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(71) Applicant *(for all designated States except US)*: **SAUDI ARABIAN OIL COMPANY** [SA/SA]; Box 5000, Dhahran, 31311 (SA).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **AL-HAJJI, Adnan** [SA/SA]; P.O. Box 5091, Saudi Aramco, Dhahran, 31311 (SA). **BOURANE, Abdennour** [FR/SA]; P.O. Box 1634, Saudi Aramco, Ras Tanura, 31311 (SA). **KOSEOGLU, Omer, Refa** [US/SA]; P.O. Box 8560, Saudi Aramco, Dhahran, 31311 (SA).

(74) Agent: CINAMON, Jay, S.; Abelman, Frayne & Schwab, 666 Third Avenue, New York, NY 10017-5621 (US).

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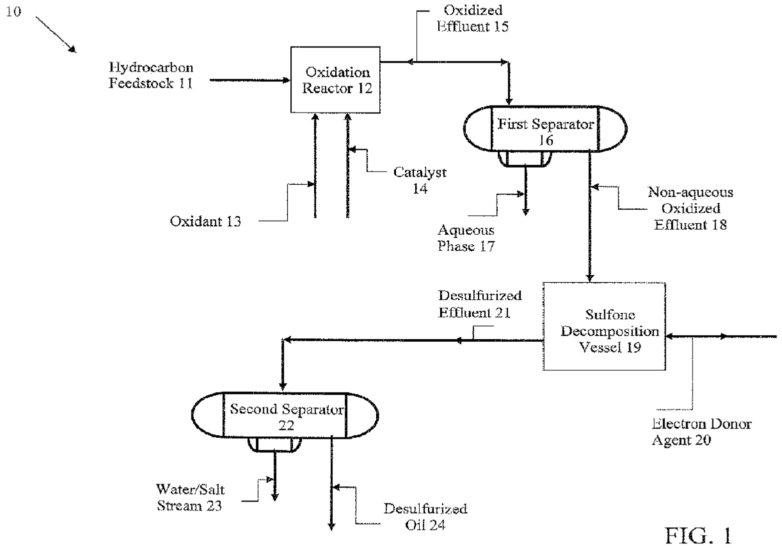

FIG. 1

(57) Abstract: A process wherein an electron donor agent is provided for the decomposition of sulfones and sulfoxides formed after the oxidative desulfurization of a sulfur-containing hydrocarbon stream.

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PROCESS FOR SULFONE CONVERSION BY SUPER ELECTRON DONORS

RELATED APPLICATIONS

[01] This application claims the benefit of U.S. Patent Application No. 13/181,043 filed July 12, 2011, the disclosure of which is hereby incorporated by reference.

FIELD OF THE INVENTION

[02] The process of the present invention relates to the removal of oxidized sulfur-containing compounds after the oxidative desulfurization of a crude oil or distilled oil, or an integrated hydrodesulfurization/oxidative desulfurization. More particularly, it relates to a process for the decomposition of remaining sulfones and sulfoxides after oxidative desulfurization.

BACKGROUND OF THE INVENTION

[03] Crude oil is the world's main source of hydrocarbons used as fuel and petrochemical feedstock. While compositions of natural petroleum or crude oils are significantly varied, all crudes contain sulfur compounds and most contain nitrogen compounds which may also contain oxygen, but oxygen content of most crude is low. Generally, the sulfur concentration in crude oils is less than about 5 weight percent, with most crude having sulfur concentrations in the range from about 0.5 to about 1.5, weight percent. Nitrogen concentration is usually less than 0.2 weight percent, but it may be as high as 1.6, weight percent.

[04] Crude oils are refined in oil refineries to produce transportation fuels and petrochemical feedstocks. Typically, fuels for transportation are produced by processing and blending of distilled fractions from the crude to meet the particular end use specifications. Because most of the crudes available today in large quantity are high in sulfur, the distilled fractions must be desulfurized to yield products which meet performance specifications and/or environmental standards.

[05] Sulfur-containing organic compounds in fuels are, indeed, a major source of environmental pollution. The sulfur compounds are converted to sulfur oxides during the combustion process and produce sulfur oxyacids and contribute to particulate emissions. Oxygenated fuel blending compounds and compounds containing few or no carbon-to-carbon chemical bonds, such as methanol and dimethyl ether, are known to reduce smoke and engine exhaust emissions. However, most compounds of this type have high vapor pressure and/or are nearly insoluble in diesel fuel, and they have poor ignition quality, as indicated by their cetane numbers. For instance, purified diesel fuels by chemical hydrotreating and hydrogenation to reduce their sulfur and aromatics contents, also causes a reduction in fuel lubricity. Diesel fuels of low lubricity may cause excessive wear of fuel pumps, injectors and other moving parts which come in contact with the fuel under high pressures. Mid distillates, a distillate fraction that nominally boils in the range 180°C -370°C, are used for fuel or a blending component of fuel for use in compression ignition internal combustion engines (Diesel engines). They usually contain from about 1 to 3 percent by weight of sulfur. The specification for mid distillate fraction have been reduced to 5-50 part per million weight (ppmw) levels from 3000 ppmw level since 1993 in Europe and United States.

[06] In order to comply with these regulations for ultra-low sulfur content fuels, refiners have to make fuels having even lower sulfur levels at the refinery gate so that they can meet the stringent specifications after blending at the gate.

[07] Low pressure conventional hydrodesulfurization (HDS) processes can be used to remove a major portion of the sulfur from petroleum distillates for the blending of refinery transportation fuels. These units are not efficient at mild conditions (i.e., 30 bars pressure) to remove sulfur from compounds where the sulfur atom is sterically hindered as in multi-ring aromatic sulfur compounds. This is especially true where the sulfur heteroatom is hindered by two alkyl groups (e.g., 4,6-dimethyldibenzothiophene). These hindered dibenzothiophenes predominate at low sulfur levels such as 50 to 100 ppmw. Severe operating conditions (i.e., higher hydrogen partial pressure, temperature, catalyst volume) must be applied to remove the sulfur from these refractory sulfur compounds. The increase of hydrogen partial pressure can only be done by increasing the recycle gas purity, or new grassroots units must be designed, which is a costly option. The use of severe operating conditions results in yield loss, less catalyst cycle and product quality deterioration (e.g., color).

[08] In order to meet the stricter specifications in the future, such hindered sulfur compounds will also have to be removed from distillate feedstocks and products. The needs drive the efforts to develop new non-conventional process technologies. Oxidative desulfurization is one of the known arts to decrease the sulfur to a low level. However, unlike the situation prevailing in the hydrodesulfurization process, where the sulfur is removed as H_2S and the nitrogen as NH_3, the oxidative desulfurization would lead to oxidized sulfur (e.g. sulfoxides and sulfones) and nitrogen compounds. For instance, the oxidative desulfurization of one thousand tons of a hydrotreated diesel containing initially 500 ppmw of sulfur would lead to the formation of 1 ton of sulfones, considering a total conversion. These oxidized compounds are then further removed by means of extraction or adsorption.

