

⑩



Europäisches Patentamt

European Patent Office

Office européen des brevets

⑪ Publication number:

**0 070 834
B1**

⑫

EUROPEAN PATENT SPECIFICATION

④⑤ Date of publication of patent specification: **10.07.85**

⑤① Int. Cl.⁴: **C 10 L 1/12, C 10 L 10/04**

②① Application number: **81902943.0**

②② Date of filing: **16.10.81**

③⑧ International application number:
PCT/SE81/00309

③⑦ International publication number:
WO 82/01375 29.04.82 Gazette 82/11

⑤④ **A PROCESS AND A COMPOSITION TO IMPROVE THE COMBUSTION OF FUELS.**

③⑩ Priority: **17.10.80 SE 8007314**

④③ Date of publication of application:
09.02.83 Bulletin 83/06

④⑤ Publication of the grant of the patent:
10.07.85 Bulletin 85/28

③④ Designated Contracting States:
AT CH DE FR GB LI NL SE

⑤⑥ References cited:
**EP-A-0 013 243
CH-A- 202 497
DE-A-2 407 508
DE-A-2 648 741
DE-A-2 938 074
FR-A- 698 152
GB-A- 485 333
GB-A-1 005 957
SE-C- 108 848
US-A-3 332 755
US-A-3 692 503**

⑦③ Proprietor: **NILSSON, Carl-Einar
Porse Geets Väg 10
S-641 37 Katrineholm (SE)**

⑦③ Proprietor: **LITTORIN, Ove Gustav
Västmannagatan 54
S-113 25 Stockholm (SE)**

⑦② Inventor: **NILSSON, Carl-Einar
Porse Geets Väg 10
S-641 37 Katrineholm (SE)**
Inventor: **LITTORIN, Ove Gustav
Västmannagatan 54
S-113 25 Stockholm (SE)**

⑦④ Representative: **Burman, Tore et al
Bergling & Sundbergh AB P.O. Box 7645
S-103 94 Stockholm (SE)**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Courier Press, Leamington Spa, England.

EP 0 070 834 B1

Description

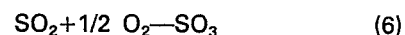
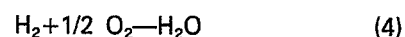
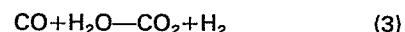
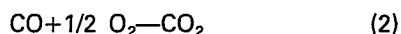
The present invention relates to a process to improve the combustion of fuels for the generation of energy, which process operates with reduced corrosion and lowered deposition on heat-transferring and other surfaces.

Synchronously with increased costs for energy generation, particularly in view of increasing crude oil prices, the techniques to make the combustion of fuels for energy generation more effective has come more and more into focus.

Several systems for improved fuel economy have been developed lately and among those there may be mentioned systems based on bringing into the combustion zone agents intended to reduce the formation of soot, slag deposits on heat-transfer surfaces, corrosion on such surfaces etc. Among such agents there may be mentioned compositions containing different types of phosphates, magnesium compounds slurried in organic carriers etc. Moreover, it has been suggested in connection with combustion of thick fuel oil to emulsify water in the oil, which has been regarded to result in a more economic and improved combustion while reducing the formation of soot and reducing deposits. Furthermore, different metal catalysts for improving the conditions in connection with combustion have been devised, see for example EP—A—13243 and CH—A—202497. However, these references do not disclose the specific metal combinations provided by the present invention.

Thus it is desired in connection with combustion of fuels of different types for energy generation to reduce the emission of dust, to reduce discharge of polyaromatics, the corrosive effect of the combustion gases on heat-transfer and other surfaces and to reduce deposition of slags and other products on said surfaces. Common to all measures hitherto proposed for the purpose of improving the combustion efficiency and to reduce the inconveniences resulting from the combustion, seems to be the fact that no scientific approach has been taken which means that with any known system one has not been able to obtain optimization of the combustion conditions and minimizing the negative effects of the combustion. Particularly in view of the present strict environmental requirements it is therefore desirable with a fundamentally new technique by which a more effective combustion of different fuels can be obtained at the same time as one avoids or at least reduces the inconveniences in the form of slag deposits, corrosion etc. arising in connection with the combustion.

