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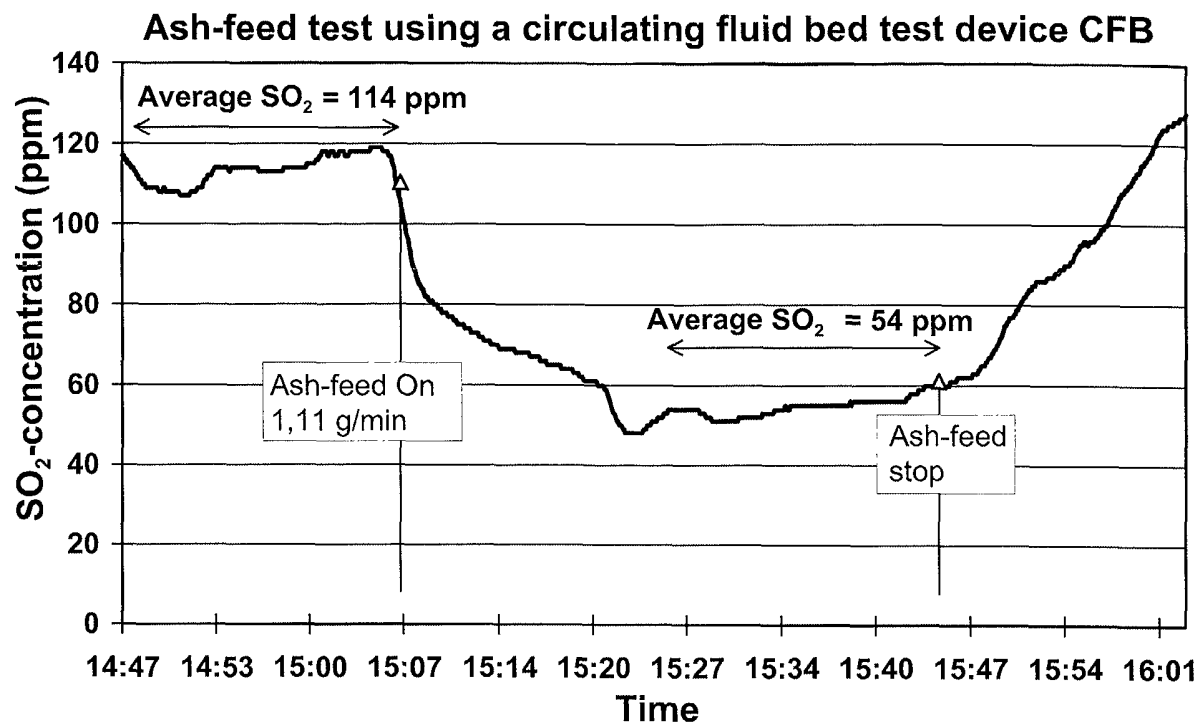
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(54) **Method for sulphur retention in a power plant**

(57) The invention relates to a method for sulphur retention in a power plant, in which, along with a fuel with a sulphur content and air, an additive is added to

the firebox of a thermal boiler, which binds the sulphur dioxide arising in connection with combustion. According to the invention, the said additive is wood ash.

**Fig. 1****EP 1 243 638 A2**

Description

[0001] The present invention relates to a method in sulphur retention in a power plant, in which an additive that binds the sulphur dioxide arising during combustion is added to a fuel with a sulphur content and the air in the firebox of a thermal boiler.

[0002] Stricter environmental regulations and emissions limits will lead in the future to an increase in the costs of cleaning the flue gases of power plants. Tighter limits (of as little as 70 mg/MJ SO₂) have been proposed for sulphur-dioxide emissions in particular, so that it is sensible to attempt to either improve the sulphur retention process, or to begin to use fuels with a lower sulphur content. The replacement of some peat or coal with wood fuels will permit a reduction of the sulphur load of a power plant. However, the high price of wood fuels, for instance, may become a limiting factor to the increase of the use of wood fuels. Wood fuels have a beneficial effect on sulphur dioxide emissions, not only due to their lower sulphur content, but also due to the alkali composition of wood ash, which permits the partial retention of sulphur in wood-ash residue. Thus at present the greatest known benefit of using wood comes from the reduction of the sulphur content of the fuel mix.