[09] Sulfur-containing compounds that are typically present in hydrocarbonaceous fuels include aliphatic molecules, such as sulfides, disulfides and mercaptans as well as aromatic molecules such as thiophene, benzothiophene, dibenzothiophene and alkyl derivatives such as 4,6- dimethyl-dibenzothiophene. These aromatic molecules have a higher boiling point than the aliphatic molecules and are consequently more abundant in higher boiling fractions.

[10] The aliphatic sulfur compounds are easily desulfurized using the hydrodesulfurization method but some of the highly branched aliphatic molecules can hinder the sulfur atom removal and are moderately harder to desulfurize.

[11] Among the sulfur-containing aromatic compounds, thiophenes and benzothiophenes are relatively easy to hydrodesulfurize, while the addition of alkyl groups to the ring compounds slightly increases the difficulty of hydrodesulfurization. Dibenzothiophenes resulting from adding another ring to the benzothiophene family are directionally harder to desulfurize and the difficulty varies greatly according to their alkyl substitution with di-beta substitution being the most difficult to desulfurize, justifying their “refractory” appellation. These so-called beta substituents hinder the heteroatom from seeing the active site on the catalyst. The economical removal of the so-called “refractory sulfur” is thus exceedingly difficult to achieve and, therefore, the removal of sulfur compounds in hydrocarbonaceous fuels to a sulfur level below about 10 ppmw is very costly by current hydrotreating techniques. In order to meet the more stringent sulfur specifications, these refractory sulfur compounds have to be removed from hydrocarbonaceous fuel streams.

[12] Among the plausible options for a cost effective reduction of the sulfur level of a hydrocarbonaceous stream it can be considered to integrate to the hydrodesulfurization process an oxidation reaction zone where the hydrocarbonaceous sulfur compounds are easily converted under very mild conditions to compounds containing sulfur and oxygen, such as sulfoxides or sulfones for example, which have different chemical and physical properties which make it possible to remove the sulfur-bearing compounds from the balance of the original hydrocarbonaceous stream. Techniques for the removal of oxidized sulfur compounds can include extraction, distillation and adsorption processing steps. However, no efficient methods have been proposed for the ultimate disposal of the sulfoxides and sulfones.

[13] Several teachings of the prior art address desulfurization processes integrating hydrodesulfurization and oxidative desulfurization steps. U.S. Pat. No. 6,174,178, incorporated herein by reference, for example, discloses an integrated process in which the hydrocarbonaceous feedstock is first contacted with a hydrodesulfurization catalyst in a hydrodesulfurization reaction zone to reduce the sulfur content to a low sulfur level. The resulting hydrocarbonaceous stream is then sent in its entirety to an oxidation zone containing an oxidizing agent where the residual sulfur is converted into oxidized sulfur compounds under mild conditions. After decomposing the residual remaining oxidizing agent the oxidized sulfur compounds produced are then extracted using a solvent resulting in a stream containing the oxidized sulfur compounds and a hydrocarbonaceous oil stream having a reduced concentration of oxidized sulfur compounds. A final step of adsorption is carried out on the latter to reach ultra low sulfur level. The reference, however, provides no teaching on the methods for ultimate disposal of the oxidized sulfur compounds.

[14] In U.S. Patent No 6,277,271, incorporated herein by reference, there is disclosed a process for the desulfurization of hydrocarbonaceous oil wherein a stream, composed of hydrocarbonaceous oil and a recycle stream containing oxidized sulfur compounds, is contacted with a hydrodesulfurization catalyst in a hydrodesulfurization reaction zone to obtain low level of sulfur. The resulting hydrocarbonaceous stream is then contacted in its entirety with an oxidizing agent in an oxidation reaction zone to convert the residual sulfur compounds into oxidized sulfur compounds. After decomposing the remaining oxidizing agent, the oxidized sulfur compounds are removed resulting in a stream containing these latter and a stream of hydrocarbonaceous oil having a reduced concentration of oxidized sulfur compounds. At least a portion of the oxidized sulfur compounds are recycled back to the hydrodesulfurization reaction zone to increase the hydrocarbon recovery from the process. However, some of the sulfones compounds formed are reduced back to the initial sulfur compounds still leaving the sulfur disposal problem not fully resolved.

[15] U.S. Patent No 6,087,544, incorporated herein by reference, discloses a process to produce distillate fuels having a sulfur level below the distillate feedstream. The distillate feedstream is first fractionated into a light fraction which contains only from about 50 to 100 ppmw of sulfur, and a heavy fraction. The light fraction is then sent to a hydrodesulfurization reaction zone to remove substantially all of the sulfur therein. Finally part of the desulfurized light fraction is then blended with half of the heavy fraction to produce a low sulfur distillate fuel. However, not all the distillate feedstream is recovered to obtain a low sulfur distillate fuel product.

[16] U.S. Patent No 6,174,178, incorporated herein by reference, discloses an integrated process in which the hydrocarbonaceous feedstock is first contacted with a hydrodesulfurization catalyst in a hydrodesulfurization reaction zone to reduce the sulfur level to a low sulfur level. The resulting hydrocarbonaceous stream is then sent in its entirety to an oxidation zone containing an oxidizing agent where the residual sulfur is converted into oxidized sulfur compounds under mild conditions. After decomposing the residual remaining oxidizing agent, the oxidized sulfur compounds produced are then extracted using a solvent resulting in a stream containing the oxidized sulfur compounds and a hydrocarbonaceous oils stream having a reduced concentration of oxidized sulfur compounds. A final step of adsorption is carried out on the latter to reach ultra low sulfur levels.

[17] U.S. Patent No 6,277,271, incorporated herein by reference, discloses a process for the desulfurization of hydrocarbonaceous oil wherein a stream composed of hydrocarbonaceous oil and a recycle stream containing oxidized sulfur compounds is contacted with a hydrodesulfurization catalyst in a hydrodesulfurization reaction zone to obtain low level of sulfur. The resulting hydrocarbonaceous stream is then contacted in its entirety with an oxidizing agent in an oxidation reaction zone to convert the residual sulfur compounds into oxidized sulfur compounds. After decomposing the remaining oxidizing agent, the oxidized sulfur compounds are removed resulting in a stream containing these oxidized sulfur compounds and a stream of hydrocarbonaceous oil having a reduced concentration of oxidized sulfur compounds. At least a portion of the oxidized sulfur compounds is recycled back to the hydrodesulfurization reaction zone to recover the hydrocarbon part of the oxidized sulfur compounds.

[18] In WO2002/18518, incorporated herein by reference, a two stage desulfurization process is placed downstream of a hydrotreater. After having been hydrotreated in a hydrodesulfurization reaction zone the entire distillate feedstream is then sent to an oxidation reaction zone to undergo an aqueous formic acid based hydrogen peroxide biphasic oxidation to convert the thiophenic sulfur compounds to the corresponding oxidized compounds, i.e. sulfones. Some of the sulfones end up in the aqueous oxidizing solution during the oxidation reaction and are further removed by a subsequent phase separation step. The oil phase containing the remaining sulfones is finally subjected to a liquid-liquid extraction step. No mention is made about the fate of the sulfones.

[19] WO2003/014266, incorporated herein by reference, discloses a process for the removal of the sulfur from a hydrocarbon stream. The hydrocarbon stream containing the sulfur compounds is sent to an oxidation reaction zone where the organic sulfur compounds are oxidized into the corresponding sulfones using an aqueous oxidizing agent. After separating the aqueous oxidizing agent from the hydrocarbon phase the resulting hydrocarbon stream is sent to the hydrodesulfurization step. The resulting hydrocarbon is substantially sulfur reduced.

