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(54) **Method for removing Impurities from Hydrocarbon Oils**

(57) A method for removing impurities from a feedstock comprising a hydrocarbon oil is provided. The method comprises contacting the feedstock with an oxygen-containing gas under conditions effective to oxidize at least a portion of the impurities, as well as contacting the feedstock with a Lewis acid under conditions effective so that any Lewis base impurity(ies) in the feedstock can react with the Lewis acid. Any impurities so oxidized and/or reacted are then removed.

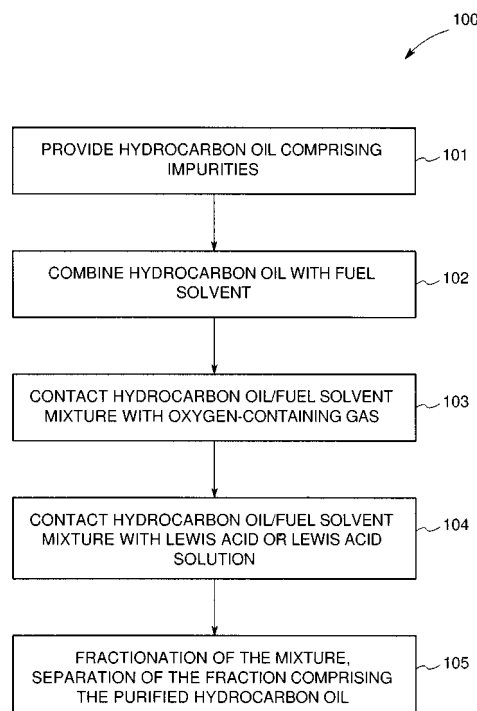


FIG. 1

Description**BACKGROUND**

[0001] Petroleum is the world's main source of hydrocarbons used as fuel and petrochemical feedstock. Because of the presence of impurities, crude oil is seldom used in the form produced at the well, but rather, is typically converted in oil refineries into the wide range of fuels and petrochemical feedstocks appropriate for their intended end-use applications. While compositions of natural petroleum or crude oils vary significantly, all crudes contain sulfur compounds. Generally, sulfur concentrations in crude oils range from about 0.5 to about 1.5 percent, but may deviate upwardly to up to about 8 percent. When combusted, sulfur containing compounds are converted to sulfur oxides (SO_x), considered to be an environmental pollutant. Catalytic oxidation of sulfur and the subsequent reaction thereof with water can result in the formation of sulfuric acid mist, thereby also contributing to particulate emissions. And so, such crudes typically must be desulfurized to yield products, which meet performance specifications and/or environmental standards.

[0002] In fact, it is likely that sulfur removal from petroleum feedstocks and products will become increasingly important in years to come. While legislation on sulfur in diesel fuel, for example, in Europe, Japan and the US has recently lowered the specification for on-road vehicles from 0.05 to 0.001 (EU) or 0.0015 (US) percent by weight, indications are that future specifications may go below this level and include off-road vehicles.

[0003] Hydrodesulfurization (HDS) has been used to remove impurities from hydrocarbon oils, and can remove a major portion of sulfur. However, conventional hydrodesulfurization processes do not effectively remove aromatic sulfur compounds, such as benzothiophene and dibenzothiophene. Intensifying certain hydrodesulfurization processing conditions, e.g., reaction temperature, hourly space velocity, etc., may result in improved removal of these more recalcitrant contaminants, however, intensification of processing conditions may add costs to an already capital intensive process. Further, using conventional hydrodesulfurization catalysts at high temperatures can result in yield loss, faster catalyst coking and product quality deterioration.

[0004] Efficient, more cost effective, methods for removal of sulfur compounds from crude oils are thus needed. Desirably, such methods would be capable of removing aromatic sulfur compounds to the very low levels required in many applications.

BRIEF DESCRIPTION

[0005] Provided herein are methods for removing sulfur impurities from a hydrocarbon oil. The method comprises contacting the hydrocarbon oil with an oxygen-containing gas under conditions effective to oxidize at least a portion of the impurities. The method further comprises contacting the hydrocarbon oil with a Lewis acid under conditions effective so that any Lewis base impurity(ies) in the hydrocarbon oil can react with the Lewis acid. Any impurities so oxidized and/or reacted are removed from the hydrocarbon oil.

[0006] Also provided are methods for removing sulfur impurities from a hydrocarbon oil. The method comprises contacting the hydrocarbon oil with a gas comprising nitrogen dioxide, or nitric oxide and oxygen, under conditions effective to oxidize at least a portion of the sulfur impurities. The hydrocarbon oil comprising oxidized sulfur impurities is then contacted with a Lewis acid under conditions effective so that any Lewis base sulfur impurity(ies) in the hydrocarbon oil can react with the Lewis acid. Any impurities so oxidized and/or reacted are then removed from the hydrocarbon oil.

DRAWINGS

[0007] These and other features, aspects, and advantages of the present invention will become better understood when the following detailed description is read with reference to the accompanying drawings in which like characters represent like parts throughout the drawings, wherein:

FIG. 1 is a flow chart schematically illustrating one embodiment of the present method;

FIG. 2 is a flow chart schematically illustrating another embodiment of the present method;

FIG. 3 is a flow chart schematically illustrating another embodiment of the present method;

FIG. 4 is a flow chart schematically illustrating another embodiment of the present method;

FIG. 5 is a flow chart schematically illustrating another embodiment of the present method; and

FIG. 6 is a flow chart schematically illustrating an additional embodiment of the present method.

DETAILED DESCRIPTION

[0008] Unless defined otherwise, technical and scientific terms used herein have the same meaning as is commonly understood by one of skill in the art to which this invention belongs. The terms "first", "second", and the like, as used herein do not denote any order, quantity, or importance, but rather are used to distinguish one element from another. Also, the terms "a" and "an" do not denote a limitation of quantity, but rather denote the presence of at least one of the referenced item, and the terms "front", "back", "bottom", and/or "top", unless otherwise noted, are merely used for convenience of description, and are not limited to any one position or spatial orientation. If ranges are disclosed, the endpoints of all ranges directed to the same component or property are inclusive and independently combinable (e.g., ranges of "up to about 25 wt.%, or, more specifically, about 5 wt.% to about 20 wt.%" is inclusive of the endpoints and all intermediate values of the ranges of "about 5 wt.% to about 25 wt.%" etc.). The modifier "about" used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., includes the degree of error associated with measurement of the particular quantity).

[0009] Provided herein are methods for removing impurities from a hydrocarbon oil. The methods comprise contacting the hydrocarbon oil with an oxygen containing gas under conditions effective to oxidize at least a portion of the impurities. The hydrocarbon oil is also contacted with a Lewis acid so that any impurities capable of acting as a Lewis base can react with the Lewis acid. Any impurities so oxidized and/or reacted are then removed from the hydrocarbon oil.

[0010] The methods disclosed herein may advantageously be applied to any hydrocarbon oil, or mixture of one or more hydrocarbon oils, comprising impurities. Exemplary hydrocarbon oils suitable for the present invention include, but are not limited to, liquid oils obtained from bitumen (often called tar sands or oil sands), petroleum, oil shale, coal, as well as synthetic crude oils produced by the liquefaction of coal, heavy crude oils, oil distillates, and petroleum refinery residual oil fractions, such as bottoms or fractions produced by atmospheric and vacuum distillation of crude oil.

