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

(11) **EP 3 441 442 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
13.02.2019 Bulletin 2019/07

(51) Int Cl.:
C10L 1/04 *(2006.01)* ***C10L 1/12*** *(2006.01)*

(21) Application number: **18175487.0**

(22) Date of filing: **01.06.2018**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **10.08.2017 PT 2017110250**

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(54) A PROCESS FOR THE REDUCTION OF THE SULPHUR CONTENT OF FUELS

(57) The present invention describes a continuous process for the removal of sulphur compounds (majority of species), that are harmful to the environment and public health and are present in hydrocarbon fuels. This process is particularly suitable for liquid fuels, more specifically for (HFO) Heavy Fuel Oils. The developed process involves the treatment of fuels (A) by means of an ultrasonic method to which an ozone generator (2) is coupled to promote the more efficient formation of peroxides and oxides of sulphur compounds (1, 2,3 and 4).

Separation of the different fuel phases (aqueous and organic phase) is promoted by the addition of a phase transfer agent (D) in a static mixer (5), the separation occurring in a centrifuge (6).

The extraction solvent (D), the catalyst (C) and the water (B) added in the process are subsequently recovered by a high recovery rate process (8). At the end of the process, the treated fuel, containing a much lower sulphur content, is gathered (13).

The several components added to treat the fuel are recovered by a distillation process (8), cooled in different heat exchangers (7, 9, 10, 11 and 12) and stored in respective collection tanks (14, 15 and 16). Water is used as a cooling fluid (E) by the heat condensing exchangers used in the process. The gases resulting from the distillation process (F) are removed by means of an exhaust-vent stream (18). The recovered reagents are returned to the process ensuring that the process occurs continuously until the desired sulphur ratio is obtained.

Residues from the desulphurisation treatment (sulphones and sulphoxides) are stored (17) for further external treatment and possible valorisation.

The present invention is suitable, for example, for marine fuels, although not limited thereto.

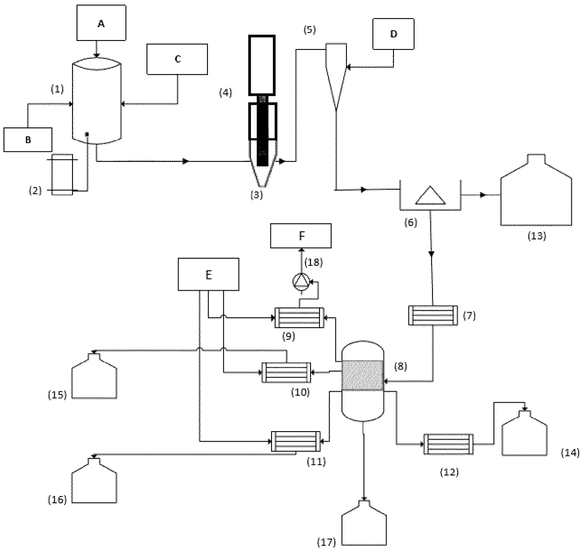

FIG. 1

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Description

Technical field of the invention

[0001] The present invention resides in the field of hydrocarbons desulphurisation. In particular, it relates to a process for the reduction of the sulphur content of petroleum products and liquid petroleum-based fuels, in particular fuels used in the maritime industry.

State of the art

[0002] Despite the constant global research and development of alternative sources of energy, fossil fuels (which can range from coal to oil-based fuels) continue to be the main and most widely used source of energy due to their wide availability, high yields and relatively low prices. The application of these energy sources is diversified and they are used as fuels in automotive, aircraft or marine engines, as well as heating energy sources for plants of all kinds. One of the problems that has concerned international communities over the years is the sulphur content present in this type of fuels, particularly in the form of organic compounds.

[0003] Industrial fuels in general and in particular marine fuels have sulphur contents that are quite high; therefore, the International Maritime Organisation (IMO)imposed sulphur content limits after 1 January 2020.

[0004] Sulphur in any of its forms reacts with oxygen in the combustion air (spontaneously or during combustion), producing sulphur oxides SO and SO2, called SO_x, of which sulphur dioxide (SO_2) is the most abundant, that in the presence of combustion moisture leads to (H_2SO_4) or sulphuric acid, responsible for the phenomenon called acid rain. This phenomenon is harmful to agriculture, wildlife, as well as extremely harmful to human beings, being associated to diseases in respiratory and heart systems, but also responsible for the cancer induction.

[0005] Sulphur is also responsible for the emission of particulate matter (known as soot) PM2.5 being particularly important, since it is related to cancer. Sulphur compounds, given their effects, tend to threaten various ecosystems, causing irreversible damage to their quality of life. In response to these concerns various regulations have been ratified and tight requirements have been imposed to reduce the sulphur content released to the atmosphere of the fuels.