[0003] The wood-ash residue that comes from power plants is generally waste, for which a final disposal location must be found. Possible final disposal applications have included fertilizer, forest improvement, landscaping, landfill, etc. However, the high heavy-metal content of wood ash has generally prevented its use as fertilizer and for forest improvement, especially if waste sludge from the forest products industry, for example, is burned with wood.

[0004] The mixing of limestone, for example, with fuel as a sorbent is known for reducing sulphur dioxide in flue gas, when the calcium oxide calcined from the limestone reacts with the flue gases to bind the sulphur dioxide arising in combustion. However, limestone must be quarried and crushed finely and then transported over long distances, thus forming a significant cost in the operating economy of a power plant.

[0005] This invention is intended to create a method, by means of which the use of limestone to reduce the sulphur dioxide in flue gases arising during combustion can be replaced with wood ash that is created as a by-product of wood combustion, but which is useless as such. The characteristic features of the method according to the invention are stated in the accompanying Claim 1. The method according to the invention is characterized at least by wood ash, which is preferably a dry, fine fly ash arising during the combustion of wood, being added to the firebox of a thermal boiler along with air and a fuel containing sulphur. The calcium content of the wood ash used in 10 - 60 %, preferably 30 - 50 %. The preferable feed rate of wood ash to the firebox is 0,5 - 5 % of the total fuel flow. Other characteristics of the method according to the invention appear in the ac-

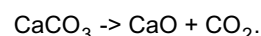
companying Claims.

[0006] The composition and properties of wood ash are advantageous for sulphur retention, as wood ash contains lime. This allows the costs of retaining sulphur in coal and peat-fired power plants to be reduced by using the lime. Savings arise from eliminating the costs of quarrying and crushing limestone, for instance, as wood ash residue can be regarded, except for transportation costs, as a practically free sorbent material. In addition, it can be assumed that the final disposal of ash will become significantly more expensive in the future, so that benefits will come from the net costs of the landfill disposal of ash. Sulphur retention brings no new detriments to the use of ash, on the contrary, the content of detrimental substances (e.g., heavy metals) tends to diminish, if the wood ash used as a sorbent is mixed with the ash of the main fuel. The replacement of even some of the limestone presently used with wood ash will significantly reduce the sulphur-retention costs of power plants.

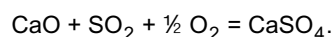
[0007] In the following, the invention is described in greater detail with the aid of tests that have been made and with reference to the accompanying figures, in which

- Figure 1 shows the measurement results of the method according to the invention using a pilot device in peat burning,
- Figure 2 shows the measurement results of the method according to the invention using a pilot device in coal burning.
- Figure 3 shows the measurement results of the method according to the invention in peat burning on a power-plant scale.

[0008] Wood ash contains a significant amount of calcium (Ca), the content of which is usually c. 200 - 400 g/kg, of which as much as 75 % is calcium oxide. When, according to the state of the art, limestone (CaCO₃) is used as a sulphur-retention sorbent in the firebox of a power plant, the limestone calcines under the effect of the temperature (+520 °C - +850 °C) into calcium oxide (CaO):



[0009] In the sulphur-retention process, the CaO reacts with the SO₂ in the flue gas to form calcium sulphate (CaSO₄):



[0010] Pilot runs made using a circulating fluid bed test device (CFB) were used to ascertain the ability of wood ashes obtained from boiler plants to bind sulphur oxides, when burning fuels with a sulphur content (e.g.,

milled peat, coal). The wood ashes used in the research came from thermal boilers burning wood fuels, preferably fly ash from a fluid bed boiler (FBC) and a grate boiler. The wood ash used should be dry and fine, like the limestone typically fed into the combustion. The pilot runs were compared with feeding limestone into a fluid bed.

[0011] The following clarifications are intended to facilitate interpretation of the results of the combustion tests being described. The binding of sulphur to the ash is depicted as the conversion of sulphur oxide. If the flue gas emissions of sulphur diminish in relation to the sulphur content entering the combustion process, this conversion is regarded as a reduction, i.e. the smaller the said conversion, the more effectively the sulphur coming from the fuel binds to the wood ash.

