Many explanations are proposed for the reduced capturing at higher temperatures, including sintering of pores of the CaO particles, decomposition of $CaSO_4$ with CO, instability of the intermediate product, $CaSO_3$, and the depletion of oxide in the region of the capturing process. Thus, the process of combusting sulfur-containing fuel, especially, bituminous coal, in a fluidized bed boiler, has, in practice, a desired operating temperature, typically, near to about 850° C. The combustion temperature has an effect to the highest obtainable steam temperature and, thereby, the thermal efficiency of the boiler.

[0007] H. Liu, et al. have suggested in an article published in Fuel (2000) 945-953 that, when using oxyfuel combustion in a fluidized bed, the calcium carbonate based sulfur capture is replaced at temperatures below 850° C. by direct sulfation from $CaCO_3$ to $CaSO_4$. This reaction enables a higher sulfation degree of the calcium, due to the porosity of the $CaCO_3$ particles generated therein by the counter-diffusion of the CO_2.

[0008] At low partial pressures of carbon dioxide, CO_2, prevailing in combustion processes using air as the oxidant gas, the equilibrium of the reaction (i) is, in the typical temperatures of fluidized bed combustion, always on the right hand side, i.e., $CaCO_3$ calcines to CaO. On the other hand, at typical partial pressures of CO_2 prevailing in a circulating fluidized bed boiler when using oxyfuel combustion, for example, at about 0.7 atm, the $CaCO_3$ does not calcine to CaO below a calcination temperature of about 870° C., and SO_2 is captured by direct sulfation. However, above the calcination temperature, $CaCO_3$ calcines to CaO, and direct sulfation should not be important.

[0009] Due to the above-mentioned reasons, there is a need for an improved combustion method of a circulating fluidized bed boiler, in order to improve the thermal efficiency of the boiler, while still effectively capturing sulfur dioxide in the furnace.

SUMMARY OF THE INVENTION

[0010] An object of the present invention is to provide a method of efficiently combusting sulfur-containing fuel in a circulating fluidized bed boiler.

[0011] According to an aspect of the present invention, a method of combusting sulfur-containing fuel in a circulating fluidized bed boiler is provided, the method comprising the steps of feeding sulfur-containing fuel into a furnace of the circulating fluidized bed boiler, combusting the fuel with oxidant gas consisting essentially of pure oxygen and circulated exhaust gas, so as to form exhaust gas having carbon dioxide and water as its main components, and feeding calcium carbonate containing material into the furnace so as to capture sulfur dioxide into calcium sulfate in the furnace, wherein the temperature in the furnace is maintained above 870° C.

[0012] According to other embodiments of the present invention, the temperature in the furnace is preferably maintained above 900° C., even more preferably, above 930° C.

[0013] As is well known to a person skilled in the art of fluidized bed combustion, the temperature in the furnace can be maintained at a desired level by controlling the fuel feeding rate or the cooling rate of the furnace. The heat absorption rate can advantageously be controlled by using a controllable heat exchange chamber arranged in the hot loop of the circulating fluidized bed boiler. The oxygen feeding rate is usually controlled so that substantially complete combustion of the fuel is obtained, and a desired excess oxygen level, typically, about 3%, remains in the exhaust gas.

[0014] The present invention is based on a series of surprising results obtained by the inventor, when adding calcium carbonate to a fluidized bed combustion reactor maintained at different temperatures, when combusting bituminous coal by using a mixture of oxygen and recirculated exhaust gas as the oxidant gas. The results will be discussed in more detail below, in the section entitled DETAILED DESCRIPTION OF THE INVENTION.

[0015] It appears that the conditions giving rise to a decreasing sulfur capture at high temperatures in air-firing fluidized bed boilers are changed in oxyfuel combustion. As a result of the change, the temperature range of decreasing efficiency appears to be removed, or at least shifted to a higher temperature. An improved sulfur capture in the furnace in oxyfuel combustion can be expected, at any temperature, on the basis of the extended time of SO_2 presence in the furnace, due to the recirculation of the exhaust gas. In addition to that, the contents of the gas in the furnace are, in oxyfuel combustion, clearly different than those in air combustion. Thus, the enhanced sulfur capture at high temperatures may be related to the higher content of CO_2 or O_2 in the furnace.