When burning fuels for energy generation the oxygen of the air reacts with the substances of the fuel while forming oxygen-containing compounds. The main reactions which are involved are in principle the following:



The invention has for its purpose to control said reactions so as to result in a more complete combustion, whereby the excess of air and the soot formation and discharge of polyaromatics are reduced. In regard to sulphur-containing fuel it is noted that it is desirable to suppress the oxidation of the sulphur dioxide to sulphur trioxide, the latter together with the water of the exhaust gases forming sulphuric acid resulting in non-desirable corrosion. The dew point for sulphur trioxide is, in a manner known per se, dependent on the sulphur trioxide contents of the gases and the carbon dioxide content. The dew point diminishes with sinking sulphur trioxide content and with increasing carbon dioxide content. Thus, it is essential to suppress the formation of sulphur trioxide and to increase the content of carbon dioxide in the combustion gases.

The technique of the instant invention is based on the one hand the insight of these basic reactions in connection with the combustion, on the other hand the components present in the fuel including contaminants. In connection with the creation of the invention it has been found that a more efficient combustion and an optimized control of the basic chemical reactions in connection herewith can be obtained if there is supplied to the combustion zone such a catalyst as to introduce into said zone at least the elements aluminium, magnesium, manganese and zinc. A particular feature of the technique of this invention is the adaptation of the dosage of the said elements after the inherent contents of the fuel of said elements. As an example there can be taken a heavy fuel oil containing magnesium. When burning such fuel oil the contents of magnesium of a catalyst composition can be reduced in the corresponding degree as the inherent content of magnesium of the fuel oil. An example to the contrary is a diesel engine fuel not containing zinc, where adding an organic zinc compound results in improved combustion and reduced corrosion.

The technique of the present invention is in general applicable to gaseous and liquid fuels. Moreover, the form of additive according to the invention may vary, inter alia in considering the fuel in question. Thus, the additive can be present in liquid form, preferably an aqueous solution, in powder form, in the form of a slurry of powder in liquid or in other solid form.

The composition used according to the invention can be supplied to the combustion zone in several ways, also in this case dependent on the fuel and the practical situation in question. Thus, the composition can be admixed with the fuel before its supply into the combustion zone, it can

be admixed with the air of combustion and, finally, it can be injected directly into the flame or into the combustion space in connection thereto.

In addition to the elements previously mentioned intended for supply to the combustion zone, i.e. aluminium, magnesium, manganese and zinc, one or several of the following elements may be added for the purpose of further improving the combustion conditions and the other conditions in connection with the combustion: cadmium, iron, tin, silicon, beryllium, copper, chromium, silver, barium, titanium, nickel, calcium, molybdenum, rubidium, vanadium, sodium, arsenic, boron, bromine, phosphorus and selenium.

The elements involved can be supplied to the combustion zone in varying quantities, from the order of from some tenths up to some tens of ppm based on the quantity of fuel. These added quantities refer to each and every element per se.

The present invention is particularly suited for application in connection with the combustion of liquid fuels, in particular so-called heavy oils for energy generation on a large scale. In this case the additive is suitably added as an aqueous solution containing soluble salts of the elements in question. Such aqueous solutions of the active elements can be supplied to the combustion zone in several ways.

In a preferred embodiment of this aspect of the invention the aqueous solution is supplied to the fuel before the combustion and is emulsified therein in accordance with conventional technique. This results in the advantage that in addition to the positive effect of the active elements on the course of combustion there is obtained also a positive effect on the combustion due to the added water. The aqueous solution can be supplied to the combustion zone in a quantity of up to about 5 % by volume based on the volume of the fuel, and up to said upper limit the evaporation of the water constitutes an acceptable additional consumption of energy. A particularly preferred quantity of additive in the form of an aqueous solution is 0.5—2 % by volume. The concentration of the active element of the additive is adapted so that in supplying the aqueous solution in the relevant quantity to the combustion zone the said element is supplied in a quantity of the order of up to some tenths of ppm based on the quantity of fuel.

In the present invention there is thus used a composition to improve the combustion of fuels for energy generation, reduced corrosion and deposition on heat-transferring and other surfaces being obtained. This composition includes at least the elements aluminium, manganese and zinc and dependent on the contents of trace elements of the fuel the composition may contain also magnesium. This composition can be in liquid form, in the form of a powder, in the form of a slurry of solid material in liquid or in another solid form. For burning liquid fuels it is preferably in the form of an aqueous solution containing soluble salts of the said elements. In order to

facilitate the admixture of the composition into liquid fuels, which is a preferred embodiment of the invention, the composition may also contain an emulsifier.