[0011] The hydrocarbon fuel oil may be subjected to the present method "as is", without pretreatment, or addition of solvents. However, in some embodiments, the addition of a fuel solvent may be desired to facilitate processing. In such embodiments, the hydrocarbon oil may optionally be provided in combination with a fuel solvent or a mixture of solvents to further liquefy, or form a slurry with, the hydrocarbon oil, and thus potentially facilitating processing. Exemplary suitable non-polar fuel solvents include, but are not limited to, petroleum ether, hexanes, pentane, cyclohexane, heptane, propane, butane, mixtures of these, and the like.

[0012] In embodiments wherein the same is desired, the ratio of the fuel solvent to the hydrocarbon oil will desirably be sufficient so that the hydrocarbon oil-fuel solvent mixture is provided with a viscosity of up to about 32.6° API gravity crude oil (from about 0.342 cSt at 17.8°C to about 23.2 cSt at 15.6° C). Ratios of fuel solvent to the hydrocarbon oil expected to be capable of providing the desired viscosity range from about 0.5:1 to about 10:1, or from about 1:1 to about 2:1. Optionally, any fuel solvent utilized may be recovered, in whole or in part, and recycled for this, or other, uses.

[0013] The hydrocarbon oil may also optionally be pretreated, e.g., to remove high molecular weight and/or particulate impurities, prior to being subjected to the present method. For example, the hydrocarbon oil may be subjected to centrifugation, or other suitable separation techniques, to remove such particulate residues. Alternatively, any particulate residues may be removed from the hydrocarbon oil (or vice versa) by filtration, decantation, and the like. If desired, an amount of fuel solvent can be utilized to enhance the processability of the hydrocarbon oil in any desired pretreatment step.

[0014] Such pretreatment may result in the removal of at least a portion of any precipitates present in the hydrocarbon oil, and as such, may reduce the interference of the same in the oxidation and Lewis acid complexation steps. For example, hydrocarbon oils may typically contain amounts of asphaltenes, which contain heteroatoms that may interfere with the removal of the impurities by competing for the oxygen-containing gas/Lewis acid. By removal of at least part of the asphaltenes prior to oxidation or the addition of the Lewis acid to the hydrocarbon oil, the efficiency of the oxidation and/or Lewis acid complexation may be improved.

[0015] The impurities desirably removed from the hydrocarbon oil by the disclosed method may include any species capable of being oxidized and/or forming a complex with a Lewis acid (referred to herein as "Lewis acid-base complexes"), either as oxidized or unoxidized. In one embodiment of the present invention, the impurities may comprise one or more of sulfur, nickel, or vanadium, i.e., the impurities may comprise any ions, salts, complexes, and/or compounds including nickel, vanadium, and sulfur. Examples of impurities comprising vanadium that may be removed by the present method include, but are not limited to vanadium porphyrins and oxides, such as for example, vanadium pentoxide. Examples of impurities comprising nickel include nickel porphyrins, salts etc.

[0016] In one embodiment, the impurities comprise organic sulfur-containing compounds, such as alkyl sulfides or aromatic sulfur containing compounds. Examples of organic sulfur-containing compounds that may typically contaminate hydrocarbon oils include thiophene and its derivatives. Exemplary derivatives of thiophene include various substituted benzothiophenes, dibenzothiophenes, phenanthrothiophenes, benzonaphthothiophenes, thiophene sulfides, and the like. The particular impurities and concentration(s) thereof, in the hydrocarbon oil may be dependent on the geographical source of the hydrocarbon oil, as well as the form and prior processing (if any) of the hydrocarbon oil.

[0017] The present method involves contacting the hydrocarbon oil comprising impurities with an oxygen-containing

gas. Any oxygen-containing gas can be used, so long as the oxidation ability and concentration of oxygen-containing species, including molecular oxygen (O_2), in the gas is sufficient so that oxidation of at least a portion of the impurities in the hydrocarbon oil can be achieved. As those of ordinary skill in the art recognize, the concentration of oxygen utilized should be chosen to avoid explosive compositions. Effective concentrations within these parameters can be between about 0.01 volume % (vol. %) and about 21 vol. %, or between about 0.5 vol. % to about 10 vol. %.

[0018] For example, air, or oxygen depleted air, ozone, nitrogen dioxide or combinations of these may be utilized as the oxygen containing gas. Advantageously, it has now been discovered that oxidation of certain impurities in hydrocarbon oils may be readily and easily oxidized by a combination of nitric oxide/air without the use of catalysts. Nonetheless, in certain embodiments air, or oxygen depleted air may be utilized, and in these embodiments, oxidation of at least a portion of the impurities in the hydrocarbon oil can be facilitated by the use of a catalyst, such as any of those comprising molybdenum, copper, manganese, cobalt, tungsten, iron, and the like.

[0019] In those embodiments wherein the oxygen-containing gas comprises nitrogen dioxide, or combinations of nitric oxide with e.g., air, catalysts are not required, and efficiencies are provided. In such embodiments, concentrations of from 1 vol. % to 20 vol. %, or from about 4 vol. % to about 10 vol. % nitric oxide in air, or nitrogen dioxide in any gas, may be utilized. The oxygen-containing gas will further desirably be provided with a pressure of at least about 1 bar, or from about 1 bar to about 200 bar, or even from about 10 bar to about 30 bar. The oxidation of at least a portion of the impurities in the hydrocarbon oil may be further facilitated by providing the hydrocarbon oil with a temperature of at least about 20°C, or from about 20°C to about 150°C, or even from about 80°C to about 120°C.

[0020] In some embodiments, the insoluble oxidation products formed via contact with the oxygen containing gas may desirably be removed, e.g., prior to contacting the hydrocarbon oil with the Lewis acid/Lewis acid solution, which may increase the efficiency with which the Lewis acid-base complexes are formed. Any method suitable to remove the oxidation products can be utilized, and exemplary methods for doing so, include for example, filtration, decantation, centrifugation, etc.

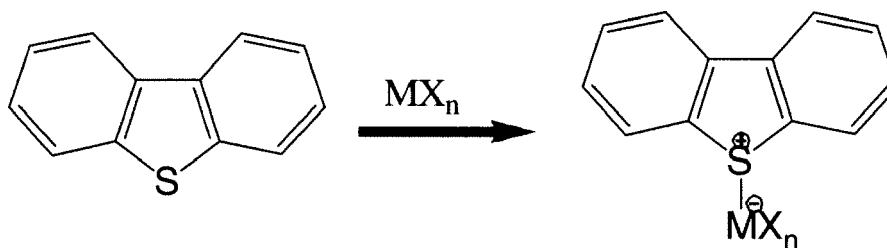
[0021] The hydrocarbon oil is also contacted with a Lewis acid. The Lewis acid may be any ion or chemical compound that can accept a pair of electrons from a corresponding Lewis base (e.g., an oxidized or unoxidized impurity). It is believed that many of the impurities typically found in hydrocarbon oils, and in particular impurities comprising sulfur, nickel, and vanadium can act as Lewis bases that, in turn, are capable of forming stable complexes with Lewis acids. Lewis acid-base complexes have low to no solubility in the hydrocarbon oil, and thus may be removed from the hydrocarbon oil.

[0022] Examples of Lewis acids suitable for use in the methods disclosed herein include one or more cations of H^+ , Li^+ , Na^+ , Be^{2+} , Mg^{2+} , Ca^{2+} , Sn^{2+} , Sn^{4+} , Al^{3+} , Ga^{3+} , In^{3+} , La^{3+} , Ce^{3+} , Cr^{3+} , Co^{3+} , Fe^{3+} , As^{3+} , Ir^{3+} , Si^{4+} , Ti^{4+} , Zr^{4+} , Th^{4+} , U^{4+} , Pu^{4+} , VO^{2+} , UO_2^{2+} , $(CH_3)_2Sn^{2+}$, and metal halogenides, alkyls, hydrides, alkoxides, for example, $BeMe_2$, $AlCl_3$, $GaCl_3$, $FeCl_3$, AlH_3 , BF_3 , BCl_3 , $B(OR)_3$, $Al(CH_3)_3$, $Ga(CH_3)_3$, $In(CH_3)_3$. Cationic Lewis acids may typically be provided in combination with a counterion, and any suitable counterion may be utilized in forming a metal salt with the Lewis acid.