[0006] Factual cases of this were, for example, the demands of the European Union to set a maximum limit of 50 parts per million (ppmw) of gasoline and diesel as of year 2005. In oil fuel, the sulphur content limit for shore industrial applications was limited to 1%. As for maritime transport industry emissions, IMO regulations to reduce sulphur oxides (SOx) emissions from ships first came into force in 2005, under Annex VI of the International Convention for the Prevention of Pollution from Ships (known as the MARPOL Convention). Since then, the limits on sulphur oxides have been progressively tightened.

[0007] Starting on 1 January 2020, the limit for sulphur in fuel oil used on ships operating outside designated emission control areas will be reduced to 0.50% m/m (mass by mass). This will significantly reduce the amount of sulphur oxides emanating from ships and should have major health and environmental benefits for the world, particularly for populations living close to ports and coasts.

[0008] The Regulation requires ship-owners to seek heavy fuel oils with low sulphur content, however, this type of fuel is scarce all around the world, and considerably more expensive than regular high sulphur content fuels.

[0009] Therefore, the development of an efficient technological solution for desulphurisation, other than scrubbers or using other fuels, would be a priority.

[0010] In line with the need to comply with the regulations and restrictions imposed, and taking into account the increase in production costs faced by the oil industry (associated with the desulphurisation methods), there is a clear need to develop a new cost-effective and cleaner technology.

[0011] By completely or partially removing sulphur from fuel composition, sulphur dioxide (SO_2) emissions are reduced.

[0012] There are currently two types of techniques available for the extraction of sulphur (S) from hydrocarbons. The most common method of desulphurising fossil fuels is the hydrodesulphurisation (HDS). According to the same process, the fuel reacts with hydrogen at high temperature (400 °C) and pressure (in the order of 100 atmospheres) in the presence of high cost solid metallic catalysts (Co/Mo or Ni/Mo), requiring large quantities of thermal energy. In said reaction, the organic sulphur is reduced to gaseous H_2S, being later oxidised to elemental sulphur (Claus process). The non-reacting H_2S from the process is harmful (extreme acute toxicity), even when present in small amounts. It is a classic process for removing sulphur from products such as natural gas and refined petroleum products such as gasoline or diesel, aircraft fuel or fuel oils, although it can only be implemented in refineries.

[0013] In addition to the tendency to release H_2S into the atmosphere (high hazard) the hydrodesulphurisation process has certain limitations, including the ability to carry out the conversion of only few organic sulphur compounds present in the fuel (such as mercaptans, thioethers and disulphides). Other compounds such as aromatics, condensed cyclic and multicyclic compounds (e.g., benzothiophenes (BT) or dibenzothiophenes (DBT)) will be difficult to remove by this technique. Recent studies related to HDS indicate, that some volatile organic sulphur compounds (VOC's) are emitted to the atmosphere even by diesel fuel with sulphur contents below 0.1 wt%.

[0014] These compounds correspond to alkyl-DBT with substitutions at positions 4 and 6. These dibenzothiophenes are refractory sulphur compounds and have low reactivity in HDS. To reduce the presence of these compounds by the conventional HDS process, the catalyst volume of the reactor will have to be increased (for example, to reduce these compounds from 0.05 wt% to 0.0015 wt%, the volume would have to be increased by 3.2 times, and if values in the order of 0.0001 % wanted to be reached, the volume of the reactor would have to be 7 times higher). This aspect demonstrates the difficulty of the HDS process in adapting to new legal requirements. Another disadvantage is related to the new imposed regulations since hydrodesulphurisation has to be carried out under more stringent conditions to achieve lower sulphur levels. Hydrodesulphurisation is also a process with higher operating costs, only compatible with large processing volumes and continuous processes, in particular applicable to large refineries (requiring high reactors and high reaction times).

[0015] U.S. Patent 8,926,825 B2 describes the use of the Hydrodesulphurisation (HDS) technique as a way of removing sulphur compounds in hydrocarbons (more specifically in diesel samples). As indicated earlier, the process, like any HDS method, uses high temperatures and pressures, which makes the method expensive and potentially dangerous. The method also describes a subsequent fractionation step in a distillation column of a more loaded undercurrent in sulphur species resistant to Hydrodesulphurisation. The chain is subject to an oxidation process in the presence of an oxidising agent (hydrogen peroxide in percentages of around 2.5 wt%) and exposed to an ultrasound system (power consuming 1Kw min/litre processed). It promotes the subsequent separation of sulphur oxides (sulphoxides and sulphones) in an absorption tower (solid/liquid absorption) using a solid alumina system as absorbent, which is extremely costly (e.g. SELEXSORB CD BASF)).

[0016] It is a process that, despite the high extraction efficiency (around 90%), has high operating costs due to the combination of various desulphurisation techniques, by the use of expensive metal absorbers and peroxides (high hazard). It is also a process only tested in diesel samples, and its effectiveness in other types of fuels (such as heavy fuel oil) has not been proven yet.

