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(54) **Use of low-corrosive fuel compositions in boilers**

(57) The use in a blue flame burner or an optimised yellow flame burner of a boiler of a fuel oil composition which comprises a base oil and one or more additives selected from antioxidants, heterogeneous nitrogen compounds and slightly hydrotreated or straight run fuel

fractions, for the purpose of reducing the levels of high temperature corrosion in one or more portions of said burner. This has particular applicability where said fuel oil composition contains no more than 500ppm sulphur.

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Description

[0001] The present invention relates to the use in boilers, including standard boilers, low temperature boilers and condensing boilers, of certain fuel compositions for the purpose of reducing the levels of high temperature corrosion in the burners thereof, and to operation of such boilers.

[0002] Such boilers are typically used for heating water for commercial or domestic applications such as space heating and water heating.

[0003] In standard and low temperature boilers, it is ensured that flue gas leaves the boiler as gas, and condensation of sulphuric acid is avoided.

[0004] Condensing boilers are described for example in EP-A-0789203, in particular a gas-fired condensing boiler. These boilers are called condensing boilers because the gases produced by combustion are cooled inside the apparatus until the water vapour contained therein condenses, so as to recover the latent condensation heat and transfer it to the water to be heated, which flows through said boilers. This latent heat is sometimes also used to pre-heat the combustion air. A problem associated with these condensing boilers is that, when using most fuels, the liquid condensate by-products of the combustion must be contained, neutralised and/or treated and channelled away for disposal, this, however, generally being unnecessary if ultra low sulphur fuel is used. Furthermore, heat exchanger materials must be capable of withstanding the corrosive liquid condensate by-products. Steps should also be taken to ensure that the burner and igniter systems, along with other system elements such as sensors, are not fouled by moisture, or condensation.

[0005] Natural gas is used as fuel in boilers. For example, in The Netherlands, which is equipped with a widespread natural gas grid, many households use a boiler for domestic heating in combination with warm water supply. The wide application of these boilers is due to their attractive energy efficiency and the presence of the natural gas supply grid.

[0006] A disadvantage of all boilers that use natural gas is that they cannot be easily applied in regions where no natural gas grid is present. A solution to this problem is to use a liquid fuel. Liquid fuels can be easily transported to and stored by the end user, for example in a storage tank connected to the boiler by copper lines. Such tanks may, for example, be underground or in basements. A disadvantage of the use of liquid fuels is, however, that a condensing boiler and/or the associated chimneys have to be made from different, more corrosion resistant, materials. This is a disadvantage for the manufacturer of condensing boilers because it would result in two types of boiler. Moreover, the apparatus using a liquid fuel would be more expensive due to the different more corrosion-resistant material required.

[0007] Conventional designs of oil burner assemblies for home heating fuel oils employ a traditional fuel/air mixing process, in which the evaporation and combustion of the fuel oil take place simultaneously. In one form of oil burner assembly for home heating fuel oils, the fuel oil is sprayed as a hollow cone and air is weakly swirled along a path which is parallel to the axis of a burner blast tube and which passes into the hollow cone so that the trajectories of the fuel oil droplets cross the air flow streamlines. This leads to a rapid evaporation giving fuel oil rich regions, which in turn ignite under local sub-stoichiometric conditions producing soot. This results in air pollution and a soot layer on the inner wall of the boiler. This leads to a decrease in efficiency as well as a waste of a fossil fuel.

[0008] The general pattern of the flame of such an oil burner assembly is one of heterogeneity in terms of fuel concentrations; the pockets of fuel lean mixture give rise to high nitric oxide concentrations from both the fuel nitrogen and the atmospheric nitrogen, while the pockets of fuel rich mixture give rise to soot. The visible flame from such a system is yellow. The yellow colour is the visible radiation from the high temperature soot particles and this completely masks other visible radiations as far as the human eye is concerned. These soot particles result from unburnt carbon.

[0009] Yellow flame burners operate on the principle that a pump delivers the fuel through an electrical pre-heater which raises the fuel temperature to approximately 70°C. The pressurised fuel is then delivered through a nozzle and forms a spray. Oxygen-containing air for combustion is introduced and distributed via a so-called swirl plate to mix vigorously with the fuel spray. At the initial system start, the spray is ignited by an ignition electrode. In yellow flame systems, only an insufficient evaporation of the fuel is achieved before the combustion takes place.

[0010] For complete combustion of the carbon, that is soot-free combustion, the step-wise combustion of carbon to carbon dioxide via the intermediate carbon monoxide stage gives rise to a visible radiation in the blue region of the light spectrum. When this occurs the blue radiation becomes visible in a soot-free or low-luminosity flame, and oil burners for such soot-free flames are known as blue flame burners.

[0011] Blue flame burners are characterised in that the combustion of the hydrocarbon fuel to carbon dioxide is performed such that part of the flue gas is recycled to the flame and more suitably to the nozzle of the burner. Recycling part of the flue gas externally of the burner may effect such recirculation of the flue gas. This is enabled by a flame tube, which is attached to the burner. This tube is provided with recirculation holes or slits through which the recirculated gases enter the front part of the flame tube. Alternatively, recycling may be achieved by swirling the combustible mixture of fuel and oxygen-containing gas, wherein at the axis of the swirling flame some recirculation of the flue gas takes place. Good evaporation of the fuel is reflected in lower emissions of soot, carbon monoxide, nitrogen oxides and hydrocarbons. The absence of soot particles formed during the combustion process results in an almost colourless

flame, i.e. blue flame.