[0023] Many of the exemplary Lewis acids listed above may also be classified as Pearson Lewis acids, and these may be particularly suitable for forming complexes with the sulfur, vanadium, and nickel impurities sometimes found in hydrocarbon oils. Accordingly, in one embodiment, the Lewis acid may comprise a hard Pearson Lewis acid. Hard Pearson Lewis acids are generally characterized by the fact they have atomic centers of a small ionic radius; have a relatively high positive charge; do not contain electron pairs in their valence shells; have a low electron affinity; are likely to be strongly solvated; and have high energy low unoccupied molecular orbitals (LUMOs). Examples of hard Pearson Lewis acids are identified in R.G. Pearson. J.Am.Chem.Soc. 1963, 85:3533-3543; R.G.Pearson, Science, 1966, 151: 172-177; R.G.Pearson, Chem. Br., 1967, 3:103-107; and R.G.Pearson, J.Chem.Ed., 1968, 45:581-587; all of which are hereby incorporated by reference herein for any and all purposes.

[0024] In one embodiment, the Lewis acid may comprise one or more of $AlCl_3$, $GaCl_3$, $FeCl_3$, which can be particularly effective at forming complexes with thiophene compounds and their derivatives, e.g., according to the following reaction scheme:

(I)



Where $MX_n = AlCl_3, GaCl_3, FeCl_3$.

[0025] The Lewis acid may desirably be provided as a solution, i.e., the Lewis acid may be provided in combination with an appropriate solvent. The solvent may desirably be an aprotic solvent, i.e., one that does not exchange protons with a substance dissolved in it. Desirably, the aprotic solvent will be one capable of easily forming two phases when mixed with the hydrocarbon oil. To facilitate separation, the aprotic solvent may be selected to solvate the positively charged species of the Lewis acid. For example, in certain embodiments, the aprotic solvent may be acetonitrile, nitromethane, 1,2-dichloroethane, or combinations thereof.

[0026] The Lewis acid may form complexes with any impurities capable of acting as Lewis bases when provided in a stoichiometric amount relative thereto. However, due to the likely presence of competing components in the hydrocarbon oil, in one embodiment, a stoichiometric excess of the Lewis acid may advantageously be provided to increase the likelihood of complexation of substantially all of the impurities in the hydrocarbon oil with the Lewis acid. For example, the Lewis acid may be provided in a slight, e.g., a 1%, stoichiometric excess relative to the impurities in the hydrocarbon oil, or, the Lewis acid may be provided in about a 300% (3 times) stoichiometric excess relative to the impurities.

[0027] Advantageously, added heat and pressure are not necessary for carrying out the Lewis acid complexation. Optionally then, the complexing of at least a portion of impurities in the hydrocarbon oil capable of acting as Lewis bases may be further facilitated by providing the hydrocarbon oil with a temperature of at least about 15°C, or from about 20°C to about 50°C, or even from about 20°C to about 35°C. The hydrocarbon oil will further desirably be provided with a pressure of at least about 1 atmosphere, or from about 1 atmosphere to about 5 atmospheres, or even from about 1 atmosphere to about 2 atmospheres, while being contacted with the Lewis acid.

[0028] The impurities so oxidized and/or reacted may then be removed from the hydrocarbon oil. More particularly, the oxidized and/or reacted impurities will move to or begin to form a separate and distinct phase from the hydrocarbon oil, and optional fuel solvent, so that a first layer comprising the hydrocarbon oil and optional fuel solvent and a second layer comprising the Lewis acid-base complexes, and optional aprotic solvent, are formed. Although the mixture is expected to be capable of separating on its own, the separation of the mixture into the first and second layers may be promoted by centrifugation, or any other suitable method.

[0029] After separation, the layers may be separated by any suitable extraction method or apparatus known in the art, such as by decantation or via a separatory funnel. Thereafter, the hydrocarbon oil treated by the disclosed method may be delivered to a point-of-use, or, may be subjected to further processing, e.g., to remove any fuel solvent originally added to the hydrocarbon oil, or to be re-treated via one or more steps of the disclosed method. If, for example, fuel solvent has been employed and is desirably removed post-processing, it may be removed by any suitable method, such as by evaporation.

[0030] The contacting steps may be performed in any order, or relatively simultaneously, but advantageously may be carried out in sequence, with the oxidation step occurring first. In these embodiments of the invention, the step of contacting the hydrocarbon oil with the Lewis acid may remove any oxidized impurities capable of acting as Lewis bases, as well as any impurities resistant to oxidation. In such embodiments, the contacting steps may act synergistically, i.e., to result in the ability to remove more impurities than may be removed via either step alone.

[0031] Either or both of the contacting steps may also be repeated in parallel or sequence to further purify the hydrocarbon oil. For example, the separated layer comprising the hydrocarbon oil may be contacted with another amount of the Lewis acid, or Lewis acid solution, and/or may be contacted with the same, or a different oxygen-containing gas any number of times. As would be appreciated by one skilled in the art, the number of times the process is performed can be dependent on the desired purity of the final hydrocarbon product, and one or more of the contacting steps can be repeated until the desired purity has been substantially achieved.

[0032] The separated layer comprising the Lewis acid may be further processed to recover the Lewis acid so that it

may be reused, whether in the disclosed method or otherwise. If recovery and recycling of the Lewis acid is desired, the layer containing the Lewis acid may be contacted with an acid capable of competing with the Lewis acid complexed with the impurities. One example of an acid capable of competing with the Lewis acid is hydrochloric acid, in concentrations ranging from about 0.001M to about 3.5 M. The acid will be preferably substituted for the Lewis acid in the Lewis acid-base complexes, so that the Lewis acid will be freed. Once freed, the Lewis acid may be recovered by any suitable method, e.g., crystallization, distillation, etc. for reuse in this, or another process, or stored until such reuse is desired.

[0033] The present invention is effective to remove a substantially higher number of impurities than other known techniques, such as HDS and solvent extraction, or either oxidation or Lewis acid complexation separately. For example, the disclosed method is capable of removing substantially all of the sulfur impurities from a hydrocarbon oil having greater than about 0.5 % by weight sulfur with an effective amount of Lewis acid. In another aspect of the present invention, the processes and systems described herein are capable of removing substantially all of the sulfur impurities (e.g. to a level of less than about 1% by weight) from a hydrocarbon oil material having greater than 3% sulfur content. Aspects of the present invention are particularly useful for gas turbine applications where it is often desirable to lower the sulfur impurity content from 4% by weight sulfur (or greater) to less than about 1% by weight sulfur. Accordingly, in one aspect, the present invention provides an efficient, low-cost process for the removal of sulfur impurities, e.g. thiophenes and their derivatives, from high sulfur-content fuels.

[0034] Referring now to FIG. 1, one embodiment of the disclosed method for removing impurities from a hydrocarbon oil is shown in flow chart form. More specifically, FIG. 1 shows method 100, wherein a hydrocarbon oil comprising impurities is provided at 101. The impurities capable of being removed by method 100 include any species capable of being oxidized and/or forming a complex with a Lewis acid, and in some embodiments, may include one or more of a sulfur, nickel, or vanadium impurity. In one particular embodiment, the impurities comprise organic sulfur-containing compounds, such as thiophene and its derivatives, including various benzothiophenes, dibenzothiophenes, phenanthrothiophenes, benzonaphthothiophenes, sulfides, such as aromatic and non-aromatic alkyl sulfides, and the like.