[0012] The optimal temperature in sulphur retention is about +800 °C in a fluid bed (FBC) and +850 °C in a circulating fluid bed (CFB), with an oxygen content of 5 - 6 %. At higher temperatures (> +1000 °C), the desulphuration efficiency decreases partly due to sintering of the CaO, so that the pores of the CaO become blocked and the particle size increases. Binding of the sulphur can also be optimized with good mixing and a sufficient amount of air, as the removal of sulphur oxide is based on oxidizing it to form a sulphate. Once the sulphur is bound as sulphate compounds, it exits the combustion along with fly ash into particle separators, such as electrical filters, where it is separated from the flue gases in a known manner.

[0013] Limestone is fed into the firebox in a suitable Ca/S ratio in relation to the sulphur content of the fuel. When calculating the calcium/sulphur ratio of the wood ash, 30 % was used as the average proportion of calcium for both wood ashes. The so-called total calcium amount in question was determined using the XRF method.

[0014] Research to validate the method according to the invention was carried out using a pilot device of the circulating fluid bed (CFB) type. In the tests, the fuel used was pure peat, with a sulphur content of 0,2 %, an ash content of 4,53 %, a moisture content of 42 %, and a thermal value of 11,4 MJ/kg. During the test when burning pure peat, the average sulphur-dioxide content of the flue gas was 114 ppm and the oxygen content 4,1 %. The maximum SO₂ content for peat containing 0,2 % sulphur was 206 ppm. The SO₂ content measured in the test corresponded to an emission of 111 mg/MJ, being thus quite low. The conversion of the sulphur in the flue gas into sulphur dioxide was correspondingly 114 ppm / 206 ppm, i.e. 55 %. 45 % of the peat's sulphur thus remained in the peat ash.

[0015] Figure 1 shows the effect of wood ash on the sulphur-dioxide emission of the circulating fluid bed combustion of peat. The feed of the wood ash commenced at 15:06, the SO₂ content dropping sharply immediately. The feed of the wood ash was terminated at 15:45, after which the SO₂ content rose slowly to the

values prevailing before the feed. When 1 g/min, i.e. 0,8 % of the total fuel flow, was fed into the reactor with the peat, an average sulphur-dioxide content of 54 ppm was measured in the flue gas when the oxygen content was 5,8 %. The measured sulphur-dioxide content corresponds to a sulphur-dioxide emission of 59 mg/MJ, the SO₂ conversion being 29,5 %. The wood ash fed in reduced the sulphur-dioxide emission by 46 %. The calculation was carried out using a process balance calculation program, which took into account factors such as the effect of the change in the oxygen content on the conversion of the sulphur oxide.

[0016] Figure 2 shows the effect of feeding wood ash on the sulphur-dioxide emission of the circulating fluid bed (CFB) combustion of Polish coal. Feed of the wood ash was commenced at 14:30 and terminated at 15:15. The calcium/sulphur ratio in the test was 1,9. In this test, fly ash from a fluid-bed boiler (FBC) was used as the sorbent. The maximum sulphur dioxide content of the flue gas was 514 ppm, using coal with a sulphur content of 0,88 %. In the test, the boiler was fed with a fuel mass flow of 1,2 g/s, the sulphur dioxide content of the flue gas being measured as 296 ppm when the oxygen content was 6,7 %. The conversion of the sulphur in the flue gas into sulphur dioxide was 57,7 %. The SO₂ content measured corresponds to an emission of 374 mg/MJ.

[0017] When wood ash was fed into the boiler with the coal at a mass flow of 0,0775 g/s, the sulphur dioxide content dropped to a level of 145 ppm. A conversion of sulphur dioxide during the feed of the wood ash of 28,2 % was obtained, corresponding to a sulphur dioxide emission of 183 mg/MJ. The effect of the wood ash caused the sulphur dioxide content to drop by as much as 51 %.