[0012] As indicated above, there are different types of boilers, which differ in how the hot exhaust gases are circulated in the boiler for optimum heat exchange and in the temperatures at which the exhaust gases finally leave the boiler through some form of exhaust pipe.

[0013] Condensing boiler technology has been available in the gas market for several years. Recently, oil-fired condensing boilers have become available. With such technology, the exhaust gas is cooled to such an extent that the water content (from hydrogen retained in the fuel itself and from humidity of the combustion air) partially condenses and releases the condensation heat, which is utilised to increase the efficiency of the system. However, due to the sulphur content of the liquid fuel itself, the condensate is acidic, which can lead to severe corrosion problems in the system if no corrosion-resistance is installed, especially in the heat exchanger and the exhaust system.

[0014] However, it has now been found that when using liquid fuels having a low sulphur content, e.g. 500ppm or less, in boilers which are fitted with burners having flame tubes, e.g. blue flame burners or optimised yellow flame burners with flame tubes (so-called transparent burners), high temperature corrosion (HTC) of the flame tubes is experienced. By "optimised" is meant optimised in terms of Nox emissions. Recirculation of the flue gas in such blue flame burners as well as in said optimised yellow flame burners leads to homogeneous temperature profiles, lower oxygen partial pressures and homogeneous profiles of gas species.

[0015] It is an object of the present invention to overcome the problem of such high temperature corrosion when using such low sulphur fuels with burners fitted with flame tubes.

[0016] In accordance with the present invention there is provided the use in a blue flame burner or an optimised yellow flame burner of a boiler of a fuel oil composition which comprises a base oil and one or more additives selected from antioxidants, heterogeneous nitrogen compounds and slightly hydrotreated or straight run fuel components, for the purpose of reducing the levels of high temperature corrosion in one or more portions of said burner.

[0017] In this specification, "reducing the levels of high temperature corrosion" means as compared to the levels of such corrosion which are caused during operation of the burner when using an alternative fuel oil composition comprising said base oil but not comprising said one or more additives.

[0018] By "straight run" fuel components is meant fractions which have been obtained in the atmospheric distillation of crude petroleum refinery feedstock. By "hydrotreated" fuel components is meant components which have been obtained by subjecting various sources of suitable hydrocarbon refinery streams to treatment with hydrogen, e.g. hydrocracking to adjust the boiling range, hydroisomerisation which can improve cold flow properties by increasing the proportion of branched paraffins, and hydrodesulphurisation to reduce sulphur content.

[0019] Said fuel oil composition preferably contains no more than 500ppm sulphur, more preferably no more than 150ppm sulphur, even more preferably no more than 100ppm sulphur, yet more preferably no more than 50ppm sulphur, most preferably no more than 10ppm sulphur.

[0020] In accordance with the present invention there is also provided a method of reducing the levels of high temperature corrosion in one or more portions of a blue flame burner or an optimised yellow flame burner of a boiler by replacing the use in said burner of a fuel oil composition comprising a base oil by a fuel oil composition which comprises said base oil and one or more additives selected from antioxidants, hydrocarbon compounds comprising one or more heteratoms selected from nitrogen, phosphorus and oxygen and slightly hydrotreated or straight run fuel fractions.

[0021] In accordance with the present invention there is still further provided a method of operating a boiler provided with a blue flame burner or an optimised yellow flame burner, which method comprises supplying to said burner a fuel oil composition comprising a base oil and one or more additives selected from antioxidants, heterogeneous nitrogen compounds and slightly hydrotreated or straight run materials, for the purpose of reducing the levels of high temperature corrosion in one or more portions of said burner.

[0022] The burner used in all aspects of the present invention is preferably fitted with a flame tube. Moreover, said burner is preferably a blue flame burner.

[0023] In a fuel oil composition used in the present invention, said antioxidants may be selected from hindered mono-, di- and poly-phenols, including ester-based hindered phenols; diarylamines; hydroquinones; alkylated p-phenylenediamines; dihydroquinolines; thioethers; trivalent phosphorus compounds; and hindered amines; and said hydrocarbon compounds comprising one or more heteroatoms selected from nitrogen, phosphorus and oxygen may be selected from heterocyclic and/or polyaromatic compounds comprising one or more heteroatoms selected from nitrogen, phosphorus and oxygen.

[0024] Particularly preferred such additives for use in the present invention are selected from IRGANOX L57, IRGANOX L135, IRGANOX L06 and IRGALUBE F10 (all ex. Specialty Chemicals Inc), trimethylphenol and esters thereof, quinoline, quinaldine and trimethylpyridine (all ex. Aldrich).

[0025] Said additives are preferably present in the amount of 10 to 500ppm, more preferably 50 to 500ppm, still more preferably 50 to 250ppm, most preferably 50 to 150ppm, and particularly about 50ppm.

