(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 042 367**
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **81850107.4**

(22) Date of filing: **11.06.81**

(51) Int. Cl.³: **C 10 L 10/00**, C 10 L 1/12, F 23 J 7/00

(30) Priority: **16.06.80 US 159457**

(43) Date of publication of application: **23.12.81 Bulletin 81/51**

(84) Designated Contracting States: **AT DE FR GB IT SE**

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(54) Method for reduction of sulfur content in exit gases.

(57) A method for reducing the emissions of sulfur dioxide and sulfur trioxide in exit gases resulting from the burning of sulfur bearing fuels, which includes the step of igniting at least a member selected from the group consisting of alkaline earth metal nitrates, alkali metal nitrates and ammonium nitrate simultaneously with the igniting of the fuel. The method provides for the burning of high sulfur content fuels while maintaining strict environmental emission requirements established for lower sulfur content fuels.

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METHOD FOR REDUCTION OF SULFUR CONTENT IN EXIT GASES

Field of the Invention

The present invention relates generally to the field of pollution control and more specifically to the reduction of sulfur dioxide and sulfur trioxide emissions in exit gases from combustion systems.

Background of the Invention

Society has become increasingly aware of the existence of the dangers of pollution in all areas of life and great emphasis has been placed on the curbing of pollution. One area of pollution has been the emissions from industrial and utility combustion plants. Federal and State Government agencies have established regulations governing the emission of sulfur dioxide and sulfur trioxide in exit gases from combustion systems. These regulations have included the establishment of maximum level requirements of the sulfur dioxide and sulfur trioxide content in the exit gases. For example, one such regulation (at the time of

this writing) requires that exit gases contain 0.2 lbs. or less of sulfur dioxide per million British Thermal units (BTUs) in the fuel. Prior to the present invention, these level requirements have prompted experts to seek the use of low sulfur content fuels, or to install expensive scrubbing systems, or both.

In some areas, the state and/or Federal agencies responsible for the control of emission levels obtained legislation regulating the sulfur content of the fuels to be burned. This legislation has demanded the burning of the low sulfur content fuels and has imposed the regulation on both buyers and sellers of fuels. The low sulfur content fuels require special processing by suppliers. The significantly higher costs or the lower sulfur content fuels are reflected in the higher costs to all consumers. The continually increasing costs for low sulfur content fuels have been an inducement to utilities and others using those fuels to find methods for improving overall efficiencies which would reduce the total cost for generating power.

High sulfur content fuels are significantly less expensive than low sulfur content fuels; high sulfur content fuels are more readily and easily available, and high sulfur content fuels have significantly higher heating values than do low sulfur content fuels. In an attempt to allow the use of high sulfur content fuels, the regulatory agencies have established programs requiring the use of scrubbing systems designed to remove the objectionable sulfur dioxide and sulfur trioxide components in the exit

gases. These scrubbers are required in installations burning fuels at 250 million BTUs per hour or higher, and where the exit gases contain more than 0.2 lbs. of sulfur dioxide per million British Thermal Units in the fuel. The scrubbers have high maintenance costs and require speciel handling of the extracted products. The scrubber units are estimated to cost between 70 - 100 million dollars each depending upon the systems to which they are attached. The regulations governing the use of scrubbers apply to new installations. Existing installations must be operated at the Environmental Protection Agency (EPA) designated levels. This significant increase in the capital investment is passed on to the consumer in the form of higher power costs. The net effects of the overall emission control and regulation, apparently, have been significantly higher fuel costs, reduced heating values of the fuels required to be used, and higher costs for generating poser.

Summary of the Invention

Briefly described, the present invention comprises a method for reducing the sulfur dioxide and sulfur trioxide content in the emission gases of combustion systems. The invented method includes the igniting of the sulfur bearing fuels or products with a member selected from the group consisting of alkaline earth metal nitrates, alkali metal nitrates and ammonium nitrate and maintaining low emission levels of sulfur dioxide and sulfur trioxide in the exit gases. The invention will in the following be described with special reference to use of alkaline earth

metal nitrate which is a preferred compound.

The alkaline earth metal is metered into the fuel system at a point in time prior to actual ignition of the fuel and at a predetermined rate which may be varied to satisfy the reduction levels desired by the user. The fuel and alkaline earth metal nitrate are ignited simultaneously and, during the igniting process, the alkaline earth metal nitrate reacts with the sulfur and oxygen present to form alkaline earth metal sulfides, sulfites, sulfates and other sulfur bearing compounds thus preventing large quantities of sulfur from forming sulfur dioxide and sulfur trioxide.