[0018] The sulphur dioxide contents of Figure 2 were measured from the flue-gas duct using a continuous-operation flue-gas analyser. The figure shows that the sulphur dioxide content of the combustion of the coal did not return to the previous emission level immediately after the ending of the feed of the wood ash, mainly due to the slight accumulation of ash on the walls of the post-separation cyclone during the feed of the wood ash. The continual deduction in the sulphur dioxide content during the wood-ash feed also seems to be due to the accumulation of ash. The calculations of average content were therefore made from short stable time periods.

[0019] The power-plant-scale sulphur-retention test, which was carried out to test the method according to the invention, took place in a circulating fluid bed boiler, in which combined combustion of peat and wood had taken place recently. The combustion plant had usually achieved the sulphur dioxide emission limit (140 mg/MJ) by using limestone in sulphur retention. During 1999, an average of about 160 tonnes of lime was consumed each month in the plant. Besides the circulating fluid bed boiler, the power plant also operates an older fluid bed boiler (FBC), which at present burns wood fuels (including woodchips, sawdust, bark, logging-waste chips).

This means that the use of the wood ash available from the fluid bed boiler in the sulphur retention of the circulating fluid bed combustion (CFB) would be extremely profitable in both financially and in terms of environmental protection.

[0020] Wood ash, which was fly ash from the fluid bed boiler, was used as the ash sorbent. The calcium content of the wood ash was about 37 %. In the fluid bed boiler, from which the wood ash came, wood, birch and spruce bark, and plywood off-cuts were burned. During the sulphur-retention test, milled peat with an average sulphur content of 0,25 % and an effective thermal value in solids of 20,89 MJ/kg, was burned in the circulating fluid bed boiler. The average moisture content of the peat was 52 - 54 %.

[0021] The following reviews in greater detail the performance and results of the sulphur-retention test, carried out over two days. The peat for combustion was transported to the circulating fluid bed boiler using two conveyor belts. During the test, feed screws of the lime were used to feed wood ash to the peat lines. The flow of peat to the boiler was kept constant during the sulphur-retention test. The average mass flow of peat to the boiler was about 13 kg/s.

[0022] The wood ash was fed into the boiler in a so-called lime/peat ratio of 1,0 - 1,5. The ratio was based on the speed of rotation of the additive and fuel feed screws. The total wood ash feed time on the two tests days was about 15 hours, the average mass flow being 0,12 kg/s. The power plant's process controllers were used to try to keep the mass flow of the wood ash into the boiler at 0,15 kg/s. In this connection, it should be noted that the process calculations were calibrated according to the weight of the lime (about 1500 kg/m³). At a wood ash mass flow of 0,15 kg/s, the calculated calcium/sulphur ratio was about 2,9.

[0023] The feed of the wood ash into the peat lines could not be stabilized during the test, because the ash arched in the feed silos and the limit switches controlling the feed did not operate properly. Figure 3 shows the amount of sulphur dioxide (mg/m³n) measured from the wet flue gas and the sulphur-dioxide emission (mg/MJ) on the second day of the test. Wood-ash feed to the peat line was commenced between 07:15 and 07:30 when the mass flow was in the order of 0,11 kg/s. At a wood-ash mass flow of 0,11 kg/s, the calculated calcium/sulphur value was about 2,1.

[0024] Prior to the feed of wood ash, the amount of sulphur dioxide in the peat line was at a level of 414 mg/m³n, the amount of sulphur dioxide averaging 120 mg/m³n during the feed of wood ash and dropping at times to as little as under 100 mg/m³n. This gives a separation of sulphur dioxide using wood ash averaging about 70 %.

[0025] It can be seen from Figure 3 that the wood ash feed operated only momentarily. However, the figure clearly shows that wood ash reduces the sulphur dioxide emission of the circulating fluid (CFB) combustion of

peat at a power-plant scale too.

[0026] In energy production, desulphuration methods are usually based on the exploitation of calcium compounds. Pilot-scale research carried out using circulating fluid bed test devices (CFB) too have shown that pure wood ash has a considerable sulphur retention potential in the circulating fluid bed combustion of peat and coal. The active substance of wood ash in sulphur retention is calcium - in the form of calcium carbonate or oxide. The recommended proportion of CaO in the composition of wood ash used in sulphur retention is roughly 40 %. The desulphuration efficiency of wood ash may also be influenced by factors other than the high calcium content. Such factors are, for example, the relatively high contents alkali metals, such as magnesium, sodium, and potassium, in wood ash and physical properties such as porosity. Naturally, it is good if there is as little sulphur as possible in the wood ash. According to the method according to the invention, pure wood-based ash can be used to replace lime in the reduction of the sulphur dioxide emissions of power-plant boilers.