[20] WO2006/071793, incorporated herein by reference, discloses a process that reduces the sulfur and/or nitrogen content of a distillate feedstock to produce a transportation fuel or blending components for transportation fuel. The hydrotreated feedstock is contacted with an oxygen-containing gas and a titanium-containing mesoporous oxidation catalyst in an oxidation/adsorption zone to convert the sulfur compounds into the corresponding sulfones that are adsorbed onto the catalyst. No mention is made about the fate of the sulfones.

[21] U.S. Patent Publication No 2005/0150819A1, incorporated herein by reference, discloses a process for removing sulfur compounds found in a hydrocarbon stream. The sulfur compounds are first introduced in a concentration zone for increasing their concentration via e.g. complexation with ammonium complexes, adsorption or extraction and then separated from the sulfur depleted petroleum feedstock. A selective oxidation of the separated sulfur compounds is then performed in the gas phase using air or oxygen in the presence of a supported catalyst into valuable oxygenated products and sulfur deficient hydrocarbons.

[22] In U.S. Patent No 6,368,495, incorporated herein by reference, a process effective for the removal of organic sulfur compounds from liquid hydrocarbons is disclosed. The process more specifically addresses the removal of thiophenes and thiophene derivatives from a number of petroleum fractions, including gasoline, diesel fuel, and kerosene. In the first step of the process, the liquid hydrocarbon is subjected to oxidation conditions in order to oxidize at least some of the thiophene compounds to sulfones. Then, these sulfones can be catalytically decomposed to hydrocarbons (e.g. hydroxybiphenyl) and volatile sulfur compounds (e.g. sulfur dioxide). The hydrocarbon decomposition products remain in the treated liquid as valuable blending components, while the volatile sulfur compounds are easily separable from the treated liquid using well-known techniques such as flash vaporization or distillation.

[23] For reductive removal of sulfones and for reductive cleavage of classic sulfonamides, different methods using alkali metals (Li, Na, K), lithium naphthalenide, SmI_2 with HMPA, or $LiAlH_4$ in the presence of nickel compounds have been reported (Jones, Simpkins et al. 1998) and (Prakash, Chacko et al. 2009). All these reduction methods are mediated by highly aggressive metal-containing reducing agents. Electrochemical reduction is also used for the reductive cleavage of aryl sulfones (Jolivet et al., Tetrahedron Letters, 43 (44), 7907-7911 2002) ($ArSO_2R$) and sulfonamides (Klein et al., Journal of Electroanalytic Chemistry; 487(1): 66-71 (2000).

[24] The reductive cleavage of sulfones and sulfonamides with tetraazaalkenes has also been reported. The compound is a neutral organic electron donor and it is a member of the family of reagents that were recently named the "super-electron-donor" reagents. (Schoenebeck, JASC, 129 (44): 13368-13369 (2007). A more powerful reducing agent was synthesized as bisimidazolylidene. This was a limited study, however, which was only done with model compounds.

SUMMARY OF THE INVENTION

[25] The process of the present invention is a method for upgrading a hydrocarbon feedstock by the removal of sulfones and sulfoxides which comprises the steps of:

a. supplying a hydrocarbon feedstock to an oxidation reactor, the hydrocarbon feedstock comprising sulfur-containing compounds;

b. contacting the hydrocarbon feedstock with an oxidant in the presence of a catalyst in the oxidation reactor under conditions sufficient to selectively oxidize sulfur compounds present in the hydrocarbon feedstock to produce a hydrocarbon stream that comprises hydrocarbons and oxidized sulfur-containing compounds;

c. separating the oxidized sulfur-containing hydrocarbon stream into an aqueous phase and a non-aqueous oxidized effluent;

d. recovering the non-aqueous oxidized effluent and contacting it with an electron donor agent to oxidize sulfones and sulfoxides present in the non-aqueous oxidized effluent; and,

e. separating and recovering the hydrocarbon stream from which the sulfones and sulfoxides have been removed.

[26] It is an object of the present invention to reductively cleave the carbon-to-sulfur bonds in the sulfones and sulfoxides remaining after oxidative desulfurization.

[27] It is another object of the present invention to effect the reductive cleavage of the carbon-to-sulfur bonds in sulfones and sulfoxides by employing electron donor agents.

BRIEF DESCRIPTION OF THE DRAWINGS

[28] FIG. 1 is a schematic representation of the sulfone decomposition process of the present invention, including the oxidative desulfurization of the hydrocarbon feedstock, which precedes the present process.

[29] FIG. 2 is a schematic representation of the sulfone decomposition process of the present invention, including the oxidative desulfurization and solvent extraction of the hydrocarbon feedstock, which precedes the present process.

[30] FIG. 3 is a schematic representation of the sulfone decomposition process of the present invention, including oxidative desulfurization, solvent extraction and adsorption of the hydrocarbon feedstock, which precedes the present process.

DETAILED DESCRIPTION OF THE INVENTION

[31] In accordance with the process of the present invention, an oxidized hydrocarbon stream containing oxides of sulfur compounds, such as sulfones and sulfoxides, are first contacted with electron donor agents to decompose the sulfur compounds at high temperatures. There is no need to use a catalyst in this process.

[32] The process of the present invention typically follows an oxidative desulfurization or an integrated hydrodesulfurization followed by an oxidative desulfurization. However, as adverted to previously, no efficient method has been disclosed for the ultimate disposal of the oxidation reaction by-products, i.e., the oxidized sulfur compounds. The process of the present invention discloses how to effect such disposal with an electron donor agent.

[33] In one aspect, the present invention provides a method for the upgrading of a hydrocarbon feedstock, particularly a hydrocarbon feedstock that includes sulfur containing compounds. In certain embodiments, the hydrocarbon feedstock will include nitrogen containing species that can also be oxidized and removed in addition to or instead of the sulfur species.

[34] As can be seen in FIG. 1, which is one embodiment of the present invention, a sulfone conversion apparatus 10 includes an oxidation reactor 12, a first separator 16, a sulfone decomposition vessel 19 and a second separator 22. A hydrocarbon feedstock 11 is introduced into the oxidation reactor 12 where the hydrocarbon feedstock 11 is contacted with an oxidant 13 in the presence of a catalyst 14. In certain embodiments, the catalyst 14 can be regenerated from this or another process, and supplied along with, or in place of, fresh catalyst.

[35] Hydrocarbon feedstock 11 can be any petroleum based hydrocarbon, and can include various impurities, such as elemental sulfur, and/or compounds that include sulfur and/or nitrogen. In certain embodiments, hydrocarbon feedstock 11 can be diesel oil having a boiling point between about 36°C and 2000°C. Alternatively, hydrocarbon feedstock 11 can have a boiling point from about 80°C to about 560°C. Preferably, hydrocarbon feedstock 11 can have a boiling point between about 180°C to about 400°C. In certain embodiments, hydrocarbon feedstock 11 can be a solid residue. In certain embodiments, hydrocarbon feedstock 11 can include heavy hydrocarbons. As used herein, heavy hydrocarbons refer to hydrocarbons having a boiling point of greater than about 360°C, and can include aromatic hydrocarbons and naphthenes, as well as alkanes and alkenes. Generally, in certain embodiments, the hydrocarbon feedstock 11 can be selected from whole range crude oil, topped crude oil, product streams from oil refineries, product streams from refinery steam cracking processes, liquefied coals, liquid products recovered from oil or tar sand, bitumen, oil shale, asphaltene, and the like, and mixtures thereof.