It is therefore, an object of the present invention to provide an easy, economical method for reducing the emissions of sulfur dioxide and sulfur trioxide in the exit gases.

Another object of the present invention is to provide a method for the burning of high sulfur content fuels while maintaining required low levels of sulfur dioxide and sulfur trioxide contents in exit gases.

Yet another object of the present invention is to provide a method for a sulfur bearing fuel combustion system which produces exit gases including emission levels of less than or equal to 0.2 lbs. of sulfur dioxide per million BTUs of fuel and thus eliminating the need for purchasing and maintaining expensive scrubber units.

Still another object of the present invention is to provide a method for a sulfur bearing fuel combustion system which makes effective use of existing fuel resources

(such as high sulfur bearing fuels), reduces, the need for fuel suppliers to produce expensive low sulfur content fuels, reduces fuel costs to utilities and industry, provides savings which can be passed on to consumers and reduces sulfur pollutants in the air. Other objects, features and advantages of the present invention will become apparent upon reading and understanding the remaining specification.

Brief Description of the Drawing

The figure is a representative schematic of a power generating plant utilizing the method of the present invention.

Detailed Description of Preferred Embodiment

Referring now in greater detail to the drawing, the figure depicts a preferred embodiment of the process of the present invention. The present invention relates to a unique and inventive application of a specific calium nitrate in power generating units 12 and other combustion systems to reduce the harmful pollutants resulting from the burning of sulfur bearing fuels and other sulfur bearing products.

Sulfur bearing fuel oil or other sulfur bearing products are fed through feed lines 14 from their storage resevoir 16 to the combustion chamber 18 of a power generating unit 12. As the fuel approaches the combustion point 19 a quantity of the calcium nitrate is injected into the feed line 14 and thus into the fuel stream. The injection of the specific compound to the fuel is done

preferably immediately prior to the combustion point 19. The calcium nitrate and the sulfur bearing fuel are ignited simultaneously at the combustion point. The calcium nitrate in the presence of the heat of the burning fuel, reacts with sulfur of the fuel oil and oxygen forming calcium sulfides, sulfites, sulfates, and other sulfur bearing compounds which generally fall out of the combustion site into waste bins 20. As more sulfur is used up in the formation of various sulfur compounds, less sulfur remains to escape through the exhaust pipes or stacks 21 in the form of oxides, i.e. sulfur dioxide and sulfur trioxide.

In the preferred embodiment of the present invention, the metals ignited with the fuel are initially present in the form of nitrates. The particular compound chosen will be a matter of the user's choice depending upon the availability, cost, wanted and unwanted side effects such as odors, benefits to combustion units, etc., and other factors.

Calcium nitrate $Ca(NO_3)_2$ reacts with the sulfur in the fuel as seen in the following chemical formulations:

$$S + O_2 \longrightarrow SO_2$$

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

$$SO_3 + H_2O \longrightarrow H_2SO_4$$

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$2H_2SO_3 + O_2 \longrightarrow 2H_2SO_4$$

$$2Ca(NO_3)_2 \xrightarrow{\Delta} 2Ca(NO_2)_2 + 2O_2$$

$$Ca(NO_2)_2 \xrightarrow{\Delta} CaO + N_2O_3 + O_2$$

$$CaO + H_2SO_4 \longrightarrow CaSO_4 + H_2O$$

Representative formulations for the reactions of the nitrates are as follows:

$$2RNO_3 \xrightarrow{\Delta} 2RNO_2 + O_2$$

$$2RNO_2 \xrightarrow{\Delta} R_2O + N_2O_3$$

$$R_2O + H_2SO_4 \longrightarrow R_2SO_4 + H_2O$$

$$2RNO_3 + H_2SO_4 \longrightarrow R_2SO_4 + HNO_3$$

where R is selected from the group consisting of ammonium, barium, calcium, lithium, magnesium, potassium, sodium and strontium.

The above formulas are submitted only as an indication of the performance of the complete class of nitrate compounds which could be used in place of the calcium nitrate shown above.

For the purposes of this invention, in the preferred embodiment, the specific nitrate compound is placed in a liquid state, solution, emulsion or dispersion, prior to mixing with the fuel. Most preferably, the compound is in an aqueous solution, although a suitable solvent or emulsifier other than water is contemplated hereby.

