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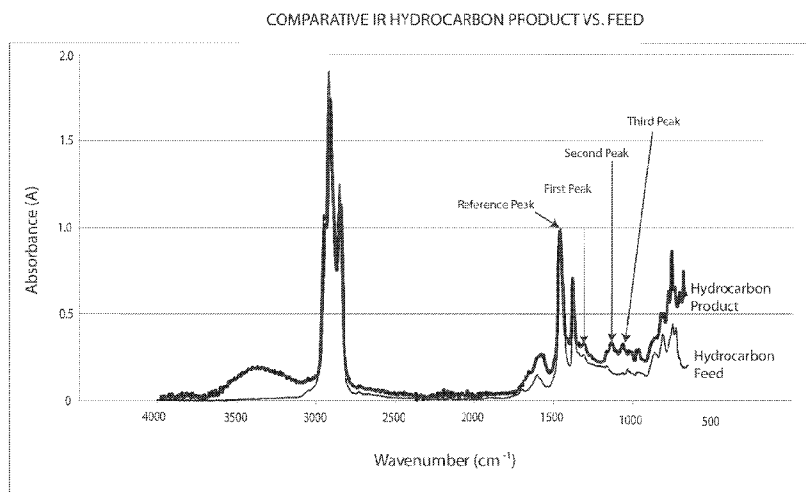


Fig. 7e

(57) **Abstract:** A hydrocarbon product having at least 0.1 grams per gram of hydrocarbon product having a boiling range distribution from an initial boiling point to approximately 739C wherein the hydrocarbon products are further characterized by an infrared spectroscopy reference peak, centered between approximately 1445 cm⁻¹ and 1465 cm⁻¹, a first infrared spectroscopy peak between approximately 1310cm⁻¹ and 1285cm⁻¹, wherein the height of the first infrared spectroscopy peak is at least approximately 28% of the height of the infrared spectroscopy reference peak and a second infrared spectroscopy peak between approximately 1135cm⁻¹ and 1110cm⁻¹, wherein the height of the second infrared spectroscopy peak is at least approximately 22% of the height of the infrared spectroscopy reference peak.

HYDROCARBON PRODUCTS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation-in-part application claiming priority and benefit of U.S. Patent Application No. 14/286,342 filed May 23, 2014, entitled “HYDROCARBON PRODUCTS”, the content of which is incorporated herein by reference.

FIELD OF THE TECHNOLOGY

[0002] The following relates generally to a hydrocarbon product having relatively low viscosity and low density while containing a significant amount of residue and micro-carbon residue.

BACKGROUND

[0003] Crude oil contains heteroatoms such as sulfur, nitrogen, nickel, vanadium and acidic oxygenates in quantities that negatively impact the refinery processing of the crude oil fractions. Light crude oils or condensates contain heteroatoms in concentrations as low as 0.001 wt %. In contrast, heavy crude oils contain heteroatoms as high as 5-7 Wt %. The heteroatom content of crude oil increases with increasing boiling point and the heteroatom content increases with decreasing API gravity. These impurities must be removed during refining operations to meet the environmental regulations for the final product specifications (e.g., gasoline, diesel, fuel oil) or to prevent the contaminants from decreasing catalyst activity, selectivity, and lifetime in downstream refining operations. Contaminants such as sulfur, nitrogen, trace metals, and total acid number (TAN) in the crude oil fractions negatively impact these downstream processes, including hydrotreating, hydrocracking and fluid catalytic cracking (FCC) to name just a few. These contaminants are present in the crude oil fractions in varying structures and concentrations.

[0004] Crudes that have one or more unsuitable properties that do not allow the crudes to be economically transported, or processed using conventional facilities, are commonly referred to as “disadvantaged crudes.” Disadvantaged crudes often contain relatively high levels of residue. Such crudes tend to be difficult and expensive to transport and/or process using conventional facilities. High residue crudes may be treated at high temperatures to convert the crude to coke. Alternatively, high residue crudes are typically treated with water at high temperatures to produce less viscous crudes and/or crude mixtures. During processing, water removal from the less viscous crudes and/or crude mixtures may be difficult using conventional means.

[0005] Disadvantaged crudes may include hydrogen deficient hydrocarbons. When processing of hydrogen deficient hydrocarbons using previously known methods, consistent quantities of hydrogen are generally needed to be added, particularly if unsaturated fragments resulting from cracking processes are produced. Hydrogenation during processing, which typically involves the use of an active

hydrogenation catalyst, may be needed to inhibit unsaturated fragments from forming coke. Hydrogen is costly to produce and/or costly to transport to treatment facilities.