[0016] Similar enhanced sulfur capture at high temperatures has been observed earlier in air-firing fluidized bed boilers when used at elevated pressures of 10 to 20 atm. In that case, the improved sulfur capture at high temperatures is probably related to changing of the sulfur dioxide capturing process to direct sulfation of $CaCO_3$, as described above. In the present case, when enhanced sulfur capture was observed at ambient pressure, and at temperatures above 870° C., the sulfur capturing process remains to be via the route including calcination of $CaCO_3$ to CaO, and direct sulfation is not important.

[0017] The efficiency of calcium carbonate based sulfur capture in a circulating fluidized bed boiler at even higher temperatures, say, above 1000° C., is not yet known. Anyhow, the present observations encourage testing of the sulfur capture up to 1000° C. and above, in order to find the full usable operation range for oxyfuel combustion of sulfur-containing fuels in circulating fluidized bed boilers, in order to obtain high steam temperatures. However, it is clear that a fluidized bed boiler cannot be operated above the softening temperature of the bed, which depends on the fuel, being, for example, about 1100° C.

[0018] The use of combustion temperatures higher than those used in conventional air-firing fluidized bed combustion allows a circulating fluidized bed boiler to generate steam at higher temperatures, while still achieving a high level of in-furnace sulfur dioxide capture. Thus, the present invention helps to facilitate improved steam cycle efficiency in supercritical and ultra-supercritical circulating fluidized bed boiler applications. The boiler is then preferably used to generate steam at a temperature of at least about 650° C., even more preferably, at least about 700° C.

[0019] Preferably, the oxygen content of the oxidant gas used in the process is about the same as that, or somewhat above that of air, i.e., about or above 21%. According to a preferred embodiment of the present invention, the oxygen content of the oxidant gas is about 28%, typically, from about 26% to about 30%. In some cases, the oxygen content of the oxidant gas may be above about 28%, for example, from about 28% to about 40%. In some other cases, the oxygen content of the oxidant gas may be from about 21% to about 28%, for example, about 24%.

[0020] In oxyfuel combustion, when the oxidant gas is a mixture of substantially pure oxygen and recycled exhaust gas, the main components of the exhaust gas are carbon dioxide, water and, for example, about 3% of excess oxygen. The oxygen content of the oxidant gas is thus determined by the recycling rate of the exhaust gas. Thus, for example, an oxygen content of 28% is obtained by recycling approximately 70% of the exhaust gas.

[0021] The average carbon dioxide content in the combustion reactor may alternatively be considered as the key parameter for advantageous oxyfuel combustion of sulfur-containing fuels in fluidized bed boilers. The carbon dioxide content in the furnace depends on the exhaust gas circulation rate and water content of the circulated exhaust gas. According to the present experiments, the average carbon dioxide content in the combustion reactor is advantageously about 70%, typically, from about 68% to about 72%. In other advantageous cases, the average carbon dioxide content in the furnace may be even higher, for example, from about 70% to about 80%, especially, when recycling dry and relatively cold exhaust gas. In still other advantageous cases, the average carbon dioxide content in the combustion reactor is lower than 70%, for example, from about 50% to about 70%.

[0022] The above brief description, as well as further objects, features, and advantages of the present invention will be more fully appreciated by reference to the following detailed description of the currently preferred, but nonetheless illustrative, embodiments of the present invention, taken in conjunction with the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] FIG. **1** is a schematic diagram of a typical circulating fluidized bed combustion reactor used for oxyfuel combustion.

[0024] FIG. **2** is a schematic diagram of experimentally observed calcium utilization in oxygen and air combustion of bituminous coal as a function of average temperature in the combustion reactor.

DETAILED DESCRIPTION OF THE INVENTION

[0025] FIG. **1** shows a schematic diagram of a typical power plant **10** used for oxyfuel combustion of sulfur-containing fuel, such as bituminous coal. The power plant **10** comprises a circulating fluidized bed (CFB) boiler **12** with a furnace **14** comprising conventional means for feeding fuel **16** and calcium carbonate, $CaCO_3$, containing sorbent **18** for capturing sulfur dioxide, SO_2, generated when combusting the fuel with an oxidant gas, to calcium sulfate, $CaSO_4$. The oxidant gas is fed to the furnace as primary oxidant gas **20**, fed through a grid at the bottom of the furnace, and secondary oxidant gas **22**, fed to the furnace at a higher level. Oxidant gas may, in some cases, be fed to the furnace at even more locations and levels.