[0017] Another technique used more recently in the removal of sulphur compounds in heavy fuels is called Oxidative Desulphurisation (ODS). This process is based on the use of a chemical reactant with high oxidation potential, in particular 50% hydrogen peroxide (H_2O_2) which causes the oxidation of free sulphur and molecular sulphur (originating sulphur oxides such as sulphones and sulphoxides). Sulphur compounds are known to be slightly more polar than hydrocarbons, however, oxides of sulphur compounds such as sulphones or sulphoxides are substantially more polar than sulphides.

[0018] Oxidating sulphides and sulphoxides or sulphones is usually easy and quick.

[0019] As such, the conversion of slightly polar sulphides into more polar sulphones or sulphoxides allows the sulphur compounds to be extracted more easily from the fuels into an aqueous phase. The ODS process has the advantage of allowing refractory sulphur compound to be removed, something that by HDS couldn't be achieved. These species are readily converted by oxidation and subsequently removed. The applicability of oxidative desulphurisation depends on the kinetics and selectivity of organic sulphide oxidation.

[0020] The oxidant is a product that, although it is not pollutant or harmful to the environment, is expensive and also potentially dangerous. This technique has the advantage of not requiring as much thermal energy as hydrodesulphurisation, nor high hydrogen pressures, being likewise compatible with smaller processing units in terms of processing capacity. It allows a safer operation as it is carried in more reasonable operatory conditions (reacting at low temperatures and pressures) and makes it easier to detect and remove sulphur species resistant to HDS. Another advantage of ODS over HDS is that it does not require hydrogen in the process (equally expensive). This technique presents, however, the inherent difficulty in the cost of the liquid oxidising agent, as well as the inherent danger of its handling.

[0021] Some studies have also demonstrated the advantage of associating ultrasonic energy, or sonification, to the oxidation process. For such purpose, an ultrasound system is used (Ultrasonic-Assisted Oxidative Desulphurisation - UAOD).

[0022] Ultrasonic-Assisted Oxidative Desulphurisation is performed by combining the fuel with the oxidising agent (hydroperoxide) in the presence of an aqueous fluid (for example water), and submitting the mixture to an ultrasonification process to increase the reactivity of the species in the blend. The UAOD process operates at ambient temperature and atmospheric pressure allowing the selective removal of sulphur compounds from hydrocarbons.

[0023] US patents 6,402,939 B1 and US 8,197,763 B2 refer to two processes where an UAOD system is used to remove sulphur in fuels.

[0024] US 6,402,939 B1 discloses a method of treating Diesel Oil where the sulphur is removed from the fuel with a yield of 13.40 to 44.70%. The method comprises two steps. In the first step, an oxidant (2 wt% hydrogen peroxide) is added to the fuel, compatibilised in an aqueous phase (water) in the presence of a solid catalyst (Tungstate: $CuSO_4$ or Fe(II), in a concentration of 10 mM to 100 mM) to regulate the activity of the OH radical and a phase transfer agent (PTA), more specifically dodecyltrimethylammonium fluoride or dodecyltrimethylammonium bromide) to accelerate the conversion of sulphides to sulphones. Two transfer agents are indicated, the first one being more selective and efficient, not leading to the formation of by-products. The mixture is sonicated for an optimum time of 7.5 minutes and kept in an ice bath (-5 to 20 °C), in order to avoid overheating resulting from the sonication process. The second stage of the treatment consists of liquid-liquid extraction (3 successive extractions with polar solvent such as Acetonitrile, Dimethylformamide (DMF) or N-Methylpyrrolidone (NMP)) or solid-liquid (using silica gel, zeolites or polymer resin).

[0025] U.S. Patent No. 8,197,763 B2 describes a method similar to the above (UAOD, for Diesel fuel treatment) with the following process differences. A phosphotungstic acid catalyst and a higher amount of oxidant (2 to 4% wt of hydrogen peroxide) are used. The exposure time to the ultrasound system is also higher (20 minutes) and the catalyst and solvents used in the process can be recovered. The yield rate of sulphur removal is from 90.30 to 97.53%.

[0026] In relation to the oxidative desulphurisation method, US 7,758,745 B2 may also be mentioned. It corresponds to a method of Ultrasound-Assisted Oxidative Desulphurisation (UAOD), presenting, nevertheless, some differences. In the process, oxidant (Hydrogen Peroxide) is used in an excessive amount (1: 1 by volume relative to the amount of the fuel to be treated), two catalysts (the first used in a first stage of the treatment (Desulphurisation of OSCs), consisting of a mixture of acetic acid and trifluoroacetic acid (20:80), and a microporous solid catalyst to be used in a second desulphurisation treatment of thiophenes in a fluidised bed reactor). A Lewis acid type at ambient temperature ionic liquid (for example trimethylammonium chloroaluminate) and a mixture of two phase transfer agents (Acetonitrile and tetraoctylammonium fluoride) are also used.