[0035] Optionally, the hydrocarbon oil may be combined with a fuel solvent to enhance the processability thereof, as shown as step 102. The optional fuel solvent may comprise any appropriate non-polar solvent such as, for example, petroleum ether, hexanes, pentane, cyclohexane, heptane, propane, butane, any other non-polar hydrocarbon solvent with a relatively low boiling point, or combinations of these. In such embodiments, The ratio of the fuel solvent to the hydrocarbon oil may be from about 0.5:1 to about 10:1, or from about 1:1 to about 2:1.

[0036] The hydrocarbon oil, or hydrocarbon oil/fuel solvent mixture is contacted with an oxygen-containing gas at step 103. The oxygen-containing gas may be any capable of oxidizing at least a portion of the impurities desirably removed from the hydrocarbon oil, e.g., air, oxygen depleted air, ozone enriched air, nitrogen dioxide, nitric oxide in air, or mixtures of these. Although catalysts comprising molybdenum, copper, manganese, cobalt, tungsten, iron, or combinations of these may advantageously be employed in those embodiments wherein the oxygen containing gas comprises air, or oxygen depleted air, advantageously, catalysts are not required in those embodiments wherein the oxygen-containing gas comprises nitric oxide or nitrogen dioxide.

[0037] As shown at step 104, the hydrocarbon oil is also contacted with a Lewis acid, either provided neat, or in combination with a solvent to provide a Lewis acid solution. Desirably, if the use of a solvent is desired or required, an aprotic solvent may be used, e.g., acetonitrile, nitromethane, 1,2-dichloroethane, or combinations thereof. The Lewis acid may be any ion or compound that can accept a pair of electrons from a corresponding Lewis base, in this case, oxidized and/or unoxidized impurities capable of acting as Lewis bases. The resulting Lewis acid-base complexes are readily separated from the hydrocarbon oil, in particular, in those embodiments wherein an aprotic solvent is utilized to provide the Lewis acid as a Lewis acid solution. The Lewis acid may desirably comprise a Pearson Hard Lewis acid, and in some embodiments, comprises AlCl_3 , GaCl_3 , FeCl_3 , or combinations of these. Any of steps 101-104 may be optionally heated or pressurized, but advantageously, the disclosed methods do not require added heat and pressure to carry out the oxidation or Lewis acid complexation.

[0038] Once the hydrocarbon oil and Lewis acid solution are combined, Lewis acid-base complexes will begin to form between the Lewis acid and any impurities of the hydrocarbon oil capable of acting as Lewis bases, and the combined solution will begin to fractionate, i.e., to form two distinct phases. One phase will comprise hydrocarbon oil (and any added fuel solvent, if present) while another phase will comprise the Lewis acid-base complexes and the aprotic solvent, if used. If desired or required, centrifugation may be utilized to facilitate the fractionation. As shown at step 105, the phases may then be separated, such as by decantation or filtration or, if the aprotic solvent used via a liquid-liquid extractor or a separatory funnel, and the purified hydrocarbon oil stored or further processed. If any fuel solvent was added to facilitate processing of the hydrocarbon oil, it may be removed from the purified hydrocarbon oil, e.g., by evaporation.

[0039] In some embodiments, it may be desirable to repeat either or both of the oxidation and/or Lewis acid complexation steps. Repetition of one or both of the oxidation and/or Lewis acid complexation steps can further reduce the amount of impurities in the hydrocarbon oil, so that more pure fractions may be obtained, or cruder grades may be started with. One such embodiment is shown in FIG. 2, in which, at step 206, the mixture is subjected to both an additional oxidation

and Lewis acid complexation step. FIG. 3 shows an additional such embodiment, wherein only the Lewis acid complexation step is repeated at step 306.

[0040] Another embodiment is illustrated in FIG. 4, which shows method 400 further comprising pre-processing purification step 407 in which particulates, or other high molecular weight impurities may be removed from the hydrocarbon oil. Hydrocarbon oils may typically contain amounts of asphaltenes, or other particulates, that may interfere with the removal of the sulfur containing impurities from the hydrocarbon oil. By removal of at least some of the asphaltenes prior to oxidation and/or the addition of the Lewis acid to the hydrocarbon oil, the efficiency of the oxidation and/or Lewis acid complexation may be enhanced.

[0041] More particularly, pre-processing purification step 407 may comprise the addition of a solvent to improve the processability of the hydrocarbon oil, and then the centrifugation of this mixture to provide the precipitation of at least a portion of any particulates or impurities having a higher molecular weight or density than the hydrocarbon oil. Pre-processing purification step may also comprise filtration, decantation, or combinations of these. The pre-treated hydrocarbon oil may then be separated from the precipitates and further processed according to the method disclosed herein.

[0042] Yet another embodiment is shown in FIG.5, wherein method 500 further comprises separation of fractionated mixture into a purified hydrocarbon oil fraction and a fraction comprising the Lewis acid complexes, and at step 508, recovery of the Lewis acid. More particularly, step 508 may involve the addition of an acid to the Lewis acid fraction, which is expected to regenerate the Lewis acid that may then recovered via any suitable method, e.g., crystallization or distillation. The Lewis acid may then be stored for future use, or as shown at step 509, recycled and reused in method 500 at step 504. Any acid capable of regenerating the Lewis acid may be used at step 508, and one example of a suitable acid is hydrochloric acid having a concentration in the range of from about 0.001 M to about 3.5 M.

[0043] In some embodiments, the oxidation products formed via contact with the oxygen containing gas may be removed prior to contacting the hydrocarbon oil with the Lewis acid/Lewis acid solution, which may increase the efficiency with which the Lewis acid-base complexes are formed. Such an embodiment is shown in FIG. 6, wherein method 600 comprises removal of formed oxidation products at step 610. Any method suitable to remove the oxidation products can be utilized at step 610, and suitable methods for doing so, include for example, filtration, centrifugation, decantation, and the like. FIG. 6 also illustrates that embodiment of the invention wherein the hydrocarbon oil is not combined with a fuel solvent prior to contacting the hydrocarbon oil with the oxygen containing gas and/or the Lewis acid.

EXAMPLE 1

[0044] 4.02 grams of a 1% solution of benzothiophene (BZT) in decalin (a model hydrocarbon oil) was weighed into a 15 ml centrifuge tube. 5.04 grams of nitromethane was added to extract the benzothiophene. The tube was shaken vigorously for about 2 minutes and then centrifuged at 2100 rpm for 10 minutes. The top phase (supernatant) was pipetted off and the sulfur content measured by XRF. Approximately 50% of the sulfur in the decalin was extracted by 5.04 g of nitromethane.

EXAMPLE 2

[0045] 4.00 grams of a 1% solution of benzothiophene in decalin, which was previously treated with NO₂ by bubbling of 3 % NO₂ in air at 75 °C during 2 hours at the rate 150 sccm in a flask equipped with a water cooled condenser, was weighed into a 15 ml centrifuge tube. 5.04 grams of nitromethane was added to extract the benzothiophene/NO₂ oxidation products. The tube was shaken vigorously for about 2 minutes and then centrifuged at 2100 rpm for about 10 minutes. The top phase (supernatant) was pipetted off and the sulfur content therein measured by XRF. Approximately 52% of the sulfur in the decalin was extracted to nitromethane.