[0027] According to the results obtained from the pilot tests, the sulphur dioxide emissions of the circulating fluid combustion of peat with a sulphur content of 0,2 %, were reduced by the use of wood ash by as much as 45 %, using a calcium/sulphur ratio of 1,5. Correspondingly, the sulphur dioxide emissions of the combustion of coal, with a sulphur content of 0,88 %, were reduced by more than 50 %.

[0028] In the sulphur retention tests, wood-based ashes of different origin were used, demonstrating that, besides controlled optimal combustion conditions, the composition of the ash is the dominant property in sulphur retention. The composition of wood ash depends greatly on the wood material burned and partly even on its origin. The manner of burning, in order to produce the wood ash, on the other hand, was found to have no significance. The heavy metal contents of wood ash that generally restrict its use as a fertilizer do not limit its sulphur-retention properties.

[0029] An example calculation of the method according to the invention can be made for a 300-MW power plant, which uses coal with a sulphur content of 0,7 weight-% as fuel. The annual fuel consumption of such a power plant is 259 300 t of coal, with an energy content of 8,33 Mwh/t, giving an annual energy amount of 2160 GWh. This contains 1815 t of sulphur, i.e. 56 722 kmol. In order to achieve the required SO₂ emission limit, lime must be added to the process usually in a Ca/S ratio of 2 - 2,5. In this case, the Ca/S ratio is assumed to be 2,0, so that the amount of lime required annually is 113 444 kmol, i.e. 11 340 t. If the price of limestone is FIM 250/t, the annual lime costs are FIM 2,8 million.

[0030] In industry and district-heating production in Finland, a total of 23,4 million bm³ (bulk m³) were used in 1994, of which bark, for instance, accounted for more than 75 %. If the present total amount of wood fuels used is reckoned to be about 25 million bm³, most of it bark

and logging waste, the ash content of the wood fuel can be calculated on this basis to be 1,5 - 2,5 %, the moisture content 55 %, and the bulk density 350 kg/bm³. The amount of wood used in 8,75 million tonnes, of which solids are 3,94 million tonnes, and ash, calculated at a 2-% content, 78 750 tonnes. The wood ash contains 39 000 tonnes of calcium and other carbonates, which can bind 5 000 tonnes of sulphur at a Ca/S ratio of 2,5, in other words, a maximum of 10 000 tonnes of SO₂ emissions can be reduced annually.

[0031] In 1996, the sulphur dioxide emissions of energy production were about 53 000 tonnes and those of industry a corresponding 48 000 tonnes. If the wood ash could be utilized in its entirety in sulphur retention, its total effect would be to reduce SO₂ emissions by about 10 %. Even though the utilization of such wood ash were only 10 - 20 % of the total amount of ash, its effect would be to clearly reduce total emissions. From the point of view of individual plants, the application of the method according to the invention will achieve highly significant benefits, in the form of an improvement of operating economy and in meeting the conditions of emissions permits.

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Claims

1. A method in sulphur retention in a power plant, in which, along with a fuel with a sulphur content and air, an additive is added to the firebox of a thermal boiler, which binds the sulphur dioxide arising in connection with combustion, **characterized in that** the said additive is wood ash.
2. A method according to Claim 1, **characterized in that** the wood ash is dry and fine fly ash arising in combustion.
3. A method according to Claim 1 or 2, **characterized in that** the calcium content of the wood ash is 10 - 60 %, preferably 30 - 50 %.
4. A method according to any of Claims 1 - 3, **characterized in that** the feed rate of the wood ash is 0,5 - 5 % of the total fuel flow.
5. A method according to any of Claims 1 - 4, **characterized in that** the fuel and the wood ash are mixed together prior to their being added to the firebox.
6. A method according to any of Claims 1 - 5, **characterized in that** the wood ash is in a solid, particulate form.