[0027] This method, despite having a considerably high sulphur removal rate (in the order of 99.90%), presents very high operating costs due to the fact that the operation is performed in different stages (one phase of Desulphurisation to remove OScs and another for the thiophenes), for considering metal catalysts that are difficult to synthesise, for using several reactive compounds that are toxic and expensive (ionic liquid, two phase transfer agents, two catalysts, and high amount of peroxide) and the high frequencies and intensities of the sonication process (50 kHz and 50 W/cm^2). The use of a high amount of oxidant may also lead to a loss of the calorific value of the fuel.

[0028] Other authors have also demonstrated the value of using other types of oxidants (such as ozone). According to the patent CN102703111A there is a batch process for desulphurising fuel oils using ultrasound (ultrasonic-assisted oxidative desulphurisation) and ozone as oxidising agent. However, the described process has some drawbacks, in particular the use of solid metal catalysts with high cost and complex preparation. The process also involves the application of high ultrasound frequencies (40 kHz), which will lead to considerable energy costs. The patent further describes a significant expense of extraction solvent in the process (three times the amount of fuel to be treated) which corresponds to significant expenditures on reagents in the process. According to examples given in the patent the technique has limited results, being a specific technique for the removal of only certain sulphur species (as a case of dibenzothiophenes) and demonstrating high yields only in cases where the concentration and sulphur in the oils was relatively low (300 to 800 ppm). Nowadays, such a result is insufficient to allow sulphur reductions in fuels such as the HFO (Heavy Fuel Oil). In the maritime industry, this type of fuel is generally purchased with sulphur concentrations of the order of 3.5%. Given the latest regulations imposed by MARPOL, it is necessary to find a process to ensure that the properties of the fuel are maintained (high calorific value), and, at the same time, guarantee sulphur removal, reaching the legal limits imposed (0.1% in the ECA zones and 0.5% outside the zones.

[0029] Thus, a clean, efficient desulphurisation solution is required which allows high yields and high rates of sulphur removal. This need is increasingly important given the shortage of heavy fuels with low sulphur content.

Brief description of the figures

[0030]

Figure 1. - Schematic of an embodiment of the process according to the present invention.

Figure 2. - Static mixer

Figure 3. - The sonotrode. **a)** Amplitude amplifier that is attached to an actuator, (at a frequency of 20,000 Hz), **b)** transfer piece, **c)** sonotrode and **d)** typical direction of vibrations (60-100 μm).

Description of the invention

[0031] The present invention contemplates a continuous Ultrasonic-Assisted Oxidative Desulphurisation (UAOD) process to which an ozone generator is coupled to promote a more efficient oxidation of the sulphur compounds (such as sulphides, disulphides, mercaptans, thiols, thiophenes, benzothiophenes and dibenzothiophenes) present in liquid fuels, more specifically Fuel Heavy Oil, for its application in the maritime industry, or Diesel. It can also be used in other applications such as power generation industry.

[0032] Ozone has an oxidising potential higher than oxygen or other oxidising species, such as hydrogen peroxide. Their formation in the process of the invention will, together with the effect of the ultrasound system, enable the sulphur compounds to be more efficiently converted to oxides and peroxides, easing their removal. The process of the invention aims to obtain low-sulphur fuel, and as a consequence emissions resulting from the combustion of those fuels are less harmful to health and the environment.

[0033] According to earlier studies the advantage of oxidising fuels with oxidant species (hydroperoxides) is known along with the use of ultrasounds. The combined effect allows an increase in the reactivity of the species present and a more selective conversion of the sulphur compounds. The reaction with the oxidising species allows the conversion of sulphur compounds present in the fuel (e.g. in the case of sulphides) to sulphur oxides (sulphones and sulphoxides). However, exposure to ultrasound promotes the thermionic decomposition of water leading to the formation of new peroxides that help the oxidising reaction of sulphur.

$$\begin{gathered}
H2O \rightarrow OH + H \\
OH + H \rightarrow H2O \\
2OH \rightarrow H2O2 \\
OH + OH \rightarrow H2 + O2 \\
2H \rightarrow H2 \\
2OH \rightarrow O + H2O \\
2O \rightarrow O2 \\
H2O + 2H \rightarrow H2O + H2 \\
H2O + H2O + O2 \rightarrow 2H2O2 \\
HO + H2O \rightarrow H2O2 + \mathrm{H} \\
O2 \rightarrow 2O \\
O2 + \mathrm{O} \rightarrow O3 \\
O2 + \mathrm{H} \rightarrow \mathrm{OOH} \\
O + \mathrm{OOH} \rightarrow \mathrm{OH} + O2 \\
O + H2O \rightarrow \mathrm{2}\ OH \\
2OOH \rightarrow H2O2 + O2
\end{gathered}$$

(EQ.1)

[0034] With the addition of ozone in situ, the present invention seeks to ensure extensive and selective oxidation, while reducing the incorporation of new elements external to the system (lower peroxide addition), and the respective production and operation costs.