[0026] As indicated, it has been found that when using such additivated fuel oil (industrial gas oil (IGO)) compositions, high temperature corrosion of flame tubes is reduced, or even removed completely, as compared to when using such

fuel compositions when not so additivated. The corrosive nature of the condensate liquid by-product is lower when compared to the condensate liquid by-product as obtained when a (low-sulphur) fuel oil not so additivated is used as fuel. It is envisaged that the corrosive nature of the fuel composition is reduced such that a condensing boiler suitable for gas firing can also be used for liquid fuel firing, possibly subject to some small adjustments to the burner. This has clear manufacturing and operational advantages.

[0027] The present invention will now be described by way of example with reference to the accompanying drawings, in which:

Figure 1 shows a schematic representation of a wall-mounted condensing boiler;

Figure 2 shows a schematic representation of a blue flame burner with external recirculation of flue gas;

Figure 3 shows a schematic representation of an optimised yellow flame burner (so-called transparent flame burner) with external recirculation of flue gas;

Figure 4 shows the loss of mass of a burner flame tube against time in respect of use of Oils A and B; and

Figure 5 shows the loss of mass of a burner flame tube against time in respect of use of Oils C and D.

[0028] In Figure 1, a boiler housing 1 contains a centrally positioned burner 2, which is shown schematically. A burner flame exists in a combustion space 3, which is enclosed by an end wall 4 and a heat exchanger tube wall 5. Flue gases can leave the combustion space 3 through openings in the wall 5 to enter an annular space 6, which is enclosed by further heat exchanger tube wall segments 7. The housing 1 further is provided with means 14 to supply cold water to the heat exchanger tube wall 4,5 and means 15 to discharge heated water from said tube wall 4,5. The housing 1 is further provided with a chimney 8 connected to space 6 for discharging flue gas. Air provided to the burner 2 via van 16 is pre-heated by flue gas leaving the housing by passing the air countercurrently along the chimney 8 in an annular space 9. In the chimney 8, water condensates and the condensate is discharged to a drain 10 via a conduit 11. An oil pump 12 is provided to supply the fuel and an expansion vessel 13 is also shown.

[0029] Figure 2 shows a blue flame burner 21 having a means 22 to supply a liquid fuel and a means 23 to supply an oxygen-containing gas. The oxygen containing gas is usually air. A nozzle 24 supplies the fuel by forming a spray. Fuel and air are mixed downstream of the nozzle 24 to form a combustible mixture which is fed to a pre-combustion space 25, which is formed by the interior of a tubular part 26. Tubular part 26 is positioned co-axially in a larger tubular part 27, which forms a final combustion space 28. Flue gas is discharged via an outlet opening 29 into an outlet space 30. Openings 31 in tubular part 27 serve as means to recycle part of the flue gas to the final combustion space 28. Openings 32 in tubular part 26 serve as means to recycle part of the gas present in the final combustion space 28 to the pre-combustion space 25.

[0030] Figure 3 shows an optimised yellow flame burner having pumping means 41 to supply a liquid fuel and a fan 42 to supply an oxygen-containing gas. The oxygen-containing gas is usually air. The fuel is dispersed in a nozzle 43 in the form of a spray and mixed with the air to form a combustible mixture, which is fed to a combustion space 44 via a conically shaped swirl plate 45. A means 46 is provided to ignite the mixture. The combustion space 44 is formed by the interior of a tubular part 47. Flue gas is discharged via an outlet opening 48 into an outlet space 49. Part of the flue gas is recycled to the combustion space 44.

[0031] Both types of burner used in the present invention are well-known and are for example described in the general textbook, "Heizung + Klimatechnik 01/02" German Version by Recknagel, Sprenger, Schramek, ISBN: 3-468-26450-8, on pages 718-719.

[0032] The operating conditions of the optimised yellow or blue flame burner may be the same as the operating conditions used for the state of the art liquid fuels. The proportion of air in excess of that required for stoichiometric combustion is known as the excess air ratio or "lambda", which is defined as the ratio of total air available for combustion to that required to burn all of the fuel. Preferably the lambda is between 1 and 2, more preferably between 1 and 1.6, and most preferably between 1 and 1.2.

[0033] The fuel used in the process of the present invention may comprise fuel fractions such as the kerosene or gas oil fractions obtained in traditional refinery processes, which upgrade crude petroleum feedstock to useful products. Preferably such fractions contain components having carbon numbers in the range 5-40, more preferably 5-31, yet more preferably 6-22, and such fractions have a density at 15°C of 650-950 kg/m³, a viscosity at 20°C of 1-80 mm²/s, and a boiling range of 150-400°C. Preferred fuel fractions are the ultra low sulphur (e.g. less than 50 ppm sulphur) fractions, which are currently on the market. Optionally, non-mineral oil based fuels, such as bio-fuels or Fischer-Tropsch derived fuels, may also form or be present in the fuel composition.