[36] Exemplary sulfur compounds present in the hydrocarbon feedstock 11 can include sulfides, disulfides, and mercaptans, as well as aromatic molecules such as thiophenes, benzothiophenes, dibenzothiophenes, and alkyl dibenzothiophenes, such as 4,6-dimethyl-dibenzothiophene. Aromatic compounds are typically more abundant in higher boiling fractions, than is typically found in the lower boiling fractions.

[37] In certain embodiments the hydrocarbon feedstock 11 can include nitrogen containing compounds, and in certain embodiments exemplary compounds can include basic and neutral nitrogen compounds, including indoles, carbazoles, anilines, quinolines, acridines, and the like.

[38] Oxidation reactor 12 can be operated at mild conditions, relative to the conditions typically used in conventional hydrodesulfurization processes for diesel type feedstock. More specifically, in certain embodiments, oxidation reactor 12 can be maintained at a temperature of between about 20°C and about 150°C, alternatively between about 30°C and about 150°C, alternatively between about 30°C and about 90°C, or between about 90°C and about 150°C. In certain embodiments, the temperature is preferably between about 30°C and about 75°C, more preferably between about 45°C and 60°C.

[39] The operating pressure of oxidation reactor 12 can be between about 1 and 30 bars, alternatively between about 1 and 15 bars, alternatively between about 1 and 80 bars, and preferably between about 2 and 3 bars. The residence time of the hydrocarbon feedstock 11 within oxidation rector 12 can be between about 1 and 180 minutes, alternatively between about 15 and 180 minutes, alternatively between about 15 and 90 minutes, alternatively between about 5 and 60 minutes, alternatively between about 30 and 60 minutes, alternatively between about 60 and 120 minutes, alternatively between about 120 and 180 minutes, and is preferably present for a sufficient amount of time for the oxidation of any sulfur or nitrogen compounds present in the hydrocarbon feedstock 11. In one embodiment, the residence time of the hydrocarbon feedstock 11 within oxidation rector 12 is between about 15 and 45 minutes. For comparison, conventional hydrodesulfurization of a diesel type feedstock is typically conducted under harsher conditions, for example, at temperatures of between about 330°C and 380°C, pressures of between about 50 and 80 Kg/cm^2, and liquid hourly space velocities (LHSV) of between about 0.5 and 2 h^{-1}.

[40] Oxidation reactor 12 can be any reactor suitably configured to ensure sufficient contacting between hydrocarbon feedstock 11 and the oxidant 13, in the presence of catalyst 14, for the oxidation of at least a portion of the sulfur and nitrogen containing compounds contained therein. Suitable reactors for oxidation reactor 12 can include batch reactors, fixed bed reactors, ebullated bed reactors, lifted reactors, fluidized bed reactors, slurry bed reactors, and the like. Certain sulfur and nitrogen compounds present in hydrocarbon feedstock 11 are oxidized in oxidation reactor 12 to sulfones, sulfoxides, and oxidized nitrogen compounds, which can be subsequently removed by separation, extraction and/or adsorption. Exemplary oxidized nitrogen compounds can include pyridine and pyrrole-based compounds or pyridine-difuran compounds. Frequently, during oxidation, the nitrogen atom itself is not oxidized, but rather the compound is oxidized to a compound that is easy to separate from the remaining compounds.

[41] Suitable oxidants can include air, oxygen, ozone, hydrogen peroxide, organic peroxides, hydroperoxides, organic peracids, peroxo acids, oxides of nitrogen, and the like, and combinations thereof. Exemplary peroxides can be selected from hydrogen peroxide, and the like. Exemplary hydroperoxides can be selected from t-butyl hydroperoxide, and the like. Exemplary organic peracids can be selected from peracetic acid, and the like.

[42] In certain embodiments, such as for hydrocarbon feedstocks having a greater concentration of sulfur than nitrogen, the mole ratio of oxidant to sulfur present in the hydrocarbon feedstock can be from about 1:1 to 50:1, preferably between about 2:1 and 20:1, more preferably between about 4:1 and 10:1.

[43] In certain other embodiments, such as for hydrocarbon feedstocks having a greater concentration of nitrogen than sulfur, for example, certain South American crude oils, certain African crude oils, certain Russian crude oils, certain Chinese crude oils, and certain intermediate refinery streams like coker, thermal cracking, visbreaking, FCC cycle oils, and the like, the mole ratio of oxidant to nitrogen present in the hydrocarbon feedstock can be from about 1:1 to 50:1, preferably between about 2:1 and 20:1, more preferably between about 4:1 and 10:1.

[44] Catalyst 14 can include at least one metal oxide having the chemical formula MxOy, wherein M is a metal selected from groups IVB, VB, or VIB of the periodic table. Certain exemplary catalysts can be homogeneous catalysts that include one or more metal oxides. Exemplary metals can include titanium, vanadium, chromium, molybdenum, and tungsten. Certain preferred metals include oxides of molybdenum and tungsten.

[45] The ratio of catalyst to oil is between about 0.1% by weight, and about 10% by weight, preferably between about 0.5% by weight, and about 5% by weight. In certain embodiments, the ratio is between about 0.5% by weight, and about 2.5% by weight. Alternatively, the ratio is between about 2.5% by weight, and about 5% by weight.

[46] Catalyst present in oxidation reactor 12 can increase the rate of oxidation of the various sulfur and/or nitrogen containing compounds in hydrocarbon feedstock 11, and/or reduce the amount of oxidant necessary for the oxidation reaction, thereby achieving completion of the reaction and oxidation of sulfur and nitrogen containing compounds in a shorter amount of time, and/or with a reduced amount of oxidant necessary to achieve oxidation of the sulfur and nitrogen containing compounds. In certain embodiments, the catalyst can be selective toward the oxidation of sulfur containing compounds. In preferred embodiments, the catalyst is selective to minimizing the oxidation of aromatic hydrocarbons present in the hydrocarbon feedstock 11.

[47] The composition of oxidant by-product will vary based upon the nature of the original oxidant employed in the process. For example, in embodiments wherein the oxidant is hydrogen peroxide, water is formed as a by-product of the oxidation reaction. In embodiments wherein the oxidant is an organic peroxide, alcohol is formed as a by-product of the oxidation reaction. By-products are typically removed during the extraction and solvent recovery steps.

[48] An oxidized effluent 15 from oxidation reactor 12, which includes an oxidized sulfur and oxidized nitrogen compounds, is discharged from oxidation reactor 12 and conveyed to a first separator 16, where the oxidized effluent 15 is separated into an aqueous phase 17 which is discharged, and a non-aqueous oxidized effluent 18 which is conveyed to a sulfone decomposition vessel 19.