EXAMPLE 3

[0046] 4.01 grams of a 1% solution of benzothiophene in decalin, which was previously treated with NO₂ as described in Example 2, was weighed into a 15 ml centrifuge tube. 5.01 grams of a 0.56M Lewis acid solution of iron (III) chloride in nitromethane was added. The tube was shaken vigorously for about 2 minutes and then centrifuged at 2100 rpm for 10 minutes. The top phase was pipetted off and the sulfur content measured by XRF. Approximately 88% of the original sulfur in the decalin was extracted using oxidation followed by treatment with Lewis acid.

EXAMPLE 4

[0047] 4.02 grams of a 1% solution of benzothiophene in decalin, which was previously treated with NO₂ as described in Example 2, was weighed into a 15 ml centrifuge tube. 2.50 grams of a 0.56M Lewis acid solution of iron (III) chloride in nitromethane was added. The tube was shaken vigorously for about 2 minutes and then centrifuged at 2100 rpm for

10 minutes. The top phase (supernatant) was pipetted off and the sulfur content measured by XRF. Approximately 82% of the original sulfur in the decalin was extracted. Thus, with only half of the Lewis acid used, most of the benzothiophene was removed from the decalin phase after the NO₂/Lewis acid treatment.

EXAMPLE 5

[0048] 4.03 grams of a 1% solution of octyl sulfide (OS) in decalin, which was previously treated with NO₂ as described in Example 2, was weighed into a 15 ml centrifuge tube. 4.0 grams of nitromethane was added to extract the octyl sulfide oxidation products. The tube was shaken vigorously for about 2 minutes and then centrifuged at 2100 rpm for about 10 minutes. The top phase was pipetted off and the sulfur content measured by XRF. Approximately 31% of the sulfur in the decalin was extracted to nitromethane.

EXAMPLE 6

[0049] 4.01 grams of a 1% solution of octyl sulfide in decalin, which was previously treated with NO₂ as described in Example 2, was weighed into a 15 ml centrifuge tube. 4.01 grams of a 0.56M Lewis acid solution of iron (III) chloride in nitromethane was added. The tube was shaken vigorously for about 2 minutes and then centrifuged at 2100 rpm for about 10 minutes. The top phase was pipetted off and the sulfur content measured by XRF. Approximately 82% of the sulfur in the decalin was removed.

EXAMPLE 7

[0050] 4.0 grams of a 1% solution of octyl sulfide in petroleum ether was weighed into a 15 ml centrifuge tube. 4.01 grams of a 0.56M Lewis acid solution of iron (III) chloride in nitromethane was added. The tube was shaken vigorously for about 2 minutes and then centrifuged at 2100 rpm for 10 minute. The top phase was pipetted off and the sulfur content measured by XRF. Approximately 44% of the sulfur in the petroleum ether was removed.

[0051] The results of Examples 1-7 are summarized in Table 1, below. Briefly, Example 3 shows that the combination of oxidation with Lewis acid treatment removes significantly more aromatic sulfur (BZT) than pure solvent extraction (Example 1) and oxidation alone (Example 2). Example 4 shows that this is true at even ½ the Lewis acid concentration, i.e., a similar sulfur removal percent was seen in Example 4 as compared to Example 3, while using Lewis acid at half the concentration of that used in Example 3. And, Example 6 shows the synergistic effect of using oxidation and Lewis acid extraction to remove aliphatic sulfur, i.e., the combination of oxidation with Lewis acid extraction removed more aliphatic sulfur than either oxidation (Example 5) or Lewis acid extraction (Example 7) alone.

Example	Sulfur source	Initial %S	Final %S	Δ (%S removed)	Comments
1	BZT	0.254	0.127	50%	Extraction only (neither oxidation nor Lewis acid treatment)
2	BZT	0.256	0.123	52%	Oxidation + extraction
3	BZT	0.256	0.031	88%	Oxidation + Lewis acid treatment
4	BZT	0.256	0.046	82%	Oxidation + Lewis acid treatment at ½ concentration of Example 3
5	OS	0.139	0.096	31 %	Oxidation + extraction
6	OS	0.139	0.025	82%	Oxidation + Lewis acid treatment
7	OS	0.426	0.239	44%	Lewis acid treatment only (no oxidation)

[0052] While various embodiments of the present invention have been shown and described herein, it will be understood that such embodiments are provided by way of example only and not of limitation. Numerous variations, changes and substitutions will occur to those skilled in the art without departing from the teaching of the present invention. Accordingly, it is intended that the invention be interpreted within the full scope of the appended claims.

Claims

1. A method for removing impurities from a hydrocarbon oil comprising:

- (a) contacting the hydrocarbon oil with an oxygen-containing gas under conditions effective to oxidize at least a portion of the impurities;
- (b) contacting the hydrocarbon oil with a Lewis acid under conditions effective so that any Lewis base impurity (ies) in the feedstock can react with the Lewis acid; and
- (c) removing any impurities so oxidized and/or reacted from the hydrocarbon oil.

2. The method of claim 1, wherein the oxygen-containing gas comprises air, ozone enriched air comprises a mixture of nitric oxide and air, nitrogen dioxide or a combination of these.

3. The method of claim 2, wherein the oxygen-containing gas comprises air, and the conditions effective to oxidize include the use of a catalyst.

4. The method of claim 3, wherein the catalyst comprises molybdenum, copper, manganese, cobalt, tungsten, iron or combinations of these.

5. The method of any preceding claim, wherein the impurities comprise sulfur, vanadium, nickel, or combinations of these.

6. The method of claim 5, wherein the impurities comprise substituted and unsubstituted benzothiophenes, dibenzothiophenes, phenanthiophenes, benzonathiophenes, alkyl sulfides, aryl sulfides or derivatives thereof.

7. The method of claim 6, wherein at least a portion of the sulfur impurities are oxidized to form sulfoxides and sulfones.

8. The method of any preceding claim, wherein the Lewis acid comprises AlCl_3 , GaCl_3 , FeCl_3 , or combinations of these.

9. The method of any preceding claim, wherein the Lewis acid is used as a solution in an aprotic solvent.

10. The method of claim 9, wherein the aprotic solvent is nitromethane.

11. The method of any preceding claim, wherein the oxidized or reacted impurities are removed by centrifugation and/or decantation.

12. The method of any preceding claim, wherein contact with the oxygen-containing gas and contact with the Lewis acid are caused to occur relatively simultaneously.

13. The method of any preceding claim, wherein at least one step is repeated at least once.

14. The method of any preceding claim, further comprising the pretreatment of the fuel oil.

15. The method of claim 14, wherein the pretreatment comprises addition of a fuel solvent, removal of insoluble particulates, or both of these.