When using the technique according to the present invention substantial advantages are obtained in connection with the combustion. Thus, the supply of the elements to the combustion zone means a more complete combustion, the oxidation of the sulphur dioxide to sulphur trioxide will be suppressed, and protection against corrosion within a broad temperature range will also be obtained. The combustion can be performed with a decrease of the excess of air, which, or course, is favourable both with regard to the coefficient of utilization and also reduces the formation of sulphur trioxide. A low excess of oxygen also, of course, results in an increased content of carbon dioxide which, as previously indicated, means lowered dew point for sulphur trioxide.

The invention will now be described by non-limiting examples.

Example 1

A fuel oil low in sulphur and of the heavy oil type is analyzed and is found to contain 5 ppms iron, 3 ppms lead, 4 ppms nickel and 25 ppms vanadium. The contents of the elements Mn, Mg, Al and Zn are less than 1/2 ppm.

As an additive there is used an aqueous solution of manganese sulphate, magnesium sulphate, aluminium sulphate and zinc sulphate. The additive is dosed in a quantity of about 1/2 percent by volume based on the quantity of fuel oil, and the concentration of the aqueous solution of the elements in question is adjusted so that the fuel oil is supplied with 10 ppms of manganese, 5 ppms of magnesium, 5 ppms of aluminium and 10 ppms of zinc, all based on the quantity of fuel oil.

The fuel oil is supplied to a boiler of a conventional type having one (1) burner and a capacity of up to about 8 tons of steam per hour. This boiler is normally operated with an excess of air of 30—50 % and an exhaust gas temperature of 250—300°C. When the boiler is operated in accordance with the technique of the present invention, i.e. while adding the aqueous solution described above containing the elements in question to the fuel oil, the exhaust gas temperature can be lowered down to about 200°C and the excess of air can be reduced to about 20—30 %.

These operational changes when applying the technique according to the present invention results in substantially improved efficiency of utilization in the combustion, reduced deposition on the heat-transferring surfaces of the boiler and substantially reduced corrosion.

Example 2

The procedure according to Example 1 is repeated but using a fuel oil which, according to analysis performed, contains magnesium in an amount of about 3 ppms. Against this background

the procedure of Example 1 is repeated but while using an additive not containing magnesium sulphide but only the remaining three elements in the same quantities. The same favourable results as in Example 1 are obtained in operating the boiler in regard to excess of air and exhaust gas temperature and other operational conditions. Moreover, by the adjusted process according to the invention overdosage of magnesium is avoided which otherwise by deposition on heat transferring surfaces will impair the heat transfer.

Example 3

An extended test was performed on a boiler provided with four pressurized air burners and a maximum steam capacity of 75 tons per hour. The fuel used which was a fuel oil low in sulphur and of the heavy oil type was analyzed with regard to trace elements. A representative sample from the oil stock containing a one year consumption contained inter alia 6 ppms of zinc, 5 ppms of Fe, 4 ppms of Mg, 16 ppms of Ni, 33 ppms of V. The contents of Mn and Al were less than 1/2 ppm.

The additive in this case was an aqueous solution consisting of MnSO_4 and $\text{Al}_2(\text{SO}_4)_3$ and the dosage was performed in the same manner as above. The sweeping frequency was reduced from once/day to once every fourth day and in spite of this the exhaust gas temperature during the sweeping intervals sank by 5–10°C on average. The exhaust gas temperature could be further reduced by 5–10°C by increased heat recovery without the formation of sulphuric acid condensate. The pH of ashes in the dust collectors increased from about 1.5 to about 3.5. The previous disturbing high and low temperature corrosion was gone. The contents of unburnt residues in ashes and exhaust gases were practically nil.

It should be observed that the present invention is not delimited to merely energy generation while using liquid fuels in accordance with the examples. When firing using gaseous fuels the additive according to the invention can be supplied to the combustion zone by atomization and supplied to for example supplied air or directly to the gaseous fuel.

Claims

1. A process for improving the combustion of gaseous or liquid fuels for the generation of energy with reduced corrosion and lowered deposition on heat-transferring and other surfaces, characterized by supplying to the combustion zone such a catalyst as to introduce into said zone at least compounds of the elements Al, Mg, Mn and Zn in a quantity active for efficient combustion.