[49] The non-aqueous oxidized effluent 18 and an electron donor agent 20 are brought into contact in the sulfone decomposition vessel 19 in order to remove the oxidized sulfur compounds.

[50] The quantity of the electron donor agent 20 employed is in the range of about 1 to about 5 mole equivalents, preferably about 1 to about 3 mole equivalents based on the sulfone content in the feedstock. The electron donor agents 20 must have the oxidation potential to reduce the sulfones and sulfoxides. While various electron donors can be employed to advantage, for example, bispyridinylidene and bisimidazolylidene, it is preferred to employ tetraazaalkenes which upon oxidation yield in radical cations and dications. It is especially preferred to employ bisbenzimidazolylidene.

[51] Upon completion of the decomposition reaction in sulfone decomposition vessel 19, a desulfurized effluent 21, from which most of the sulfur has been removed, exits sulfone decomposition vessel 19 and is conveyed to a second separator 22 where it is mixed with water to effect washing and cleaning of the reaction by-product salt. In a second separator 22, a separation is effected, resulting in a water/salt stream 23 which is disposed of and a stream of desulfurized oil 24 which is recovered.

[52] As can be seen in FIG. 2, which is another embodiment of the present invention, a sulfone conversion apparatus 110 includes an oxidation reactor 112, a first separator 116, an extraction vessel 125, a sulfone decomposition vessel 119 and a second separator 122. A hydrocarbon feedstock 111 is supplied to the oxidation reactor 112, where the hydrocarbon feedstock 111 is contacted with an oxidant 113 in the presence of a catalyst 114. In certain embodiments, the catalyst can be regenerated from this or another process or supplied along with, or in place of, fresh catalyst. The characteristics of the hydrocarbon feedstock 111 and the oxidation reactor 112, as well as the operation conditions of the oxidation reactor 112, have been discussed previously with respect to the embodiment of FIG. 1.

[53] Upon completion of reaction in oxidation reactor 112, an oxidized effluent 115, containing oxidized sulfur and oxidized nitrogen compounds, is discharged from oxidation reactor 112 and conveyed to the first separator 116.

[54] In the first separator 116, the oxidized effluent 115 is separated into an aqueous phase 117 and a non-aqueous oxidized effluent 118.

[55] The non-aqueous oxidized effluent 118 is supplied to the extraction vessel 125 where it is contacted with a stream of an extraction solvent 126.

[56] The extraction solvent 126 can be a polar solvent, and in certain embodiments, can have a Hildebrandt solubility value of greater than about 19. In certain embodiments, when selecting the particular polar solvent for use in extracting oxidized sulfur and nitrogen containing species, selection may be based upon, in part, solvent density, boiling point, freezing point, viscosity, and surface tension. Exemplary polar solvents suitable for use in the extraction step can include acetone (Hildebrand value of 19.7), carbon disulfide (20.5), pyridine (21.7), dimethyl sulfoxide (DMSO) (26.4), n-propanol (24.9), ethanol (26.2), n-butyl alcohol (28.7), propylene glycol (30.7), ethylene glycol (34.9), dimethylformamide (DMF) (24.7), acetonitrile (30), methanol (29.7), and the like. In certain embodiments, acetonitrile and methanol, due to their low cost, volatility, and polarity, are preferred. In certain embodiments, solvents that include sulfur, nitrogen, or phosphorous, preferably have a relatively high volatility to ensure adequate stripping of the solvent from the hydrocarbon feedstock.

[57] In preferred embodiments, the extraction solvent is non-acidic. The use of acids is typically avoided due to the corrosive nature of acids, and the requirement that all equipment be specifically designed for a corrosive environment. In addition, acids, such as acetic acid, can present difficulties in separation due to the formation of emulsions.

[58] Extraction vessel 125 can be operated at a temperature of between about 20°C and 60°C, preferably between about 25°C and 45°C, even more preferably between about 25°C and 35°C. Extraction vessel 125 can operate at a pressure of between about 1 and 10 bars, preferably between about 1 and 5 bars, more preferably between about 1 and 2 bars. In certain embodiments, extraction vessel 125 operates at a pressure of between about 2 and 6 bars.

[59] The ratio of the extraction solvent 126 to non-aqueous oxidized effluent 118 can be between about 1:3 and 3:1, preferably between about 1:2 and 2:1, more preferably about 1:1. Contact time between the extraction solvent 126 and non-aqueous oxidized effluent 118 can be between about 1 second and 60 minutes, preferably between about 1 second and about 10 minutes. In certain preferred embodiments, the contact time is less than about 15 minutes. In certain embodiments, extraction vessel 125 can include various means for increasing the contact time between the extraction solvent 126 and the non-aqueous oxidized effluent 118, or for increasing the degree of mixing of the two solvents. Means for mixing can include mechanical stirrers, agitators, trays, or like means.

[60] A desulfurized oil 127 and a stream of sulfones and sulfoxides 128 are produced from the extraction vessel 125. While the desulfurized oil 127 is recovered the sulfones and sulfoxides stream 128 is conveyed to the sulfone decomposition vessel 119 where it comes into contact with an electron donor agent 129, in accordance with the process of the present invention as disclosed herein with respect to the method of FIG. 1.

[61] Upon completion of sulfone decomposition in vessel 119, a desulfurized effluent 130, which exits therefrom and is mixed with water and sent to the second separator 122 to remove reaction by-products with a stream of salt, resulting in a water/salt stream 131 and a stream of recovered desulfurized oil 132 is recovered.

[62] In another embodiment of the method of the present invention, as shown in FIG. 3, a sulfone conversion apparatus 210 includes an oxidation reactor 212, a first separator

216, an extraction vessel 225, an adsorption zone 233, a sulfone decomposition vessel 219 and a second separator 222. A hydrocarbon feedstock 211 is supplied to the oxidation reactor 212 where the feedstock 211 is contacted with an oxidant 213 in the presence of a catalyst 214.

[63] After completion of the reaction in oxidation reactor 212, an oxidized effluent 215 containing oxidized sulfur and oxidized nitrogen compounds is discharged from oxidation reactor 212 and conveyed to the first separator 216. In the first separator 216, the oxidized effluent 215 is separated into an aqueous phase 217 which is discharged, and a non-aqueous oxidized effluent 218 which is conveyed to the extraction vessel 225.

[64] After completion of the extraction in extraction vessel 225, in accordance with the method disclosed previously with respect to FIG. 2, an extracted effluent 235 is conveyed to the adsorption zone 233. After suitable residence time in contact with a suitable adsorption material, a desulfurized oil 236 is produced and recovered, and a stream of sulfones and sulfoxides 237 is removed.

[65] Exemplary adsorbents can include activated carbon, silica gel, alumina, natural clays and other inorganic adsorbents. It can also include polar polymers that have been applied to silica gel, activated carbon and alumina.