[0034] In the case of such Fischer-Tropsch derived fuels, the fuel oil composition will preferably comprise more than 50 wt%, more preferably more than 70 wt%, of a Fischer-Tropsch derived fuel component. Such a Fischer-Tropsch derived fuel component is any fraction of the middle distillate fuel range, which can be isolated from the (hydrocracked) Fischer-Tropsch synthesis product. Typical fractions will boil in the naphtha, kerosene or gas oil range. Preferably, a Fischer-Tropsch product boiling in the kerosene or gas oil range is used because these products are easier to handle

in for example domestic environments. Such products will suitably comprise a fraction larger than 90 wt% which boils between 160 and 400°C, preferably to about 370°C. Examples of Fischer-Tropsch derived kerosene and gas oils are described in EP-A-0583836, WO-A-97/14768, WO-A-97/14769, WO-A-00/11116, WO-A-00/11117, WO-A-01/83406, WO-A-01/83648, WO-A-01/83647, WO-A-01/83641, WO-A-00/20535, WO-A-00/20534, EP-A-1101813, US-A-5766274, US-A-5378348, US-A-5888376 and US-A-6204426.

[0035] The Fischer-Tropsch product will suitably contain more than 80 wt% and more suitably more than 95 wt% iso and normal paraffins and less than 1 wt% aromatics, the balance being naphthenics compounds. The content of sulphur and nitrogen will be very low and normally below the detection limits for such compounds. For this reason the sulphur content of the fuel oil composition may be very low.

[0036] The fuel composition used in the present invention may, if required, contain one or more additives as described below.

[0037] Detergents, for example polyolefin substituted succinimides or succinamides of polyamines, for instance polyisobutylene succinimides or polyisobutylene amine succinamides, aliphatic amines, Mannich bases or amines and polyolefin (e.g. polyisobutylene) maleic anhydrides. Succinimide dispersant additives are described for example in GB-A-960493, EP-A-0147240, EP-A-0482253, EP-A-0613938, EP-A-0557516 and WO-A-98/42808. Particularly preferred are polyolefin substituted succinimides such as polyisobutylene succinimides. More particularly preferred are OMA 350 and OMA 4130D (ex. Octel), F7661 and F7685 (ex. Infineum); stabilisers, for example KEROPON ES 3500 (ex. BASF), FOA 528A (ex. OCTEL); metal-deactivators, for example IRGAMET 30 (ex. Specialty Chemicals); cold flow improvers, for example KEROFLUX 3283 (ex. BASF), R433 or R474 (ex. Infineum); combustion improver, for example ferrocene, methylcyclopentadienylmanganese-tricarbonyl (MMT); anti-rust agents, for example RC 4801 (ex. Rhein Chemie), a propane-1,2-diol semi-ester of tetrapropenyl succinic acid, or polyhydric alcohol esters of a succinic acid derivative, the succinic acid derivative having on at least one of its alpha-carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group containing from 20 to 500 carbon atoms, e.g. the pentaerythritol diester of polyisobutylene-substituted succinic acid, KEROKORR 3232 (ex. BASF) or SARKOSYL 0 (ex. Ciba); re-odorants, for example KOMPENSOL (ex. Haarmann & Reimer); biocides, for example GROTA MAR 71 (ex. Schuelke & Mayr); lubricity enhancers, for example OLI 9000 (ex. Octel), EC 832 and PARADYNE 655 (ex. Infineum), HITEC E580 (ex. Ethyl), VEKTRON 6010 (ex. Infineum) and amide-based additives such as those available from Lubrizol, for example LZ 539 C; dehazers, for example alkoxyated phenol formaldehyde polymers such as those commercially available as NALCO EC5462A (formerly 7D07) (ex. Nalco) and TOLAD 2683 and T-9318 (ex. Petrolite); antistatic agents, for example Stadis 450 (ex. Octel); and foam reducers, for example the polyether-modified polysiloxanes commercially available as TEGOPREN 5851 and TEGO 2079 (ex. Goldschmidt) and Q 25907 (ex. Dow Corning), SAG TP-325 (ex. OSi) and RHODORSIL (ex. Rhone Poulenc).

[0038] It is particularly preferred that the additive include a lubricity enhancer, especially when the fuel composition has a low (e.g. 500ppm or less) sulphur content. In the additivated fuel composition, the lubricity enhancer is conveniently present at a concentration between 50 and 1000ppm, preferably between 100 and 1000ppm.

[0039] The total content of the additives may be suitably between 0 and 1 wt% and preferably below 0.5 wt%.

[0040] The present invention will now be described by reference to the following examples:

Example 1

[0041] To a blue flame burner type BE 1.1-21 (ex. Buderus AG), having a flame tube, fitted in a low temperature boiler S 115 (ex. Buderus AG), were fed at a constant power level (1) an ultra low sulphur fuel oil (Oil A); (2) such a fuel oil (Oil A) additivated according to the present invention by inclusion of 50ppm of each of a phenolic antioxidant IRGANOX L135, an aminic antioxidant IRGANOX L57 and a friction modifier/antioxidant IRGALUBE F10 (Oil B); (3) an ultra low sulphur fuel oil, containing 3ppm of nitrogen compounds (Oil C); and (4) such a fuel oil (Oil C) additivated according to the present invention by inclusion of 140ppm of a mixture of heterogeneous nitrogen compounds 50 wt% quinaldine, 40 wt% quinoline and 10 wt% trimethylpyridine (Oil D). Oils A and C had the properties as listed in Table 1. The oils contained the same standard additive package. The boiler was operated such that condensation of water as present in the flue gas took place on both the heat exchanging surfaces of the boiler as well as in the chimney.