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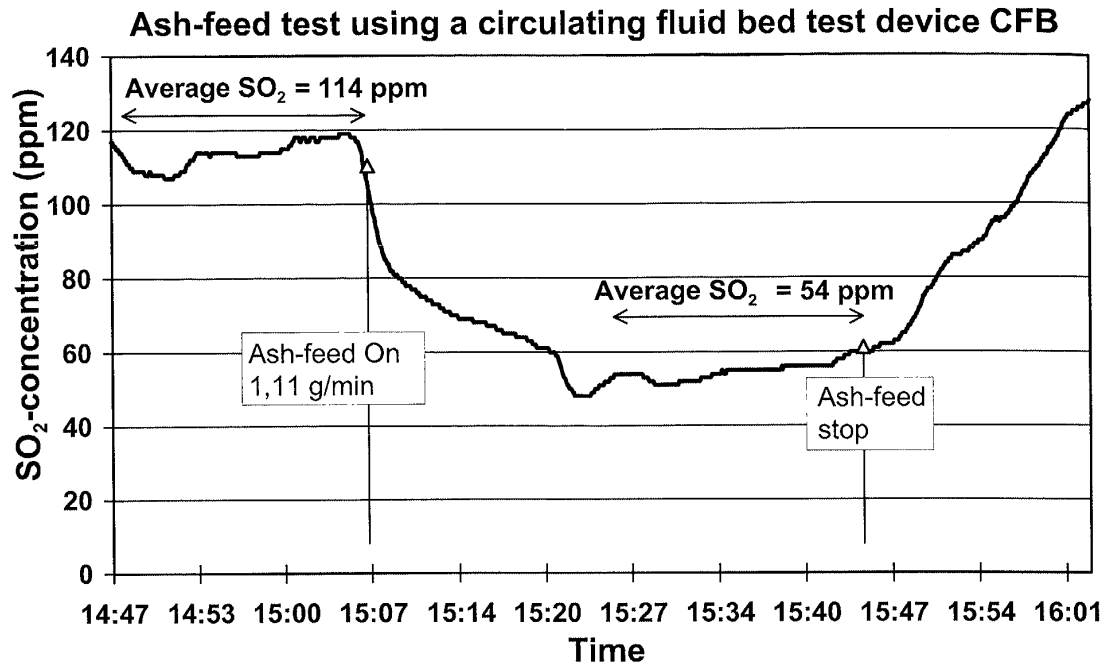