[66] The adsorption zone 233 can be a column operated at a temperature of between about 20°C and 60°C, preferably between about 25°C and 40°C, even more preferably between about 25°C and 35°C. In certain embodiments, the adsorption zone can be operated at a temperature of between about 10°C and 40°C, alternatively between about 35°C and 75°C. In certain embodiments, the adsorption zone can be operated at temperatures of greater than about 20°C, or alternatively at temperatures less than about

60°C. The adsorption zone can be operated at a pressure of up to about 15 bars, preferably up to about 10 bars, even more preferably between about 1 and 2 bars. In certain embodiments, the adsorption zone can be operated at a pressure of between about 2 and 5 bars. In an exemplary embodiment, the adsorption zone can be operated at a temperature of between about 25°C and 35°C and a pressure of between about 1 and 2 bars. The weight ratio of the stripped oil stream to the adsorbent is between about 1:1 and about 20:1, alternately between about 5:1 and about 15:1. In alternate embodiments, the ratio is between about 7:1 and about 13:1, with an exemplary ratio being about 10:1.

[67] The stream of sulfones and sulfoxides 238 discharged from the extraction vessel 225 is conveyed to the sulfone decomposition vessel 219 where it is brought into contact with an electron donor agent 239 in the same manner and under the same conditions as previously described with respect to the methods of FIGs. 1 and 2.

[68] Upon completion of the sulfone decomposition reaction in vessel 219, a desulfurized effluent 240, from which most of the sulfur has been removed, exits from the sulfone decomposition vessel 219 and is conveyed to the second separator 222 where it is mixed with water to effect cleaning of reaction by-product salt. In second separator 222, a separation is effected, resulting in a water/salt stream 241 which is disposed of and a stream of desulfurized oil 242 which is recovered.

Example 1

[69] A hydrotreated straight run diesel oil containing 500 ppmw of elemental sulfur, 0.28wt% of organic sulfur and a density of 0.85 KG/L was oxidatively desulfurized in accordance with the process of FIG. 2. The reaction conditions were, as follows:

Catalyst: Molybdenum based Mo (VI)

Reaction time: 30 minutes

Temperature: 80°C

Pressure: 1kg/cm^2

[70] During the extraction 93kg of bisimidazolylidene was employed as the electron donor agent. The extraction was conducted at 110°C, a pressure of 1kg/cm^2 and at an LHSV of 0.1 h^{-1}.

[71] The material balance for the oxidation and extraction steps are shown in Tables 1 and 2, respectively. The desulfurized diesel oil contained 40 ppmw of sulfur.

ODS

Stream Name		Diesel	Oxidant	Catalyst	Catalyst	Diesel Oxidized
Stream Type		Feed	Oxidant	Catalyst	Waste	Product
Stream #	Unit	111	113	114	117	118
Phase		Oil	Aqueous	Aqueous	Aqueous	Oil
Diesel	Kg	1000			3	995
Acetic Acid	Kg			136	34	86
H_2O_2	Kg		2			
H_2O	Kg	0	4		3	0
Na_2WO_4	Kg			1	1	
Total	Kg	1000	6	141	41	1082

Extraction

Stream Name		Diesel Oxidized	CH_3OH	Desulfurized Oil	Sulfones
Stream Type		Feed	Solvent	Product	Product
Stream #	Unit	118	126	127	128
Phase		Oil	Solvent	Oil	Oil
Diesel	Kg	995		879	
Diesel Reject	Kg				93
Acetic Acid	Kg	86			
Methanol	Kg		1082	7	
Total	Kg	1082	1082	886	93

Sulfone Decomposition

Stream Name		**Sulfones**	**Recovered Hydrocarbons**	**Desulfurized Oil**
Stream Type		Feed	Product	Product
Stream #	Unit	52	34	35
Phase			Oil	Oil
Sulfones	Kg	93		
Recovered Hydrocarbons	Kg		87	973
Total	Kg	93	87	973

[72] While certain representative embodiments and details have been shown for purposes of illustrating the invention, it will be apparent to those skilled in the art that various changes in the methods disclosed herein may be made without departing from the scope of the invention, which is defined in the appended claims.

What is claimed is:

1. A method of upgrading a hydrocarbon feedstock by removal of sulfones and sulfoxides therefrom, which comprises the steps of:

   a. supplying a hydrocarbon feedstock to an oxidation reactor, the hydrocarbon feedstock comprising sulfur-containing compounds;

   b. contacting the hydrocarbon feedstock with an oxidant in the presence of a catalyst in the oxidation reactor under conditions sufficient to selectively oxidize sulfur compounds present in the hydrocarbon feedstock to produce a hydrocarbon stream that comprises hydrocarbons and oxidized sulfur-containing compounds;

   c. separating the oxidized sulfur-containing hydrocarbon stream into an aqueous phase and a non-aqueous oxidized effluent;

   d. recovering the non-aqueous oxidized effluent and contacting it with an electron donor agent to oxidize sulfones and sulfoxides present in the non-aqueous oxidized effluent; and,

   e. separating and recovering the hydrocarbon stream from which the sulfones and sulfoxides have been removed.

2. The process according to claim 1, wherein from about 1 to about 5 mole equivalents of an electron donor agent is used based on the sulfone and sulfoxide content of the feedstock.

3. The process according to claim 2, wherein from about 1 to about 3 mole equivalents of an electron donor agent is used.

4. The process according to claim 1, wherein the decomposition is effected at a temperature from about 100°C to about 300°C.

5. The process according to claim 4, wherein the decomposition is effected at about 100°C to about 200°C.

6. The process according to claim 5, wherein the decomposition is effected about 100°C to about 150°C.

7. The process according to claim 1, wherein the decomposition is conducted at a pressure of about 3kg/cm^2 to about 30kg/cm^2.

8. The process according to claim 1, wherein the decomposition is conducted at about 0.05h^{-1} to about 4.0h^{-1}.

9. The process according to claim 1, wherein the electron donor agent must have an oxidation potential sufficient to effect reductive cleavage of the sulfones and the sulfoxides.

10. The process according to claim 9, wherein the electron donor is a tetraazaalkene.

11. The process according to claim 8, wherein the bisimidazole is bisimidazolylidene.

12. The process according to claim 1, wherein the hydrocarbon feedstock is crude oil, oil, shale oil, coal liquids, intermediate refinery products and distilled fractions thereof.

13. The process according to claim 9, wherein the electron donor agent has at least a half potential of -1.2V in dimethylformanide when referenced to a saturated calomel electrode.

14. The process according to claim 12, wherein the hydrocarbon feeds stock boils in the range of about 36°C to about 2000°C.

15. The process according to claim 1, wherein after step c), the non-aqueous oxidized effluent is subjected to solvent extraction.

16. The process according to claim 15, wherein the solvent is a polar solvent.

17. The process according to claim 15, wherein the extraction is conducted between about 20°C and about 60°C and at a pressure between about 1 and about 10 bars.

18. The process according to claim 15, wherein after the step of extraction, the extracted effluent is subjected to adsorption.

19. The process of claim 18, wherein the adsorbent materials are selected from the group consisting of activated carbon, silica gel, alumina, natural clays, polar polymers applied silica gel, activated carbon and alumina.

20. The process according to claim 18, wherein the adsorption zone is operated between about 20°C and about 60°C and at a pressure between about 1 and about 15 bars.