With reference again to the figure, the calcium nitrate preferably in the form of an aqueous solution of salt, is stored in a metering tank 22 from

which the solution is metered into the fuel line 14. Where large quantities must be used, the solution is held in a holding tank 23 from which it is pumped to the metering tank 22. The solution (thus the alkaline earth metal nitrate) is metered into the fuel line 14 at the point of combustion 19 or just prior to the point of combustion at a variable rate based on a unit quantity of sulfur bearing fuel or other sulfur bearing products and on the amount of reduction desired in the sulfur dioxide and sulfur trioxide in the exit gases.

Although the preferred embodiment calls for metering the alkaline earth metal nitrate into the system at the point of combustion or immediately prior thereto, it is within the scope of this invention to "pretreat" the fuel or other sulfur bearing product. That is, the alkaline earth metal nitrate, in its appropriate form, is injected into the liquid fuel (or dispersed onto a solid fuel) at any time prior to ignition, even for example, while the fuel is in the storage resevoir 16.

As a result of the combustion of a sulfur bearing fuel containing the described chemical there is a significant reduction in the sulfur content of exit gases. This reduction is further supported by spectrographic analysis date which indicate the increased formation of various sulfur compounds and other reaction products in excess of those normally formed without the use of the described chemical treatment of sulfur bearing fuels in the described combust-

ion system. The calcium level in the spectrophotometrically measured ash remained essentially the same throughout the treatment schedule. This indicates the formation of a consistant calcium reaction product irrespective of the length of the time the described chemical was added to the fuel. However, other elements as spectrophotometrically measured in the ash show significant increases in reaction products during the length of time the described chemical was added to the fuel. The longer the described chemical was added to the fuel, the higher were the reaction products of these other elements in the ash. Therefore, these additional reactions appear to be catalytic and the results of the addition of the described chemical to the fuel are supported by the chemical analyses of the sulfur content of the ash. One of the more important reaction products contains vanadium and the spectrographic data clearly shows that the use of the described chemical resulted in additional vanadium products containing sulfur as well as vanadium products containing other elements. In addition, other metals as indicated in the spectrographic analyses have formed reaction products and the overall effect of the treatment of the sulfur bearing fuel with the described chemical is the formation of reaction products in excess of those expected. The relatively low use level of the described chemical indicates a catalytic formation of various sulfur compounds and other reaction products not previously obtained.

Whereas some references in this disclosure may discuss the present invention in terms relating to the treatment of liquid fuels and products, no limitations are intended thereby. Rather, the fuel and sulfur bearing products discussed herein expressly include solid fuels and products, such as a sulfur bearing coal. The term "injecting into the fuel" shall be read to include the "dispersing onto" solid fuels. "Fuel Stream" and "fuel Line" shall be read to include the appropriate reference to handling of solid fuels.

EXAMPLES

Applicant offers the following examples as samples of the invented process, depicting a preferred embodiment.

PREAMBLE: ≠≠6 fuel oil with 1.8 % sulfur content was ignited and burned at a rate of twenty-four (24) gallons per minute (1440 gal/hr) in a typical manner known in the art, in a power unit of a generating station. The power unit was operated at full power, and exit gases were exhausted into and through the station's exhaust stack. For purposes of later comparison, repeated samplings and analyses of the exhaust gases were made at a point half way up the stack. The analyses of the exit gases resulting from the fuel burned in accordance with the prior art methods showed consistantly similar measurements of the total sulfur (SO_2 + SO_3) content of the exit gases, which averaged to approximately 2.69 mg sulfur (SO_2 + SO_3) per 15 liters of exit gas.

Example 1 In accordance with the present invented process, a solution of calcium nitrate was added to and ignited with the fuel oil at a rate of four (4) gallons of calcium solution per hour. The solution was injected into the fuel stream by known metering methods and devices, at a point immediately prior to the point of ignition. Metering of the solution into the fuel stream immediately prior to ignition aided in assuring that the solution was ignited at the same rate at which it was metered into the fuel stream. The power unit continued to operate at full power and exit gases were exhausted through the stack in the typical manner. Repeated samplings and analysis of the exit gases taken as above mentioned, discloses that the fuel oil with 1.8 % sulfur, burned in accordance with the method of the present invention, consistently resulted in exit gases averaging 0.19 mg sulfur (SO_2 + SO_3) per 15 liters of exit gas.