Fig. 1

Fluid bed boiler fly ash feed test using a circulating fluid bed test device

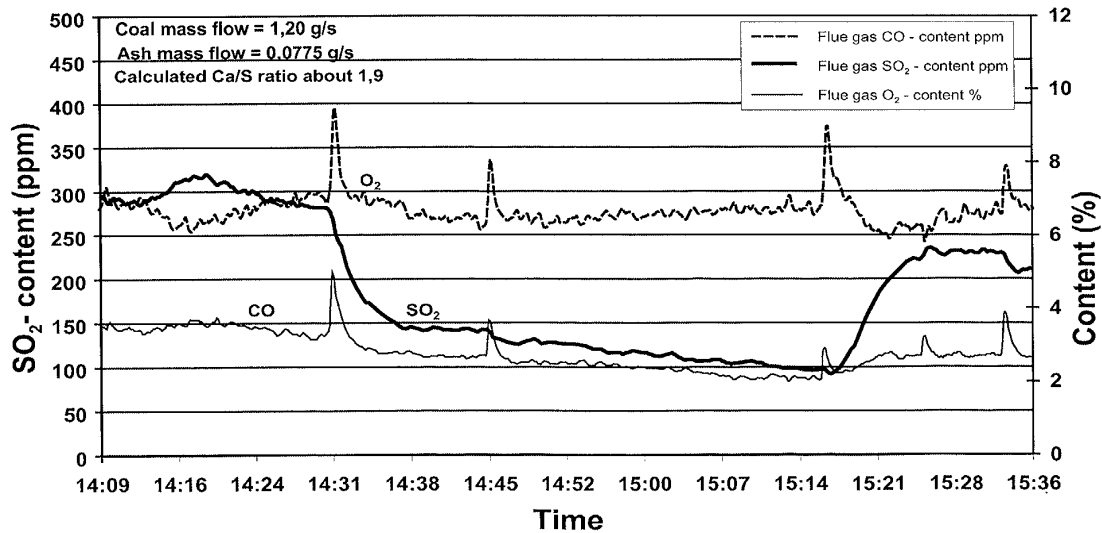


Fig. 2

Power-plant test using a CFB-boiler,
wood ash feed to peat line

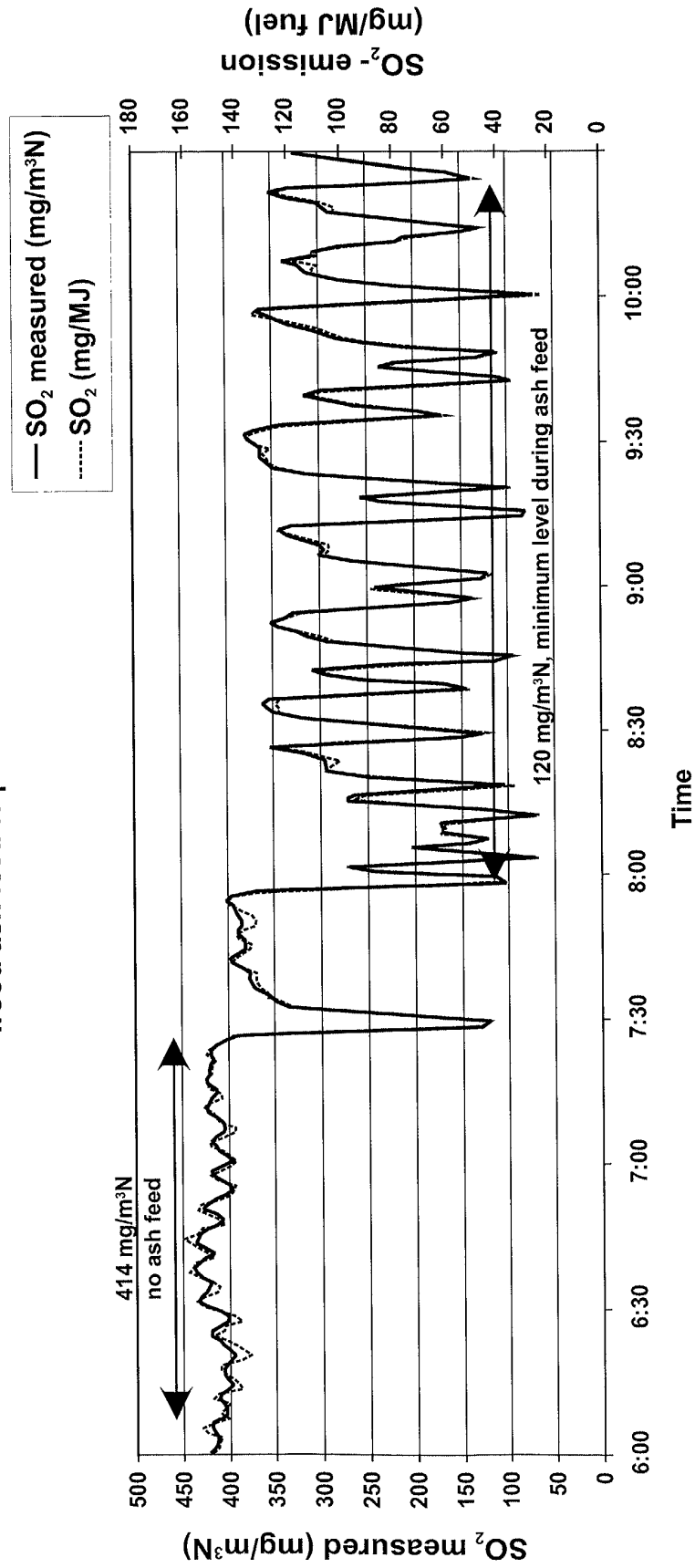


Fig. 3