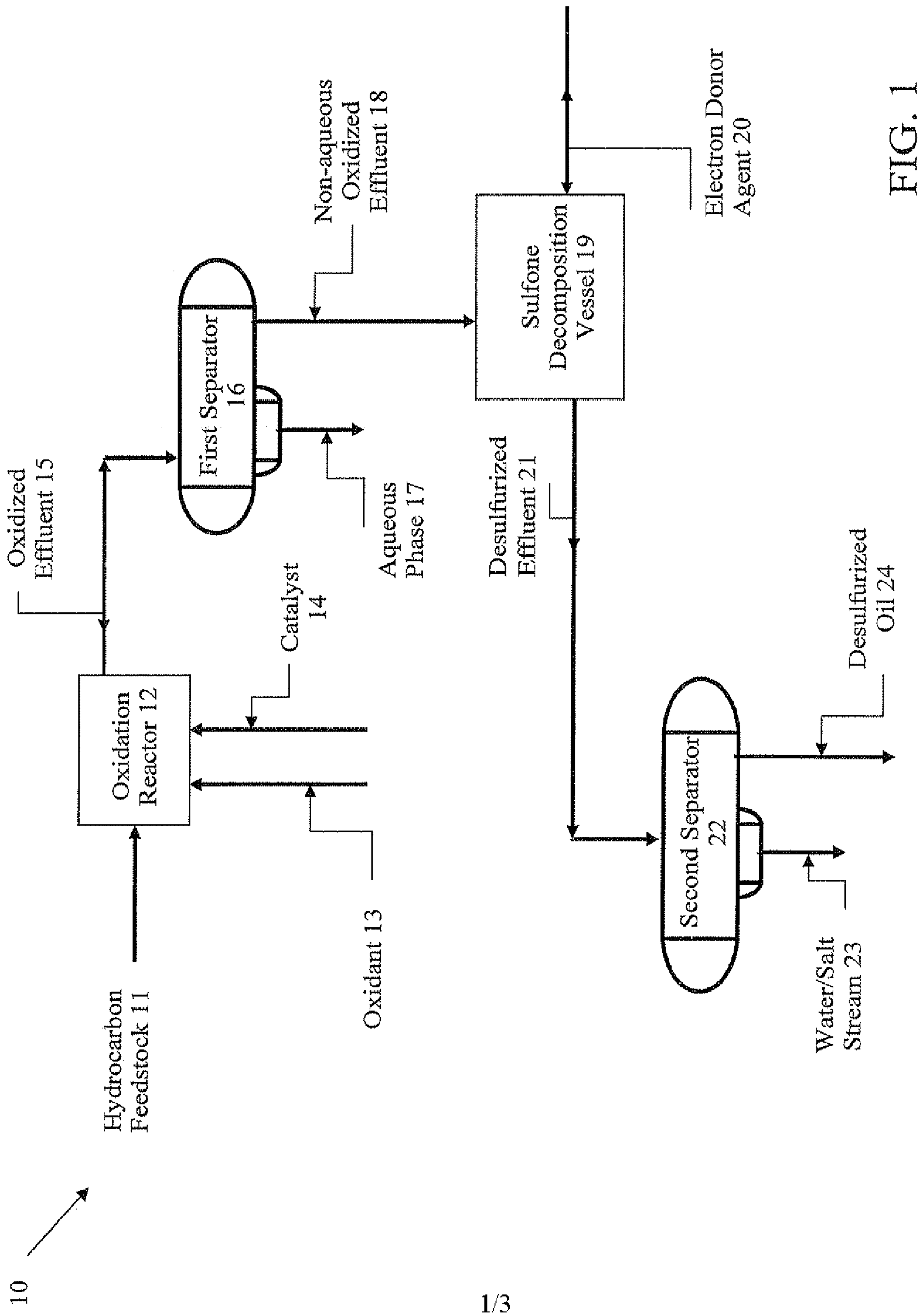
10
Hydrocarbon Feedstock 11
Oxidation Reactor 12
Oxidant 13
Catalyst 14
Oxidized Effluent 15
First Separator 16
Aqueous Phase 17
Non-aqueous Oxidized Effluent 18
Sulfone Decomposition Vessel 19
Electron Donor Agent 20
Desulfurized Effluent 21
Second Separator 22
Water/Salt Stream 23
Desulfurized Oil 24

FIG. 1

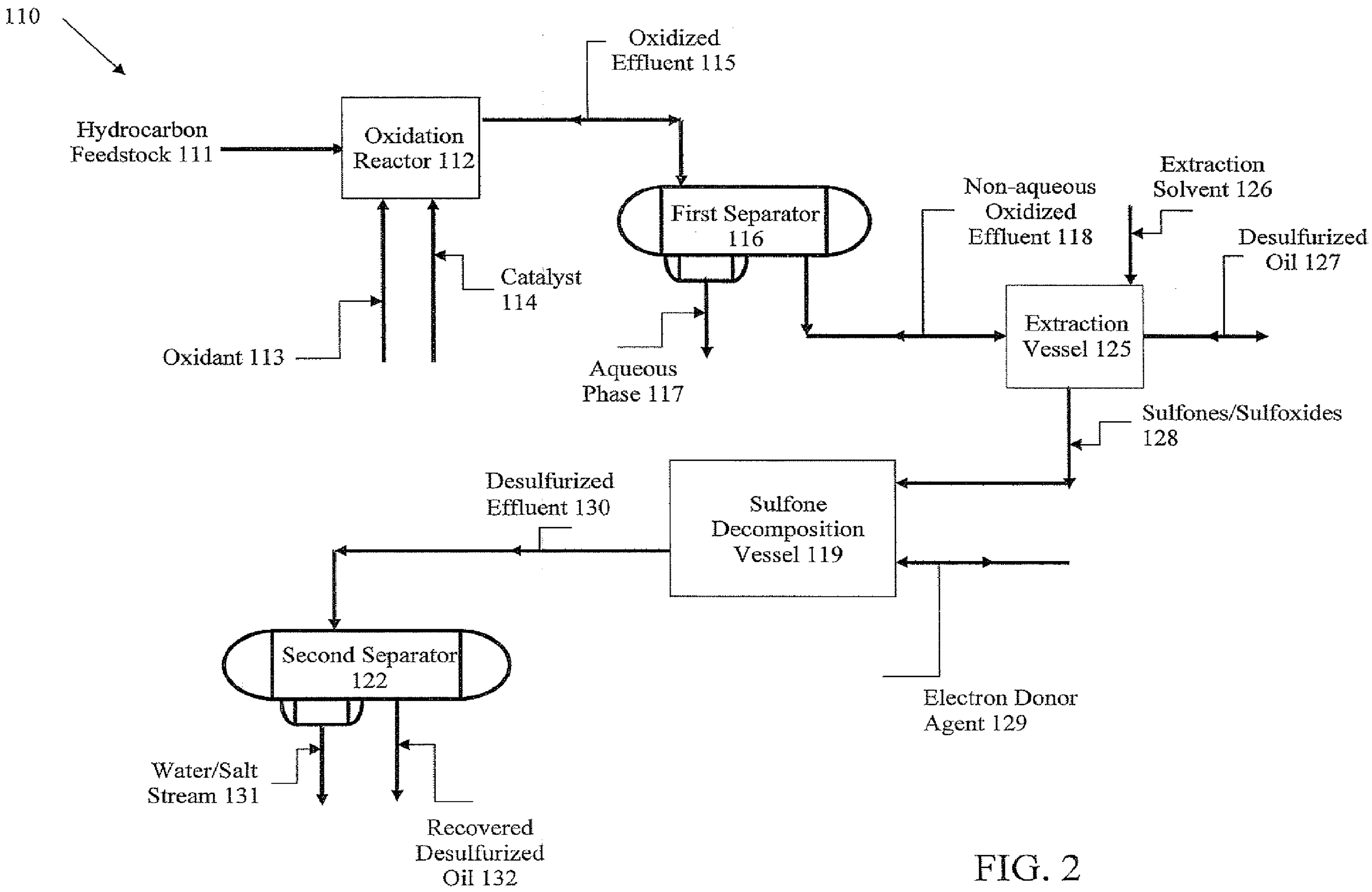
110
Hydrocarbon Feedstock 111
Oxidation Reactor 112
Oxidant 113
Catalyst 114
Oxidized Effluent 115
First Separator 116
Aqueous Phase 117
Non-aqueous Oxidized Effluent 118
Extraction Solvent 126
Desulfurized Oil 127
Extraction Vessel 125
Sulfones/Sulfoxides 128
Sulfone Decomposition Vessel 119
Electron Donor Agent 129
Desulfurized Effluent 130
Second Separator 122
Water/Salt Stream 131
Recovered Desulfurized Oil 132