[0035] The addition of ozone allows not only the oxidation of sulphur species present in the fuel but also the conversion of the water present in the fuel composition to hydrogen peroxide, thereby increasing its oxidising potential. For this, the ozone is produced in a generator suitable for that purpose.

[0036] Peroxides, as well as the ozone added, give rise to sulphur oxides which are easier to remove than in their initial state.

[0037] The peroxides formed in the ozone addition step are members of the peroxide group of hydrogen and water-soluble hydroperoxide.

[0038] Based on the foregoing, the present invention contemplates a method for reducing the sulphur content in liquid fossil fuels comprising:

a) A heating and stirring step (1) of the fuel (A), preferably at a temperature of from 30 to 90 ° C;

b) A stage of ozone addition of the fuel in the same mixer, using ozone that will be produced in situ by a generator (2). In this step, the agitation is maintained while ozone is added to the system as an oxidising agent to the fuel. This step will be carried out at the temperature reached in a), preferably for a time comprised between 30 and 60 minutes;

c) A step for mixing the fuel obtained in b) with a liquid catalyst (acetic acid) (C), which can preferably be in a proportion of 1 to 10% by volume of the mixture and, optionally, water (B), preferably in a proportion of 0 to 30% of the volume of the mixture, at the temperature reached in a), preferably for 30 to 50 minutes;

d) A sonication step applied to the mixture obtained in c) for the oxidation of the sulphur and emulsion compounds of the fuel (3) and (4);

e) An extraction step ((5) and (6)) of the oxidised sulphur compounds obtained in d) by the addition of a polar aprotic solvent (acetonitrile) (D);

f) A step of recovering the liquid catalyst (C), the extraction solvent (D) and optionally the water (B) used in the process by means of a fractional distillation (8, 9, 10 and 11),

g) A step in which recovered reagents (water, catalyst and extraction solvent) are returned to the process (continuous treatment);

h) A step of obtaining the fuel with a reduced sulphur content.

[0039] In a preferred embodiment, the fuel obtained in the method of the present invention in step h) is subjected to an additional centrifugation step (6) to remove excess water.

[0040] The fuel obtained as the final product has a substantially reduced sulphur content, with a minimum yield of 50% per cycle compared to the initial sulphur value (starting with sulphur fuel in the order of 3.5% by weight).

[0041] Ozone reagent (O_3) has a high oxidising potential, potential even higher than that of hydrogen peroxide (H_2O_2) (2.07 V and 1.77 V respectively).

[0042] With the incorporation of an ozone generator in the process based on the "corona" effect (application of an electric discharge arc to an air flow) of the atmospheric oxygen (the source of atmospheric air or pure oxygen), this oxidant can be prepared by a continuous process adjusted to the sulphur content and fuel flow being treated. This gives rise to an economic and operational safety advantage compared to the addition of other types of oxidants, not least of all because the present process does not require significant amounts of energy (low cost of production), does not take up too much space, and is fast, safe and efficient.

[0043] The use of ozone in the system also adds operational advantages. The fact that the oxidising agent, ozone (O_3), is prepared in situ through an ozone generator coupled to the process (no consumables required - outside air supplied), allows saturation of water (existing in the fuel and / or added) that will serve as a cavitation agent in ultrasonic cavitation chambers, allowing minimal use of reactants (leads to the formation of peroxides that will oxidise sulphur compounds present in the fuel).

[0044] The developed method thus allows the formation of oxidising species resulting from the thermionic decomposition of water in the sonication process and from the generation of ozone.

[0045] In particular embodiments of the invention, the oxidising species which allow the conversion of sulphur into sulphur oxides are removed at a later stage by a liquid-liquid extraction process with a polar aprotic solvent, preferably Acetonitrile (D), implying a number of passages of solvent suitable to the desired yield. Acetonitrile acts as a Phase Transfer Agent (PTA), leading to the transfer of the sulphones to the aqueous phase (formed by an aqueous solution of solvent, catalyst and sulphones), maintaining the organic phase formed by the treated fuel (with lower sulphur content). The extraction process preferably involves three solvent passages (not being completely required) to ensure a more efficient separation between the aqueous phase and the organic phase. The transfer agent should be added in equal proportion in volume to that of the fuel to be processed. Ozone concentration can also be controlled by using sensors that accurately measure the quantity from ppm (parts per million) to ppb (parts per billion).

[0046] Another advantage of the invention is the use of a commercially available liquid catalyst (advantage over other previously described methods) and the possibility of recovering the extraction solvent in a high yield by fractional vacuum distillation, as well as catalyst and water added in the process, with a high recovery rate at the end of the treatment.

[0047] The fact that the recovered chemicals are returned to the process ensures economical savings and, by functioning as a continuous process, can also permit higher flow rates treated and less inoperative times (as seen in other references).