Table 1

	Oil A	Oil C
Density (at 15 °C) in kg/m ³	831.3	836
Sulphur content (wt%)	7	37
Kinematic viscosity at 20 °C (mm ² /s)	4.468	5.267

Table 1 (continued)

	Oil A	Oil C
Flash point (°C)	70	68

[0042] The condensate liquid was collected with a drain and high temperature corrosion of the flame tube was observed and evaluated.

[0043] The results for Oils A and B above are presented in Figure 4, where it can be seen quite clearly that when using Oil A, there was a continual loss of mass of the flame tube with time. This was caused by the high temperature corrosion of the flame tube. However, when using additivated Oil A, i.e. Oil B, according to the present invention, there was no loss of mass of the flame tube with time. This was because there was no high temperature corrosion of the flame tube.

[0044] The results for Oils C and D above are presented in Figure 5, where it can be seen quite clearly that when using Oil C, there was a continual loss of mass of the flame tube with time. This was caused by the high temperature corrosion of the flame tube. However, when using additivated Oil C, i.e. Oil D, according to the present invention, there was no loss of mass of the flame tube with time. This was because there was no high temperature corrosion of the flame tube.

[0045] Oil D was tested for a duration of 981 hours, whilst Oil C was tested for a duration of 593 hours. It was found that the high temperature corrosion of the flame tube using Oil D was substantially lower than that when using comparison Oil C. This demonstrates that although the burner was exposed to Oil D for far longer than it was exposed to Oil C, the high temperature corrosion was still far lower.

Claims

1. The use in a blue flame burner or an optimised yellow flame burner of a boiler of a fuel oil composition which comprises a base oil and one or more additives selected from antioxidants, heterogeneous nitrogen compounds and slightly hydrotreated or straight run fuel fractions, for the purpose of reducing the levels of high temperature corrosion in one or more portions of said burner.
2. The use according to claim 1, wherein said fuel oil composition contains no more than 500ppm sulphur.
3. The use according to claim 1 or 2, wherein said fuel oil composition contains 10 to 500ppm of each of said one or more additives.
4. A method of reducing the levels of high temperature corrosion in one or more portions of a blue flame burner or an optimised yellow flame burner of a boiler by replacing the use in said burner of a fuel oil composition comprising a base oil by a fuel oil composition which comprises said base oil and one or more additives selected from antioxidants, hydrocarbon compounds comprising one or more heteroatoms selected from nitrogen, phosphorus and oxygen and slightly hydrotreated or straight run fuel fractions.
5. The method according to claim 4, wherein said fuel oil composition contains no more than 500ppm sulphur.
6. The method according to claim 4 or 5, wherein said fuel oil composition contains 10 to 500ppm of each of said one or more additives.
7. A method of operating a boiler provided with a blue flame burner or optimised yellow flame burner, which method comprises supplying to said burner a fuel oil composition comprising a base oil and one or more additives selected from antioxidants, heterogeneous nitrogen compounds and slightly hydrotreated or straight run fuel fractions, for the purpose of reducing the levels of high temperature corrosion in one or more portions of said burner.
8. The method according to claim 7, wherein said fuel oil composition contains no more than 500ppm sulphur.
9. The method according to claim 7 or 8, wherein said fuel oil composition contains 10 to 500ppm of each of said one or more additives.

Fig.1.