[0026] Exhaust gas produced by combusting the fuel with the oxidant gas in a fluidized bed formed in the furnace **14** is led from the furnace through a particle separator **24** to an exhaust gas channel **26**. The temperature in the furnace **14** may be controlled to a desired value, to be discussed later, by controlling the fuel feed rate and by a heat exchanger **28** advantageously connected to a return leg arranged for leading separated particles from the particle separator **24** to the lower portion of the furnace **14**. The temperature and, advantageously, temperature distribution in the furnace can be monitored by temperature measuring means **30**, such as thermocouples, arranged at one or more suitable locations in the furnace.

[0027] An exhaust gas recycling channel **32** is branched off from the exhaust gas channel **26**, so as to recycle a portion of the exhaust gas back to the furnace **14**. The exhaust gas recycling channel **32** advantageously comprises means, such as a fan **34** and a damper **36**, for controlling the exhaust gas recycling rate. The rest of the exhaust gas is conveyed through an end portion **38** of the exhaust gas channel **26** for final processing.

[0028] As is conventional, the furnace **14** usually comprises evaporation surfaces, not shown in FIG. **1**, and the exhaust gas channel **26** further comprises heat exchanger surfaces **40**, for example, superheaters, reheaters and economizers, for generating steam by the boiler **12**. For the sake of simplicity, FIG. **1** only shows one such heat exchanger surface **40**, but, in practice, the exhaust gas channel system usually comprises multiple superheating, reheating and economizer surfaces for recovering heat from the exhaust gas.

[0029] A gas-gas heat exchanger **42**, for example, a regenerative heat exchanger, is advantageously also arranged in the exhaust gas channel **26**, downstream of the steam generating heat exchange surfaces **40**, for transferring heat from the exhaust gas to the recycling portion of the exhaust gas. The exhaust gas channel **26** also usually comprises conventional units for cleaning particles and gaseous pollutants from the exhaust gas, which units are schematically represented in FIG. **1** only by a dust separator **44**. Between the gas-gas heat exchanger **42** and the dust separator **44**, there is shown a further heat exchanger **40'**, a low-pressure economizer, which may alternatively be arranged downstream of the dust separator or in the exhaust gas recycling channel **32**.

[0030] In accordance with the main object of oxyfuel combustion, i.e., to recover carbon dioxide from the exhaust gas, having carbon dioxide as its largest component, the end portion **38** of the exhaust gas channel **26** is equipped with exhaust gas processing means, schematically represented by a carbon dioxide processing unit **46**, for cooling, cleaning and compressing carbon dioxide. The carbon dioxide processing unit **46** usually comprises a dryer for completely drying all water from the exhaust gas, and a separator for separating a stream of non-condensable gas **48**, such as oxygen, and other possible impurities, from the carbon dioxide. A stream of carbon dioxide **50** is typically captured in a liquid or supercritical state, at a pressure of, for example, about one hundred ten bars, so that it can be transported to further use or to be stored in a suitable place.

[0031] FIG. **1** separately shows a condensing gas cooler **52**, located upstream of the carbon dioxide processing unit **46**, for initially removing water from the exhaust gas. The condensing gas cooler may be arranged either in the end portion **38** of the exhaust gas channel **26**, as in FIG. **1**, or upstream of the branch point of the recycling exhaust gas channel **32**. In the latter case, the water content in the recycling exhaust gas and in the furnace **14** is minimized.