The solution of this example was 50 % aqueous solution of technical grade calcium nitrate. The calcium nitrate, tech., is that supplied by Hummel Chemical Company, Inc., having the chemical formula $5Ca(NO_3)_2\ NH_4NO_3\ 10H_2O$. The following chemical formulations and explanation illustrate the theoretical reactions evidenced in this example:

$$2Ca(NO_3)_2 \longrightarrow 2Ca(NO_2)_2 + 2O_2$$

$$Ca(NO_2)_2 \longrightarrow CaO + N_2O_3 + O_2$$

$$CaO + H_2SO_4 \longrightarrow CaSO_4 + H_2O$$

$$NH_4NO_3 \longrightarrow N_2O + 2H_2O$$

$$2N_2O \longrightarrow 2N_2 + O_2$$

H_2SO_4 is formed when SO_2/SO_3 is in the presence of water vapor. Since both water vapor and SO_2/SO_3 are present upon combustion of sulfur bearing fuels, H_2SO_4 mist is formed as temperatures drop. When aqueous alkali metal compounds are atomized into or onto the sulfur bearing fuel at the hottest part of the flame, at combustion point, the above reactions take place almost instantaneously converting the SO_2/SO_3 into neutral alkali sulfates as a dense precipitating particulate.

Example 2 The calcium nitrate solution of Example 1, at a rate of six (6) gallons per hour, and the ≠≠6 fuel oil with 1.8 % sulfur, at a rate of 1416 gallons per hour, were burned together in the power unit of operating at full power. Samplings and analysis disclosed a sulfur content in the exit gases of approximately 0.058 mg sulfur ($SO_2 + SO_3$) per 15 liters of exit gas.

Example 3 Example 2 above was repeated this time igniting and burning two (2) gallons per hour of the calcium nitrate solution together with the ≠≠6 fuel oil with 1.8 % sulfur at 1416 gallons per hour. The analysed sulfur content of the exit gases was approximately 0.33 mg sulfur ($SO_2 + SO_3$) per 15 liters of exit gas.

To emphasize the impact of the present invention, the sulfur content of the exit gases in the above examples will be converted to pounds of sulfur dioxide per million BTUs in the fuel. This is the measurement used by the U.S. Environmental Protection Agency which has set a maximum

content for new facilities at 0.2 lbs. $SO_2/10^6$BTU: Using a common conversion factor computed for the power unit used in Examples 1, 2 and 3 and established on the worst possible conditions as 100 % conversion of sulfur in the fuel to sulfur dioxide, the following figures (in specific units previously described) are computed and compared:

Prior art methods	(approx)	1.855 lbs $SO_2/10^6$BTU
Example 3	(approx)	0.2299 lbs $SO_2/10^6$BTU
EPA maximum	(approx)	0.2000 lbs $SO_2/10^6$BTU
Example 1	(approx)	0.1322 lbs $SO_2/10^6$BTU
Example 2	(approx)	0.0404 lbs $SO_2/10^6$BTU

The sulfur dioxide content was calculated on the basis of factors derived from a calculated quantity of sulfur in the fuel, namely 0.9203 lbs. of sulfur per million British Thermal Units of fuel which is equivalent to 1.8406 lbs. of sulfur dioxide per million BTUs of fuel.

Example 4 Six (6) gallons or 68.34 pounds per hour of the described alkaline earth metal nitrate solution were injected into the fuel oil feed line. The fuel oil feed rate was 1,452 gallons or 11,700 pounds per hour. The sulfur content of the untreated fuel oil was 1.78 %. This is equal to 208.26 pounds or 6.4959 pound moles per hour of sulfur available for reaction with the elements in the fuel oil, the additive, the boiler surfaces, and with oxygen to form sulfur dioxide, sulfur trioxide, other oxides of sulfur, and other products some of which

may contain sulfur. The reactions will occur at temperatures of 2,300 to 2,800 deg. F and, in some instances, at higher temperatures. The total amount of sulfur measured as sulfur dioxide and sulfur trioxide in the exit gases during treatment of the fuel oil with this quantity of alkaline earth metal nitrate solution was 0.2889 pound moles per hour. This leaves 6.2070 pound moles per hour of sulfur reacting with elements in the fuel oil treated with 0.2047 pound moles per hour of calcium in the alkaline earth metal nitrate solution. There were 6.0023 pound moles per hour of sulfur removed in excess of the stoichiometric ratio of sulfur to calcium.