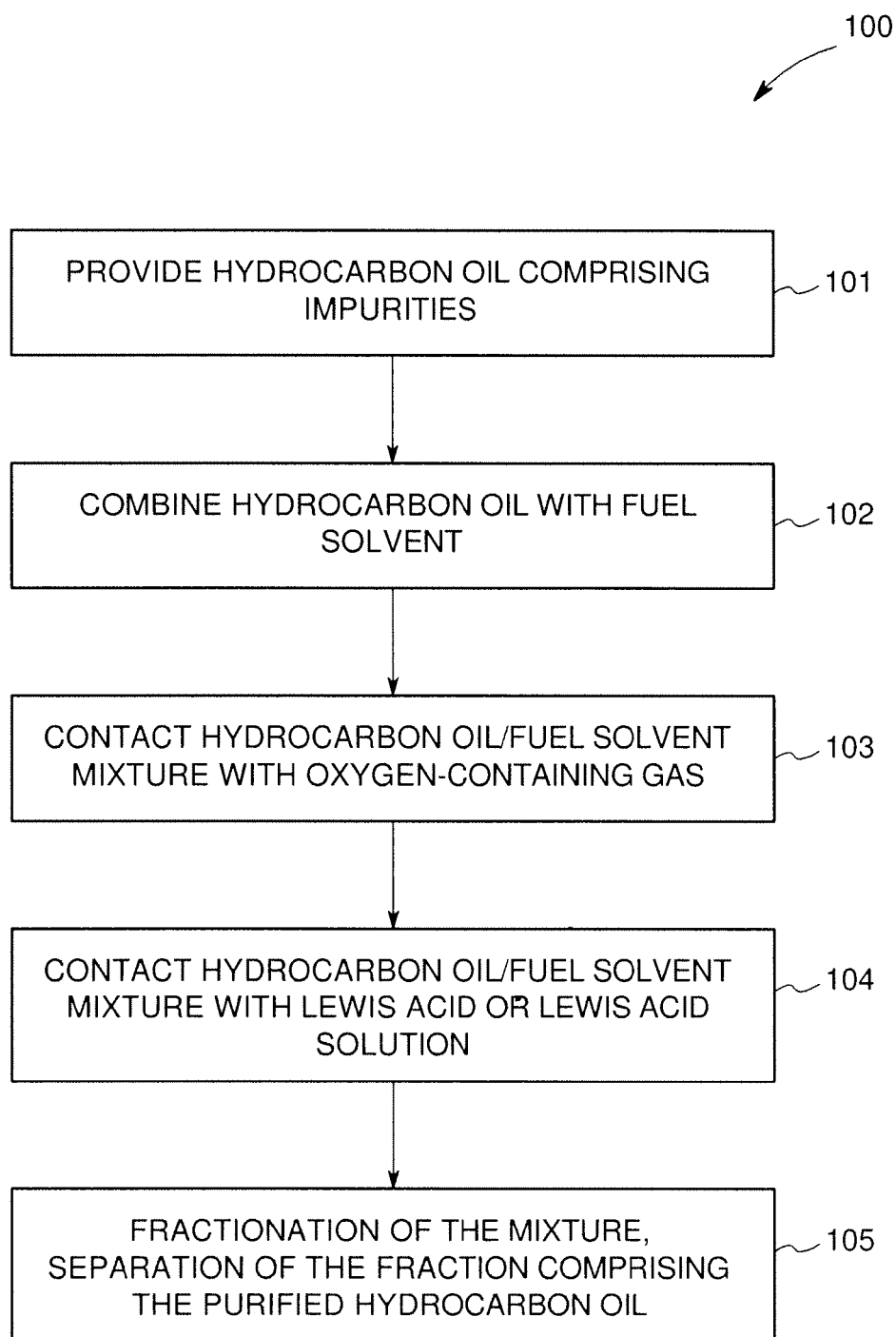


FIG. 1

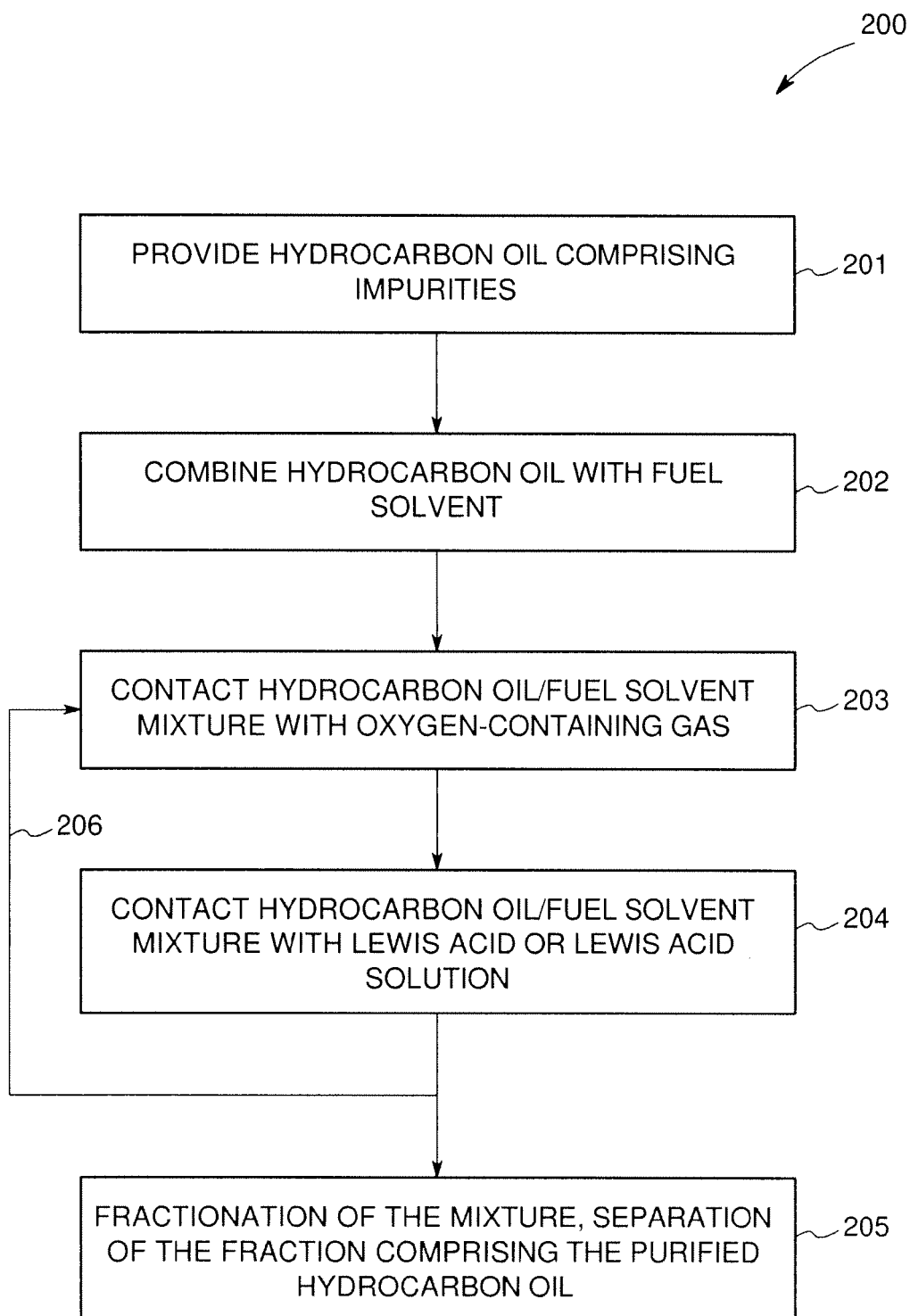


FIG. 2

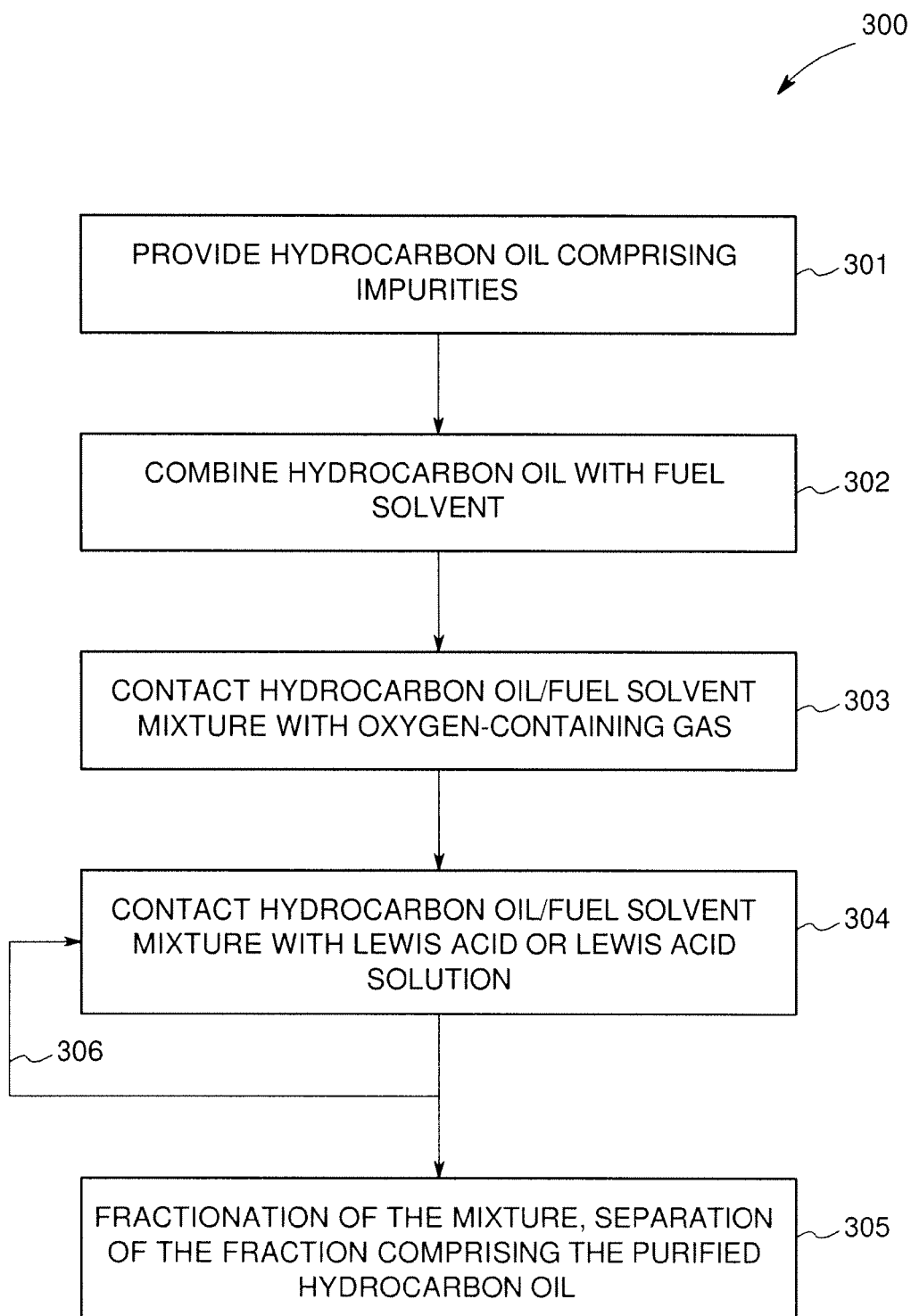


FIG. 3

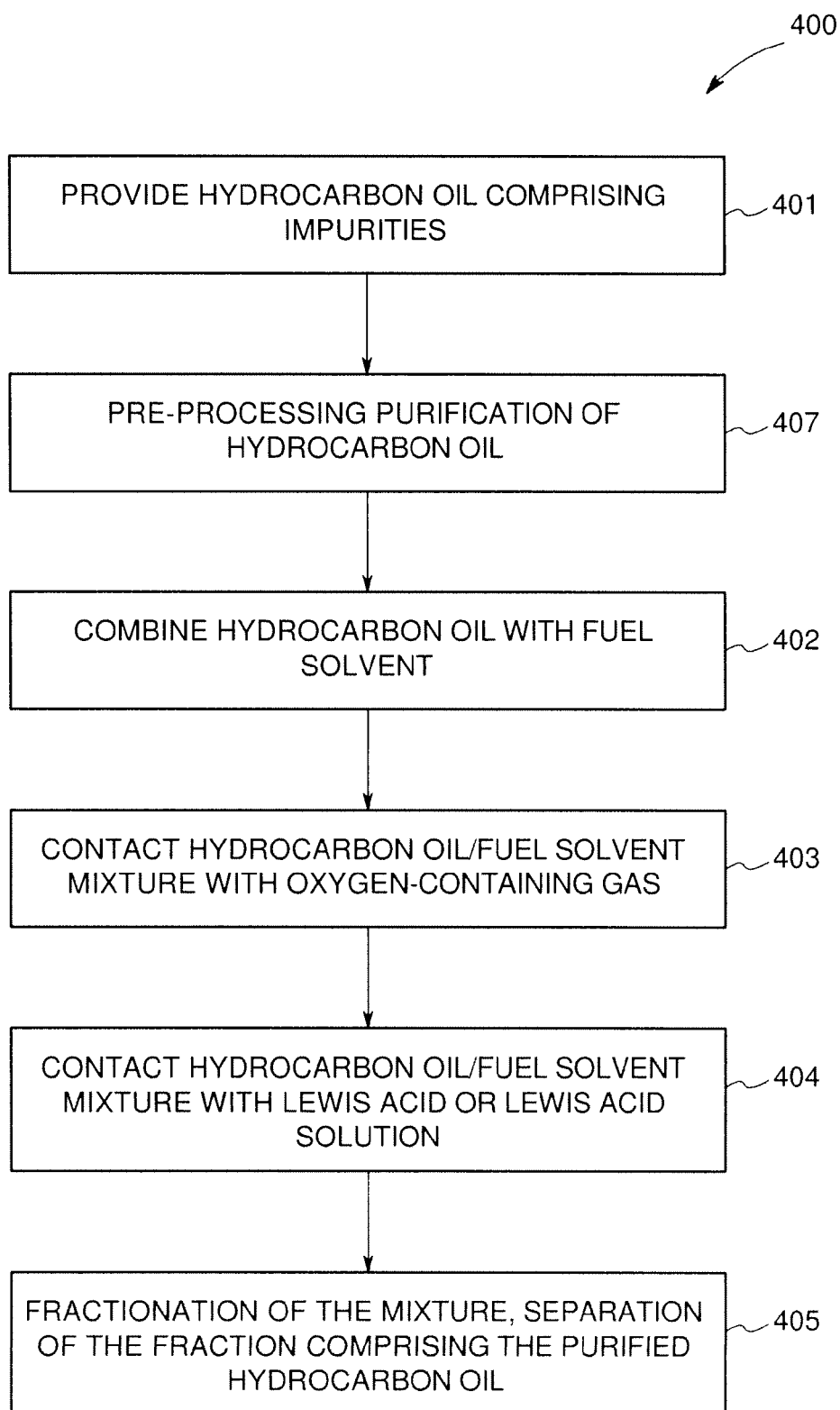


FIG. 4

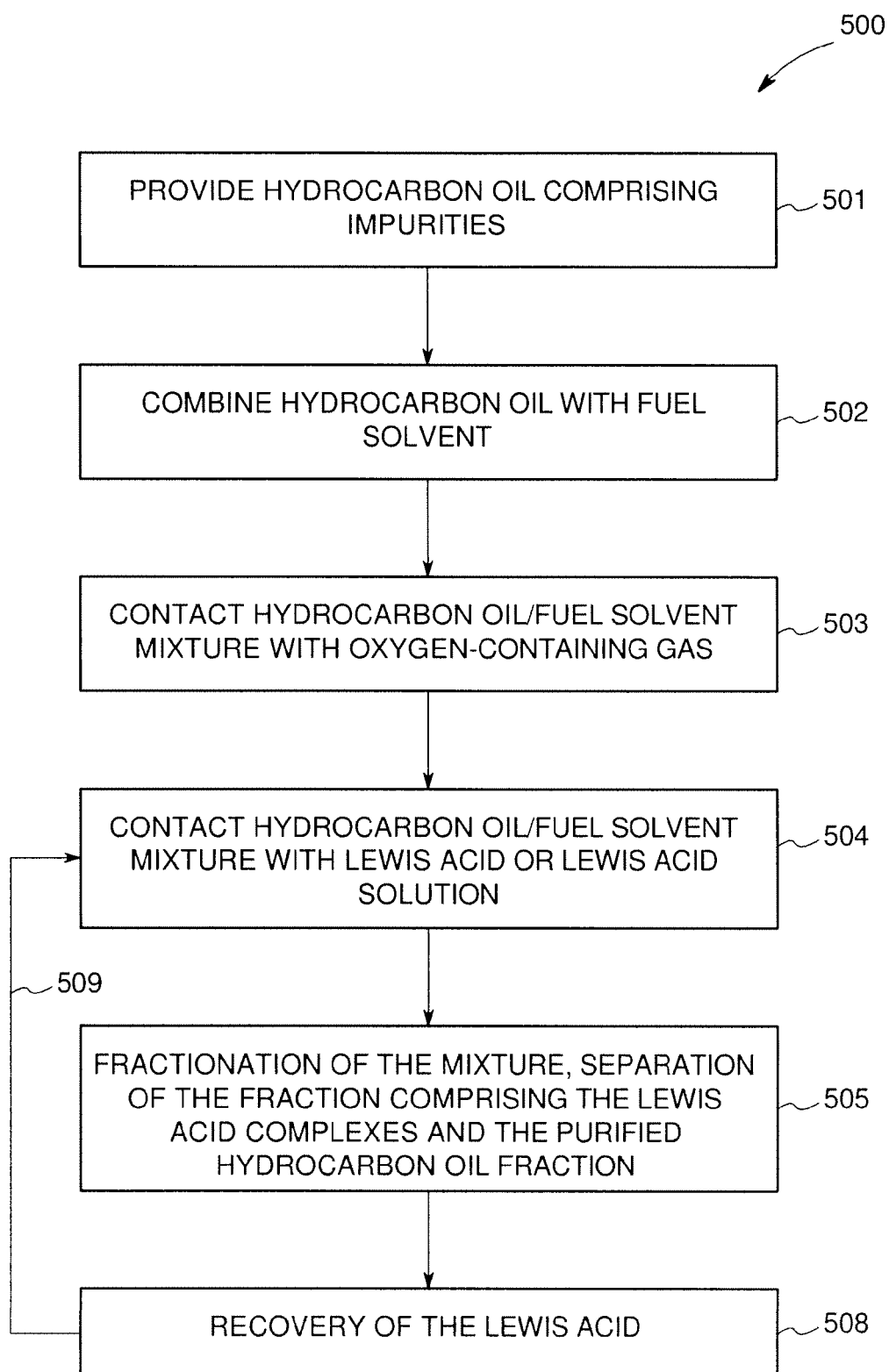


FIG. 5

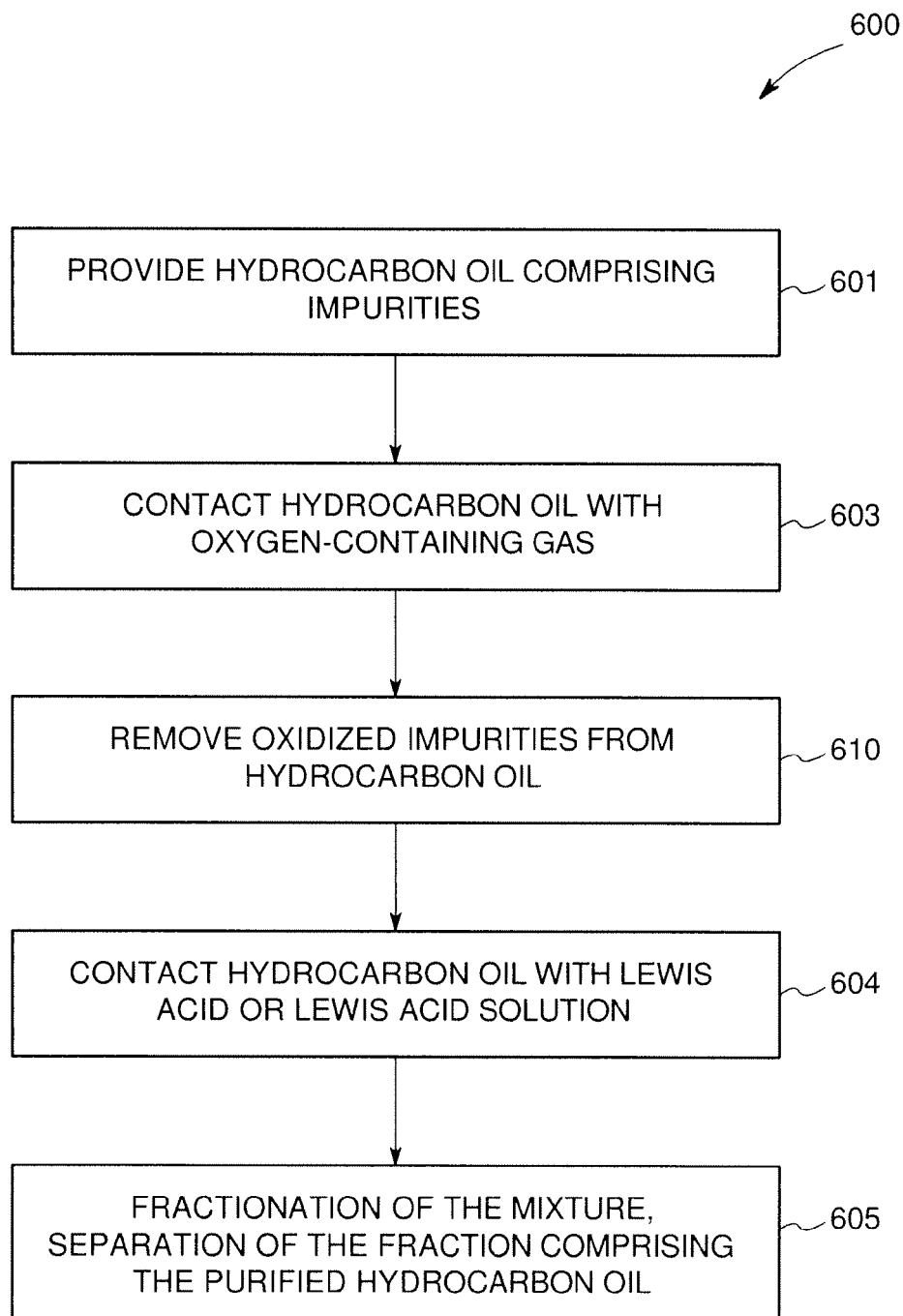


FIG. 6



EUROPEAN SEARCH REPORT

Application Number
EP 10 15 8906

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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 25 August 2010	Examiner Nazario, Luis
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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EUROPEAN SEARCH REPORT

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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 25 August 2010	Examiner Nazario, Luis
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**ANNEX TO THE EUROPEAN SEARCH REPORT
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The members are as contained in the European Patent Office EDP file on
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25-08-2010

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