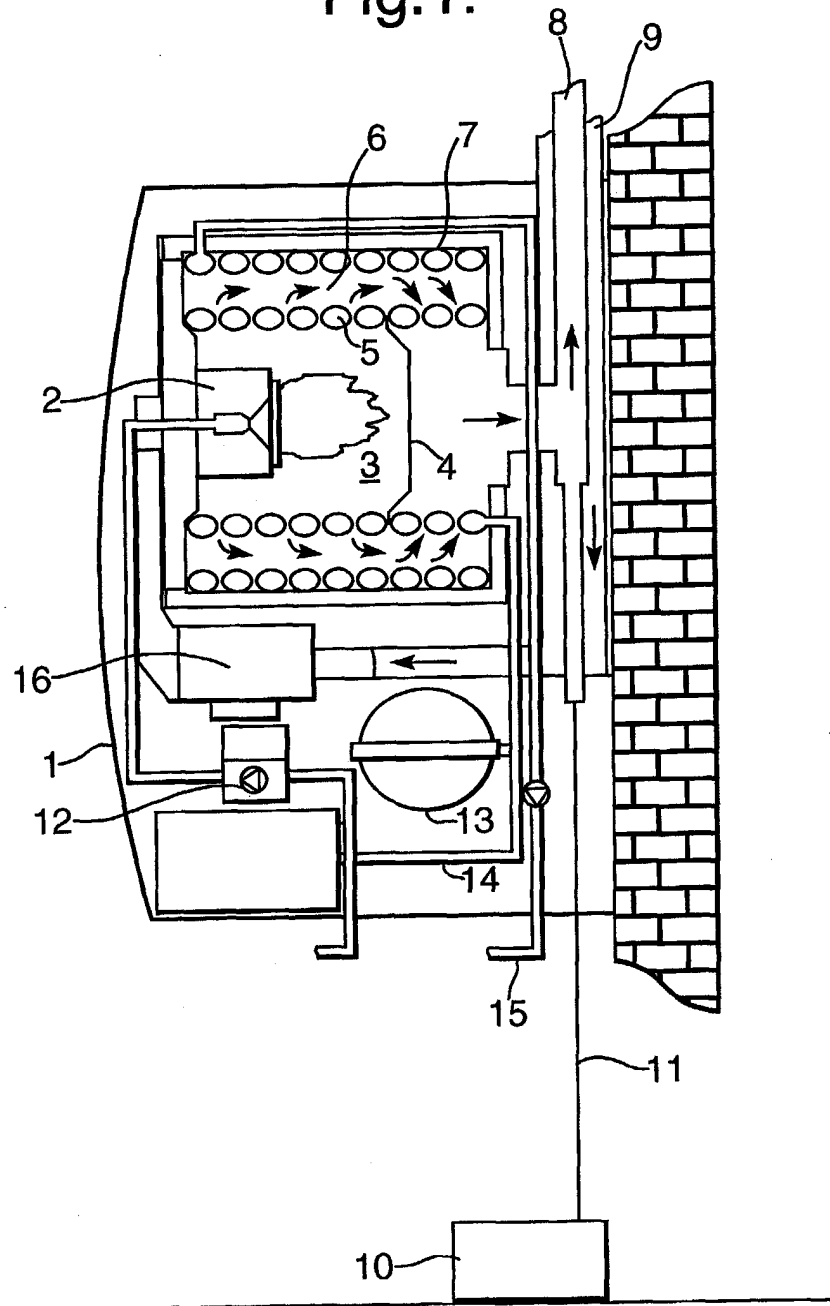


Fig.2.

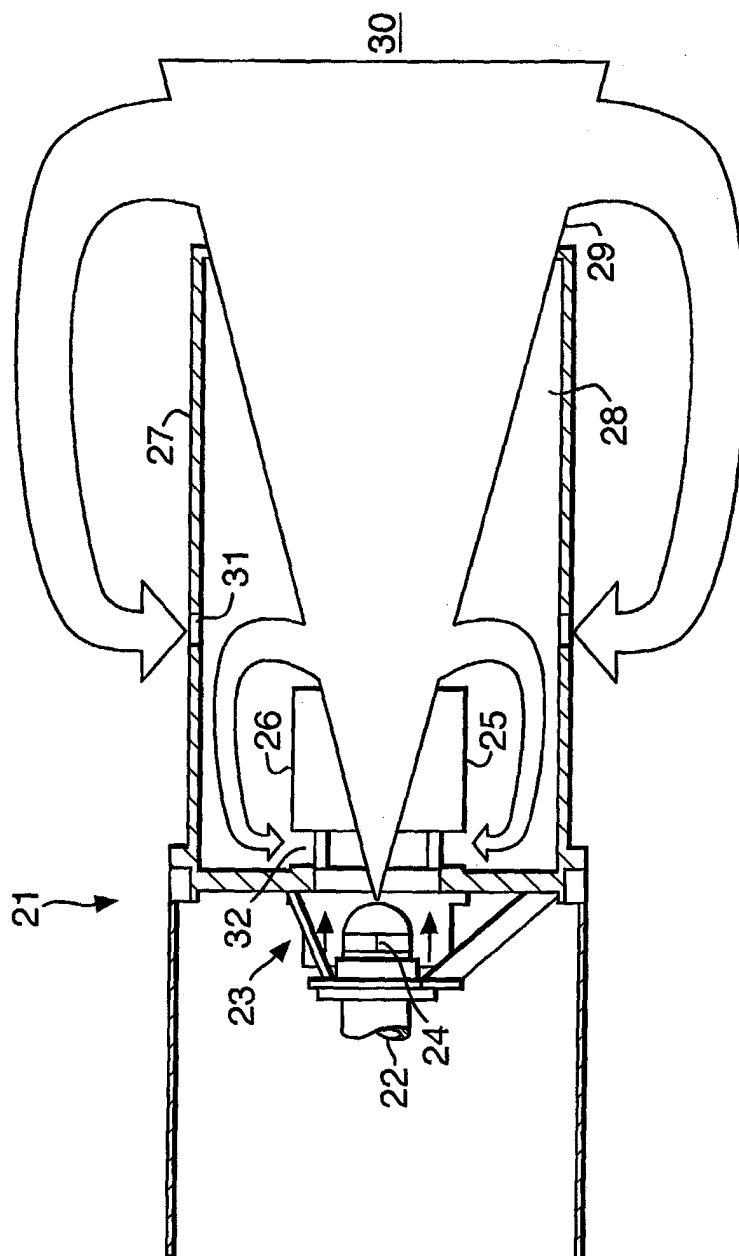


Fig.3.