[0048] The amount of extraction solvent used can also be lower than that tested by other references - in the case of the patent CN102703111A), which is considered a significant saving for an equally superior yield. The recovery will be done as a function of the different boiling points of the different components among themselves and in relation to the sulphones

[0049] From an economic point of view, part of the energy savings are related to the fact that the process can also use lower temperatures and pressures compared to previous desulphurisation processes (for example in the case of Hydrodesulphurisation). Energy consumption by ultrasound (20 kHz) is also considered to be low, but it is the necessary amount for the desired result (lower than that seen by other prior techniques).

[0050] From a safety point of view, the process developed presents no danger in terms of storage and handling since the oxidising agent is prepared on demand and exists only in saturated aqueous solution. It is a clean oxidant because it only oxidises and does not form undesirable side products.

[0051] The present invention has also an advantage from an environmental point of view compared to other processes described above, since it is a process compatible with the desulphurisation of relatively modest flow rates and can therefore be implemented on board ships, allowing them to burn with the appropriate Sulphur content (S). By-products (sulphones and sulphoxides) can be treated as oily wastes by using existing dedicated systems used on board and disposed of in the usual way (17).

[0052] Thus, the process of the present invention enables sulphur compounds to be removed with high yield from the fuel, based on a process which has a low energy consumption and which is adaptable to different production capacities.

[0053] The process does not require high temperatures nor pressures, and is safer than conventional desulphurisation processes.

[0054] In addition, it has lower operating costs than conventional desulphurisation processes such as Hydrodesulphurisation and Oxidative Desulphurisation per se.

[0055] Compared with other ozone-using techniques described above, the present invention allows the treatment of heavy fuel oils with significantly higher sulphur content (3.5% by weight), making use of liquid catalysts that are easier to obtain, using smaller amounts of extraction solvent (considerable savings), and requiring less energy and respective costs in using ultrasound technology (20 kHz compared to 40 kHz). Also, the present invention contemplates the recovery of reactants, and by-product segregation for disposal.

Detailed Description of the Invention

[0056] The sulphur present in the fuel consists of a wide variety of compounds which correspond to hydrocarbons containing one or more sulphur atoms covalently linked to the reminiscent molecular structure. Among the mentioned compounds are thiols, thioethers, sulphides, disulphides, mercaptans, among others. Some of the more refractory compounds correspond to aromatic or nonaromatic heterocycles, which may range from thiophenes to benzothiophenes or dibenzothiophenes.

[0057] The present invention is intended to promote the oxidation of said species (making them easier to eliminate) to obtain a cleaner final product, while possessing a high calorific value for the intended applications. The invention describes a continuous process for removing sulphur species from hydrocarbons, which is revolutionary in comparison to other identified techniques.

[0058] **Figure 1** shows a diagram of an embodiment of the process, in which the following steps are carried out:

Ozonation of fuel and sulphur catalysis

[0059] In a static mixer (1) heating and stirring (at 750 rpm) of the high sulphur liquid fuel (A) at an optimum temperature (preferably above 40 ° C) is promoted, however depending on the density and viscosity of the product, varying between 30 and 90 ° C) with ozone (O_3) (produced in a generator by a continuous process based on the "corona" effect (2)) and in some cases saturated water (B) in ozone at an optimum temperature (40° C, $H_2O + O_3$). The ozonation process should take place for an appropriate period of time that depends on the Ozone generator capacity (dm^3/h).

[0060] In those cases where it is considered necessary to add water (B) to the fuel (to achieve the desired treatment yield), it should be incorporated in a percentage between 0 and 30% (V/V), preferably 10%).

[0061] The water will work in these situations as aqueous fluid, allowing a better compatibility between the formed peroxides and the fuel.

[0062] After the ozonisation, the catalyst, acetic acid (CH_3COOH) (C), is added in the same static mixer (1), and the reaction is promoted for 5 to 30 minutes (preferably 15 minutes) at an optimum temperature (between 30 and 90°C, preferably at 40°C).

[0063] The addition of the catalyst to the system aims to increase the reactivity of the process. The addition of this component should be in a ratio of 1-10% (V/V) (preferably 9% (V/V)).

[0064] The reaction mixture is subsequently introduced into a cavitation chamber (3) within which a titanium sonotrode (4) resonating at about 20 kHz and amplitude between 50-100% is fitted. Preferred sonication conditions will be 20 kHz and 100% amplitude. Within the cavitation chamber (3) thermionic decomposition of the water in its various peroxides, as well as the intimate contact of those and the ozone with the free and molecular sulphur (guaranteeing complete homogeneity and stability of the emulsion) react. The sonication process should be maintained for a period of time between 10 and 30 minutes (the tests performed demonstrate that the optimal sonication time depends on the fuel flow rate).

Thermionic decomposition of water

[0065] The mixture comprising fuel, ozone saturated water (O_3) and catalyst enters the cavitation chamber (3) in a continuous flow exiting the chamber as a function of the time, temperature and ultrasound energy required for the optimisation of the process.