[0032] The oxidant gas is preferably produced by mixing a stream of substantially pure oxygen **54**, produced from an air stream **56** in an air separation unit (ASU) **58**, and at least a portion of the recycling portion of the exhaust gas in a mixing unit **60**. The air separation unit produces a gas stream consisting essentially of pure oxygen, containing, typically, at least about 95% oxygen. The recycling rate of the exhaust gas is advantageously adjusted such that the resulting gas flow rate in the furnace **14** obtains a desired value, whereby the average O_2 content of the oxidant gas is, typically, close to that of air, preferably, from about 21% to about 28%. In some other cases, the oxygen content of the oxidant gas may be higher, for example, from about 28% to about 40%. It is also possible to introduce the streams of recycled exhaust gas and substantially pure oxygen separately, or multiple streams with different O_2 contents, produced in separate mixing units, at, for example, different heights, into the furnace **14**.

[0033] FIG. **2** shows a diagram of experimentally observed calcium utilization, in percents, in otherwise similar oxyfuel combustion and air combustion processes of bituminous coal as a function of average temperature in the combustion reactor. The calcium utilization is defined as:

Calcium utilization=RET/(Ca/S),

where RET is sulfur retention [%], and Ca/S is calcium to fuel sulfur feed ratio [mol/mol]. Experimental points of oxyfuel combustion are shown as black squares, whereas points measured in air combustion are shown as hatched triangles.

[0034] As can be seen in FIG. **2**, the calcium utilization decreases with temperature in air combustion, from about 50% at 800° C. to about 30% at 900° C. In oxyfuel combustion, the calcium utilization does not show any clear decrease in the temperature range extending up to 930° C. To the contrary, the calcium utilization seems to increase, from slightly above 50% to near to 60%, when increasing the temperature from 800° C. to 900° C.

[0035] The measurements suggest, surprisingly, that, when using oxyfuel combustion, sulfur-containing fuels, especially, bituminous coals, can be advantageously combusted in a circulating fluidized bed boiler at a temperature, which is preferably higher than 870° C., more preferably, higher than 900° C. and, even more preferably, higher than 930° C., while still obtaining efficient sulfur capture in the furnace. Such a combustion process renders operation possible to generate steam at a higher temperature than conventionally, preferably, at a temperature of at least 650° C., even more preferably, at least about 700° C., and to thereby obtain an improved thermal efficiency of the boiler.

[0036] While the invention has been described herein by way of examples in connection with what are, at present, considered to be the most preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments, but is intended to cover various combinations or modifications of its features, and several other applications included within the scope of the invention as defined in the appended claims.

1. A method of combusting sulfur-containing fuel in a circulating fluidized bed boiler, the method comprising the steps of:

(a) feeding sulfur-containing fuel into a furnace of the circulating fluidized bed boiler;

(b) combusting the fuel with oxidant gas consisting essentially of pure oxygen and circulated exhaust gas, so as to form exhaust gas having carbon dioxide and water as its main components; and

(c) feeding calcium carbonate containing material into the furnace so as to capture sulfur dioxide into calcium sulfate in the furnace,

wherein the temperature in the furnace is maintained above 870° C.

2. A method according to claim **1**, wherein the temperature in the furnace is maintained above 900° C.

3. A method according to claim **1**, wherein the temperature in the furnace is maintained above 930° C.

4. A method according to claim **3**, wherein the circulating fluidized bed boiler generates steam at a temperature of at least about 650° C.

5. A method according to claim **4**, wherein the circulating fluidized bed boiler generates steam at a temperature of at least about 700° C.

6. A method according to claim **1**, wherein the sulfur-containing fuel is bituminous coal.

7. A method according to claim **1**, wherein the oxygen content of the oxidant gas is at least about 21%.

8. A method according to claim **5**, wherein the oxygen content of the oxidant gas is from about 21% to about 28%.

9. A method according to claim **5**, wherein the oxygen content of the oxidant gas is at least about 28%.

10. A method according to claim **7**, wherein the oxygen content of the oxidant gas is from about 28% to about 40%.

11. A method according to claim **1**, wherein the average carbon dioxide content in the furnace is about 70%.

12. A method according to claim **1**, wherein the average carbon dioxide content in the furnace is from about 50% to about 70%.

13. A method according to claim **1**, wherein the average carbon dioxide content in the furnace is from about 70% to about 80%.

14. A method according to claim **2**, wherein the sulfur-containing fuel is bituminous coal.

15. A method according to claim **3**, wherein the sulfur-containing fuel is bituminous coal.

* * * * *