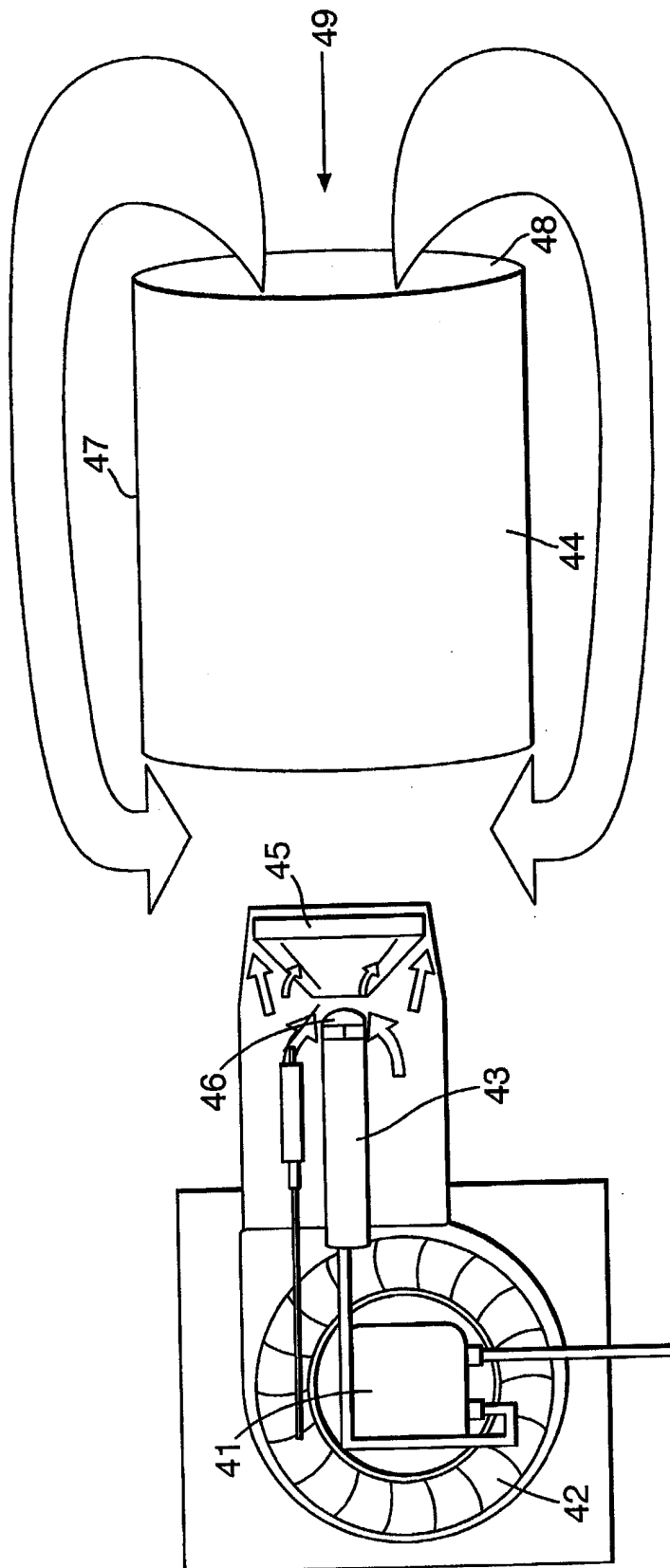


Fig.4.