[0066] Inside the cavitation chamber (3), an intimate admixture is formed comprising ozone (O_3) and oxidising agents and peroxides resulting from the thermionic decomposition of water **(EQ.1)** resulting from cavitation by ultrasonication. The mixture of these oxidising agents with the free sulphur and with the molecular sulphur contained in the fuel (in the form of Sulphides, Mercaptans, Thiols and Thiophenes), results in the formation of sulphoxides and sulphones. The method is based on the joint use of two effects, oxidation of free and molecular sulphur with ozone (O_3) and oxidation by peroxides.

Separation and removal of sulphones, sulphides and sulphoxides from the fuel being treated

[0067] The product exiting the cavitation chamber is then mixed in a static mixer (5), with polar solvent (Acetonitrile-phase separation agent, PTA- (D)), in a volumetric ratio equivalent to that of the fuel to be processed (1:1). The solvent being added has low affinity with the fuel and high polarity, so that it can make the sulphones, sulphides and sulphoxides separate from the liquid fuel in the centrifuge (6), going along with the aqueous phase. Various passages of the polar solvent acetonitrile (D) can be made in order to ensure a more efficient separation between the aqueous and the organic phase. According to the laboratory tests, it has been found that more than one wash in order to achieve a more efficient removal of the sulphur compounds.

[0068] The solution consisting of acetonitrile, distilled water, acetic acid (catalyst), sulphoxides and sulphones, is then subjected to a unitary operation (fractional distillation- (8)) to recover the extraction solvent, catalyst and added water in the process (with high recovery rate due to differences in boiling points compared to the sulphones (≈200°C)). The recovery process consists of a vacuum fractional distillation with three condensers, shell and tube heat exchangers (8), the fuel being preheated in the heat exchanger (7). The recovered compounds (depending on their boiling temperatures) are then condensed in the heat-exchangers (9, 10, 11 and 12 and 11) to be reincorporated into the process (continuous process) after being recovered. Acetonitrile, distilled water and acetic acid are stored in the tanks 14, 15 and 16. The boiling temperature of the different compounds to be recovered will be: 82 °C for the extraction solvent, 100° C for water and 118 °C for acetic acid. The sulphones and sulphoxides which are by-products of the process which are stored in the tank (17) for further treatment. On the other hand any other vapours (F) released in the distillation step may be extracted by means of an exhaust line placed in the process (18).

Measurement of sulphur content

[0069] The initial value of the sulphur content of the fuel (A) as well as the value after treatment (13) can be determined using an X-Ray Fluorescence (FRX) technique, which follows ASTM D4294 standard.

Claims

1. A method for reducing the high sulphur content in liquid fossil fuels **comprising:**

    a) A step of heating and mixing the fuel with water (1);

    b) An ozonation step (2) in which, while maintaining agitation, ozone is added as an oxidising agent to the fuel at the temperature reached in a);

c) A step of mixing the fuel obtained in b) with a liquid catalyst (C) and, optionally, water (B), at the temperature reached in a), by static mixer.

d) A stage of sonication (3,4) by applying ultrasound to the mixture obtained in c) for the oxidation of the sulphur compounds and emulsion of the fuel;

e) A step of extraction of the oxidised sulphur compounds obtained in d) by means of a polar aprotic solvent (acetonitrile)and density difference (stling);

f) A step of recovering the liquid catalyst, the extraction solvent and, optionally, the water used in the process, and by means of centrifugation.

g) A step of obtaining the fuel having a reduced sulphur content.

2. The method according to claim 1, **characterised by comprising** a heating step a) is carried out at a temperature of between 30 and 90 ° C.

3. The method according to claim 1 and 2, **characterised by** comprising an ozonation step b) is carried out for between 30 and 60 minutes.

4. The method according to any one of the previous claims, **characterised by** comprising a mixing step c) is carried out for 5 to 30 minutes, and in that the liquid catalyst is a carboxylic acid, or in particular acetic acid, in a ratio of 1 and 10% of the volume of the mixture.

5. The method according to claim 4, **characterised by** addition of water in a proportion of 0 to 30% by volume of the mixture.

6. The method according to any one of the preceding claims, **characterised by** comprising a sonication stage, sonication step d) being carried out for a time between 10 and 30 minutes, at a frequency of between 20 and 50 kHz and at a range of 50 and 100%.

7. The method according to any of the previous claims, **characterised by** comprising an extraction step e) which is carried out by means of a liquid-liquid separation process, where the solvent used is a polar aprotic solvent with a nitrile group (acetonitrile) in equal volume proportion to the fuel to be treated.

8. The method according to any of the previous claims, **characterised by** comprising a recovery step f) is carried out on the basis of differences in the boiling points of the different compounds to be recovered in relation to the sulphones.

9. The method according to claim 8, **characterised by** comprising a recovery step f) which is carried out by means of a vacuum fractional distillation.

10. The method according to claim 8, **characterised by** comprising a return of recovered components to the system (continuous process).

11. The method according to any of the previous claims, **characterised by** the fact that the fuel obtained in (g) is subjected to an additional centrifugation step to eliminate excess water.