2. A process according to claim 1, characterized by adapting the dosage of the said compounds after the inherent contents of the fuel of said elements.

3. A process according to claim 1 or 2 for the combustion of liquid fuels, particularly so-called

heavy oils, characterized by maintaining said compounds dissolved in an aqueous solution which is supplied to the combustion zone.

4. A process according to claim 3, characterized thereby that the aqueous solution is supplied to the fuel before combustion and is emulsified therein.

5. A process according to claim 3 or 4, characterized by supplying the aqueous solution to the combustion zone in a quantity of up to about 5% by volume based on the volume of the fuel.

6. A process according to claim 5, characterized by supplying the aqueous solution in an amount of 0.5–2% by volume.

7. A process according to any preceding claim, characterized thereby that each of the said compounds are supplied in a quantity of from some tenths up to some tens of parts per million based on the elements and the quantity of fuel.

Patentansprüche

1. Verfahren zur Verbesserung der Verbrennung gasförmiger oder flüssiger Brennstoffe für die Energieerzeugung mit verminderter Korrosion und geringerer Ablagerung auf wärmeübertragenden und anderen Oberflächen, dadurch gekennzeichnet, daß man der Verbrennungszone einen solchen Katalysator zuführt, daß in diese Zone wenigstens Verbindungen der Elemente Al, Mg, Mn und Zn in einer für wirksame Verbrennung aktiven Menge eingeführt werden.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß man die Dosierung dieser Verbindungen nach den Eigengehalten des Brennstoffes an diesen Elementen anpaßt.

3. Verfahren nach Anspruch 1 oder 2 zur Verbrennung flüssiger Brennstoffe, besonders sogenannter Schweröle, dadurch gekennzeichnet, daß man diese Verbindungen in einer wäßrigen Lösung gelöst hält, die der Verbrennungszone zugeführt wird.

4. Verfahren nach Anspruch 3, dadurch gekennzeichnet, daß die wäßrige Lösung dem Brennstoff vor der Verbrennung zugeführt und darin emulgiert wird.

5. Verfahren nach Anspruch 3 oder 4, dadurch gekennzeichnet, daß man die wäßrige Lösung der Verbrennungszone in einer Menge von bis zu etwa 5 Volumen-%, bezogen auf das Volumen des Brennstoffs, zuführt.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß man die wäßrige Lösung in einer Menge von 0,5 bis 2 Volumen-% zuführt.

7. Verfahren nach einem der vorausgehenden Ansprüche, dadurch gekennzeichnet, daß jede dieser Verbindungen in einer Menge von einigen Zehnteln bis zu einigen zehn Teilen je Million, bezogen auf die Elemente und die Brennstoffmenge, zugeführt wird.

Revendications

1. Procédé pour améliorer la combustion de

combustibles gazeux ou liquides afin d'engendrer de l'énergie avec une corrosion réduite et un dépôt moindre sur les surfaces de transfert de chaleur et les autres surfaces, caractérisé en ce qu'il consiste à alimenter à la zone de combustion un catalyseur tel qu'on introduit dans ladite zone au moins des composés des éléments Al, Mg, Mn et Zn en quantité active pour une combustion efficace.

2. Procédé selon la revendication 1, caractérisé en ce qu'on adapte la dose desdits composés d'après les teneurs intrinsèques des combustibles desdits éléments.

3. Procédé selon l'une des revendications 1 ou 2 pour la combustion de combustibles liquides notamment d'huiles dites lourdes, caractérisé en ce qu'on maintient lesdits composés dissous dans une solution aqueuse qui est alimentée à la zone de combustion.

4. Procédé selon la revendication 3, caractérisé en ce que la solution aqueuse est alimentée au combustible avant la combustion et est émulsifiée dans celui-ci.

5. Procédé selon l'une des revendications 3 ou 4, caractérisé en ce qu'on alimente la solution aqueuse dans la zone de combustion selon une quantité allant jusqu'à environ 5 % en volume calculée sur le volume de combustible.

6. Procédé selon la revendication 5, caractérisé en ce qu'on alimente la solution aqueuse selon une quantité de 0,5 à 2 % en volume.

7. Procédé selon l'une quelconque des revendications 1 à 6, caractérisé en ce que chacun desdits composés est alimenté en une quantité allant de quelques dixièmes à quelques dizaines de parties par million calculée sur les éléments et la quantité de combustible.

20

25

30

35

40

45

50

55

60

65

5