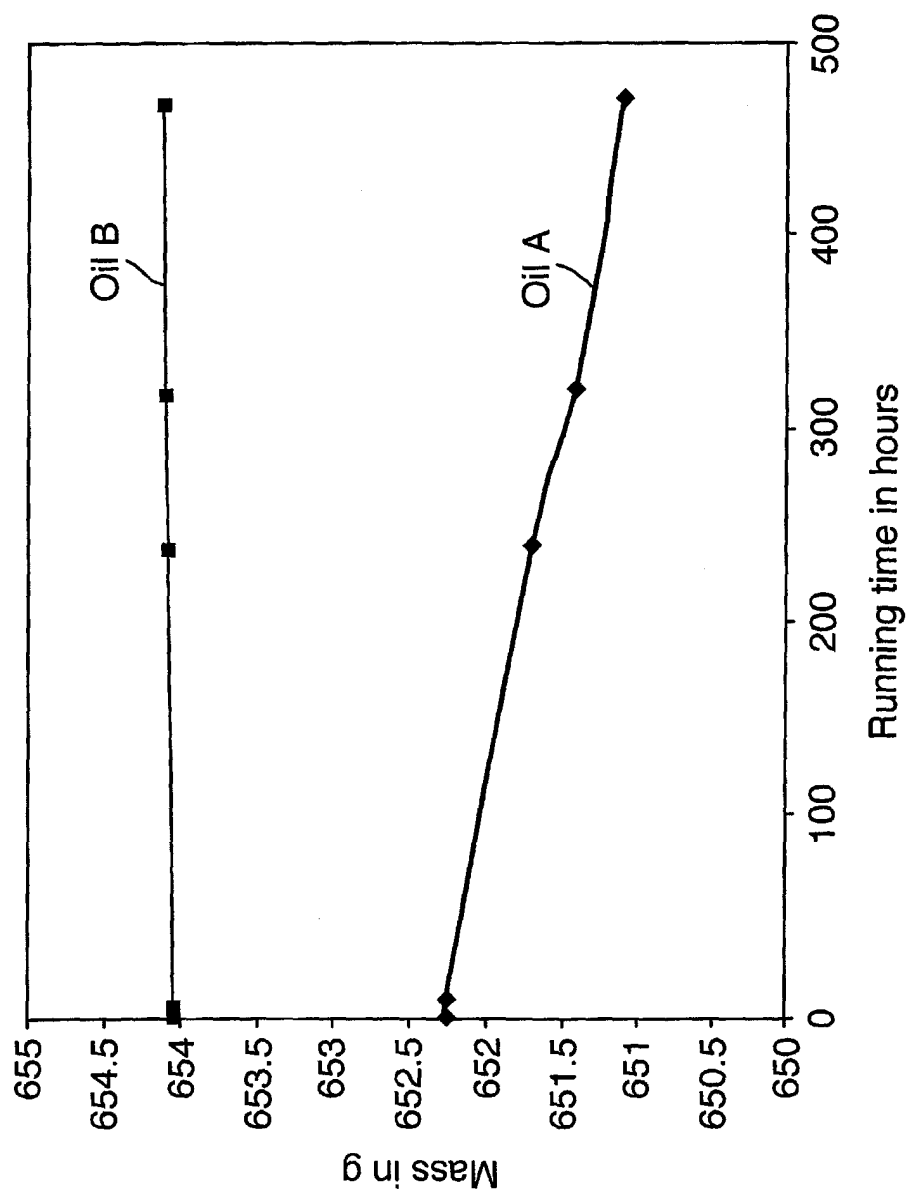
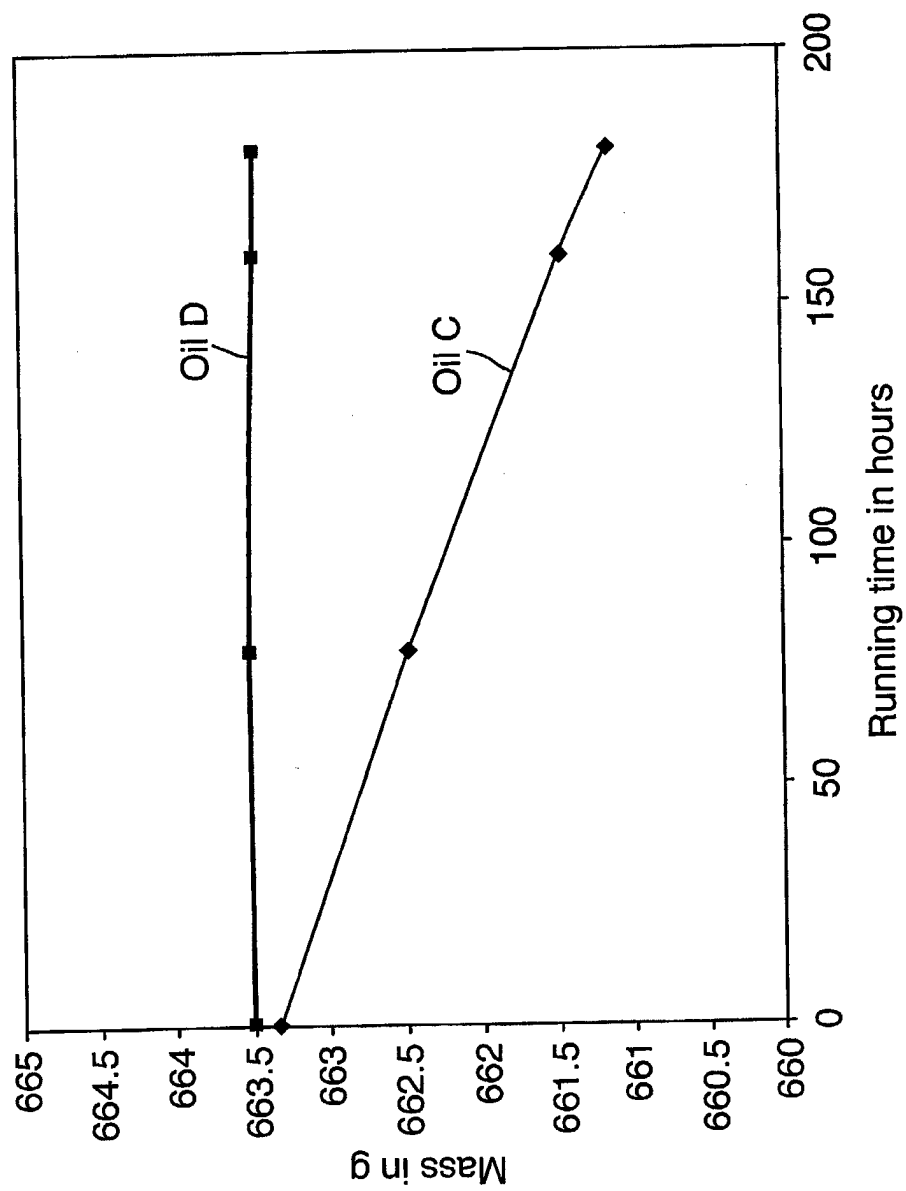


Fig.5.





European Patent
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EUROPEAN SEARCH REPORT

Application Number
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Place of search Munich		Date of completion of the search 18 August 2004	Examiner Bertrand, S
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EPO FORM 1503 03/82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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