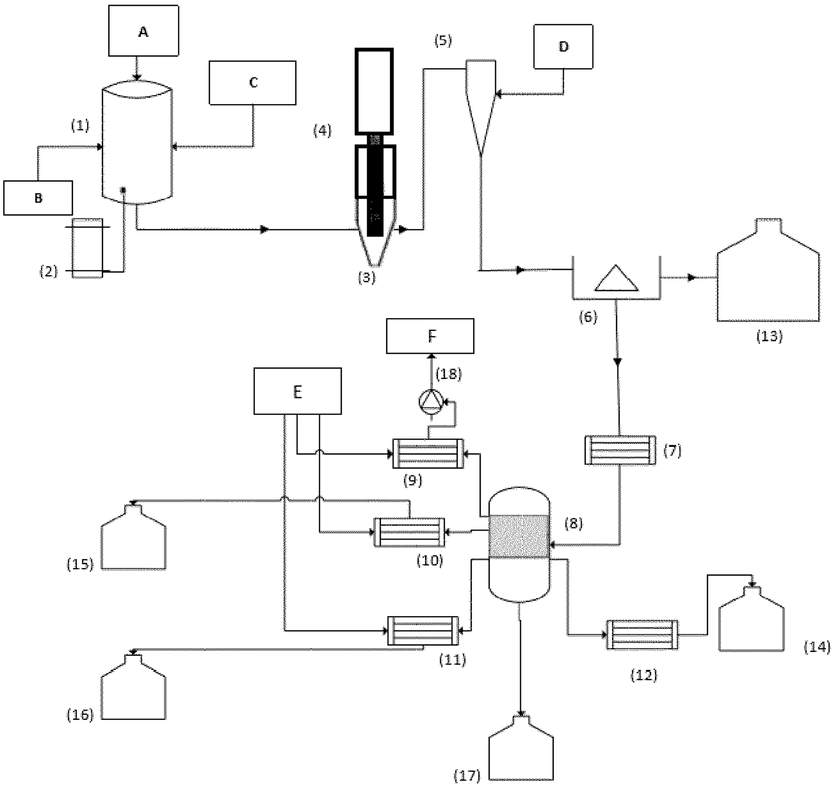

FIG. 1

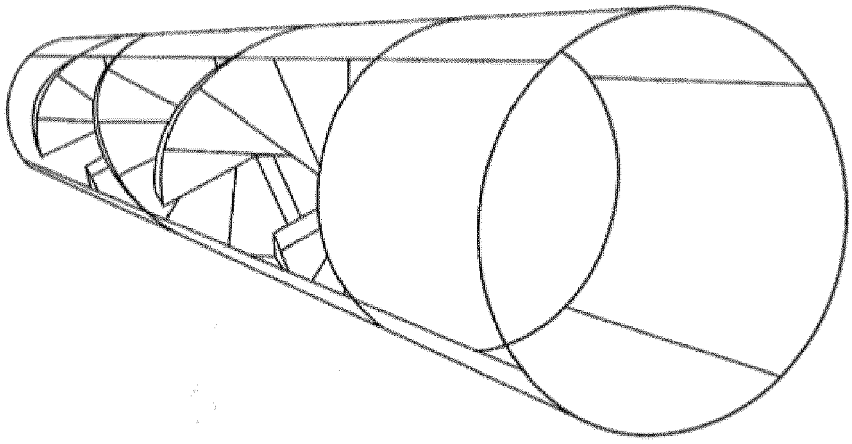

FIG. 2

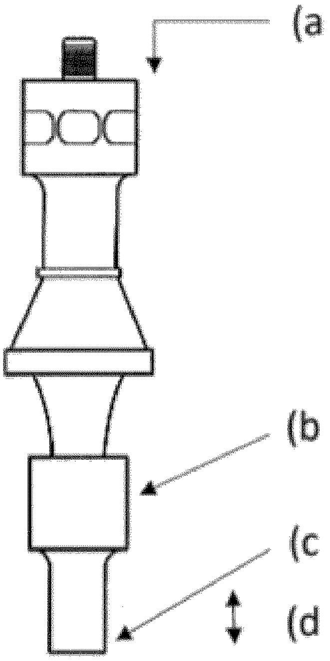

FIG. 3

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EUROPEAN SEARCH REPORT

Application Number
EP 18 17 5487

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
Y,D	DATABASE WPI Week 201330 Thomson Scientific, London, GB; AN 2013-A79109 XP002786296, & CN 102 703 111 A (UNIV SHANDONG) 3 October 2012 (2012-10-03) * the whole document * -----	1-11	INV. C10L1/04 C10L1/12
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			TECHNICAL FIELDS SEARCHED (IPC)
			C10L

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	7 November 2018	Pöllmann, Klaus

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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L : document cited for other reasons
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 18 17 5487

07-11-2018

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 102703111 A	03-10-2012	NONE	

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