FIG. 2

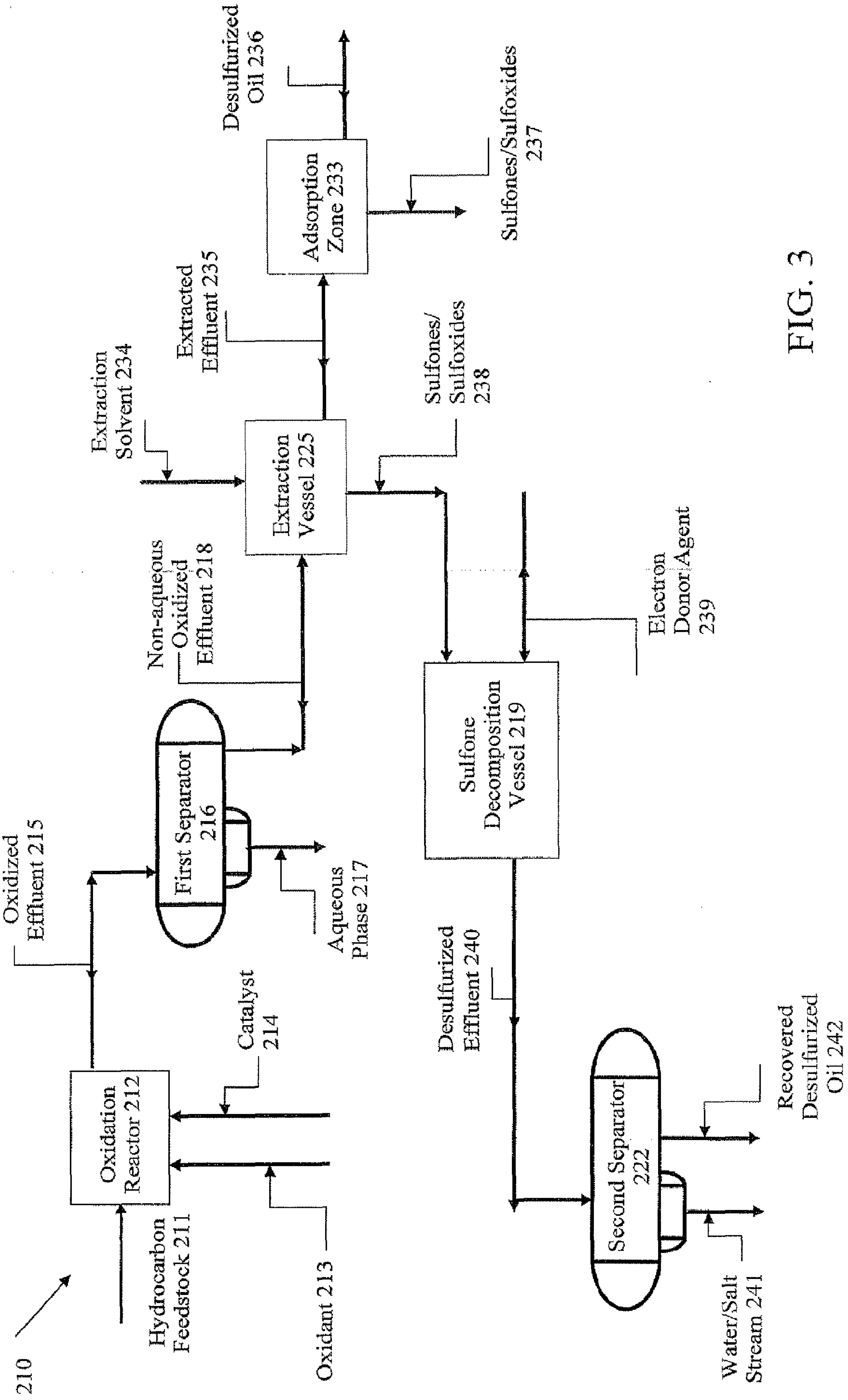
210
Hydrocarbon Feedstock 211
Oxidant 213
Oxidation Reactor 212
Catalyst 214
Oxidized Effluent 215
First Separator 216
Aqueous Phase 217
Non-aqueous Oxidized Effluent 218
Extraction Solvent 234
Extraction Vessel 225
Extracted Effluent 235
Sulfones/ Sulfoxides 238
Adsorption Zone 233
Desulfurized Oil 236
Sulfones/Sulfoxides 237
Sulfone Decomposition Vessel 219
Electron Donor Agent 239
Desulfurized Effluent 240
Second Separator 222
Water/Salt Stream 241
Recovered Desulfurized Oil 242

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/043118

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10G17/04 C10G27/04 C10G53/14 C07C317/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10G C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/200206 A1 (AL-SHAHRANI FARHAN M [GB] ET AL) 13 August 2009 (2009-08-13) claims 1,14 paragraph [0041] -----	1-20
A	FRANZISKA SCHOENEBECK ET AL: "Reductive Cleavage of Sulfones and Sulfonamides by a Neutral Organic Super-Electron-Donor (S.E.D.) Reagent", JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol. 129, no. 44, 1 November 2007 (2007-11-01), pages 13368-13369, XP55037726, ISSN: 0002-7863, DOI: 10.1021/ja074417h cited in the application figure 1 ----- -/--	1-20

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 11 September 2012	Date of mailing of the international search report 20/09/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Bernet, Olivier

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/043118

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2011/056941 A1 (SAUDI ARABIAN OIL CO [SA]; UNIV OXFORD [GB]; ARAMCO SERVICES CO [US];) 12 May 2011 (2011-05-12) the whole document -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/043118

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009200206 A1	13-08-2009	CA 2662627 A1	13-09-2007
		CN 101522570 A	02-09-2009
		EP 2001802 A2	17-12-2008
		US 2009200206 A1	13-08-2009
		WO 2007103440 A2	13-09-2007
WO 2011056941 A1	12-05-2011	EP 2496538 A1	12-09-2012
		US 2011213187 A1	01-09-2011
		WO 2011056941 A1	12-05-2011