Example 5 Four (4) gallons or 45.56 pounds per hour of the described alkaline earth metal nitrate solution were injected into the fuel oil feed line. The fuel oil feed rate was 1,477 gallons or 11,500 pounds per hour. The sulfur content of the untreated fuel oil was 1.78 %. This is equal to 204.70 pounds or 6.3849 pound moles per hour of sulfur. Using the general information supplied in example ≠≠1 (above), the total amount of sulfur measured as sulfur dioxide and sulfur trioxide in the exit gas was 0.9389 pound moles per hour. This leaves 5.4460 pound moles per hour of sulfur reacting with 0.1365 pound moles per hour of calcium. There were 5.3095 pound moles per hour of sulfur removed in excess of the stoichiometric ratio of sulfur to calcium.

C L A I M S

1. A method of reducing the sulfur content of exit gases resulting from combustion of sulfur bearing fuels or like products, said method comprising the step of igniting the sulfur bearing fuel in the presence of at least one member selected from the group consisting of the alkaline earth metal nitrates, alkali metal nitrates and ammonium nitrate.

2. A method as claimed in claim 1, wherein a mixture of the sulfur bearing fuel with said at least one member is ignited.

3. A method as claimed in claim 1 or 2, wherein the alkaline earth metal nitrate is calcium nitrate.

4. A method as claimed in claims 1-3, wherein a mixture of calcium nitrate and ammonium nitrate is ignited together with the sulfur bearing fuel.

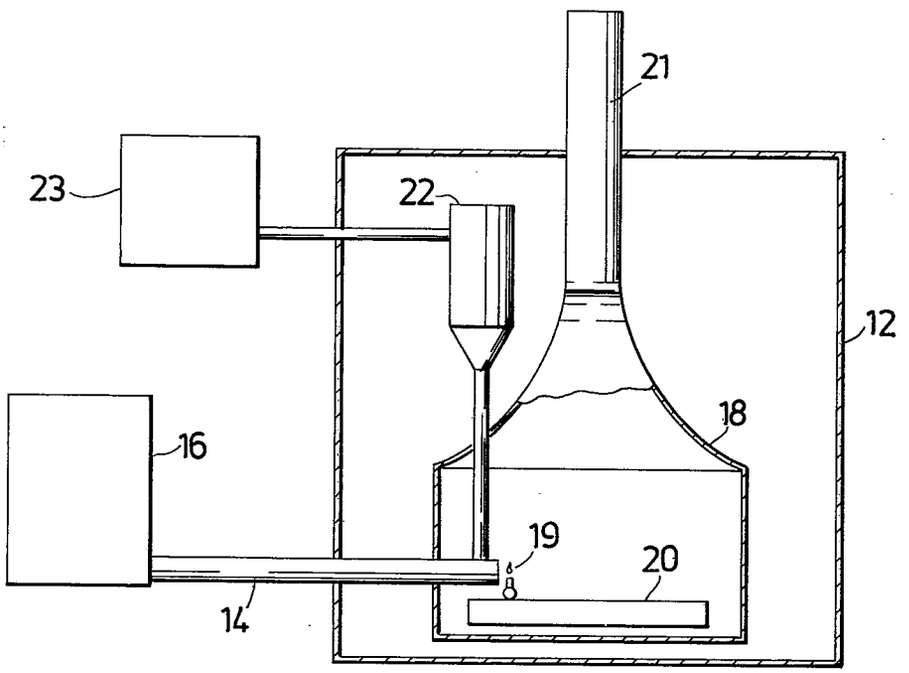
5. A method as claimed in claim 4, wherein the mixture represents a double salt of calcium nitrate and ammonium nitrate.

6. A method as claimed in claim 1 or 2, wherein the alkaline earth metal nitrate is magnesium nitrate.

7. A method as claimed in claims 3-6, wherein the alkaline earth metal nitrate is placed in solution prior to combining with the sulfur bearing product.

8. A method as claimed in claims 3-6, wherein the alkaline earth metal nitrate is placed in a dispersion prior to combining with the sulfur bearing product.

9. A method as claimed in claims 3-6, wherein the alkaline earth metal nitrate is placed in emulsion prior to combining with the sulfur bearing product.


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