[0006] Coke may form and/or deposit on catalyst surfaces at a rapid rate during processing of disadvantaged crudes. It may be costly to regenerate the catalytic activity of a catalyst contaminated by coke. High temperatures used during regeneration may also diminish the activity of the catalyst and/or cause the catalyst to deteriorate. Disadvantaged crudes may include acidic components that contribute to the total acid number (TAN) of the crude feed. Disadvantaged crudes with a relatively high TANs may contribute to corrosion of metal components during transporting and/or processing of the disadvantaged crudes. Removal of acidic components from disadvantaged crudes may involve chemically neutralizing acidic components with various bases. Alternately, corrosion-resistant metals may be used in transportation equipment and/or processing equipment. The use of corrosion-resistant metal often involves significant expense, and thus, the use of corrosion-resistant metal in existing equipment may not be desirable. Another method to inhibit corrosion may involve addition of corrosion inhibitors to disadvantaged crudes before transporting and/or processing of the disadvantaged crudes. The use of corrosion inhibitors may negatively affect equipment used to process the crudes and/or the quality of products produced from the crudes. Disadvantaged crudes may contain relatively high amounts of metal contaminants, for example, nickel, vanadium, and/or iron. During processing of such crudes, metal contaminants, and/or compounds of metal contaminants, may deposit on a surface of the catalyst or the void volume of the catalyst. Such deposits may cause a decline in the activity of the catalyst.

[0007] Disadvantaged crudes often include organically bound heteroatoms (for example, sulfur, oxygen, and nitrogen). Organically bound heteroatoms may, in some situations, have an adverse effect on catalysts. Alkali metal salts and/or alkaline-earth metal salts have been used in processes for desulfurization of residue. These processes tend to result in poor desulfurization efficiency, production of oil insoluble sludge, poor demetallization efficiency, formation of substantially inseparable salt-oil mixtures, utilization of large quantities of hydrogen gas, and/or relatively high hydrogen pressures.

[0008] Some processes for improving the quality of crude include adding a diluent to disadvantaged crudes to lower the weight percent of components contributing to the disadvantaged properties. Adding diluent, however, generally increases costs of treating disadvantaged crudes due to the costs of diluent and/or increased costs to handle the disadvantaged crudes. Addition of diluent to disadvantaged crude may, in some situations, decrease stability of such crude.

[0009] Other processes for improving the quality of crude include hydrocracking. Hydrocracking, however, generally has a high cost associated with expensive catalysts and pressure vessels. In addition, hydrocracking, under certain conditions, may also create olefins. Olefins are unstable and may, in some situations, decrease the stability of crude. Therefore, olefin-containing crudes may require the addition of expensive additives to permit transportation in pipelines. *See* U.S. Pat. Nos. 3,136,714 to Gibson et al.; 3,558,747 to Gleim et al.; 3,847,797 to Pasternak et al.; 3,948,759 to King et al.; 3,957,620 to Fukui et al.; 3,960,706 to McCollum et al.; 3,960,708 to McCollum et al.; 4,119,528 to Baird, Jr. et al.; 4,127,470 to Baird, Jr. et al.; 4,224,140 to Fujimori et al.; 4,437,980 to Heredy et al.;

4,591,426 to Krasuk et al.; 4,665,261 to Mazurek; 5,064,523 to Kretschmar et al.; 5,166,118 to Kretschmar et al.; 5,288,681 to Gatsis; 6,547,957 to Sudhakar et al.; 7,598,426 to Fang et al.; 7,648,625 to Bhan et al.; 7,678,264 to Bhan; 7,749,374 to Bhan et al.; 7,918,992 to Bhan; 8,088,706 to Domokos et al.; 8,372,777 to Bhan et al.; 8,409,541 to Reynolds et al.; 8,450,538 to Bhan et al.; 8,481,450 to Bhan; 8,492,599 to Bhan et al.; 8,530,370 to Donaho et al.; 8,562,817 to Milam et al.; 8,562,818 to Milam et al.; 8,608,946; and U.S. Patent Application Publication Nos. 20030000867 to Reynolds; 20030149317 to Rendina; 20060231456 to Bhan; 20060231457 to Bhan; 2006023476 to Bhan; 20070000810 to Bhan et al.; 20070295646 to Bhan et al.; 20080083650 to Bhan et al.; 20080087575 to Bhan et al.; 20080135449 to Bhan et al.; 20090188836 to Bhan et al.; 20100055005 to Bhan et al.; 20100098602 to Bhan et al.; 20110178346 to Milam et al.; and 20110192762 to Wellington et al, all of which are incorporated herein by reference, describe various processes and systems used to treat crudes. The process, systems, and catalysts described in these patents, however, have limited applicability because of many of the technical problems set forth above.

[0010] In sum, disadvantaged crudes generally have undesirable properties, for example, relatively high residue, a tendency to corrode equipment, and/or a tendency to consume relatively large amounts of hydrogen during treatment. Other undesirable properties include relatively high amounts of undesirable components including relatively high TANs, organically bound heteroatoms, and/or metal contaminants. Such properties tend to cause problems in conventional transportation and/or treatment facilities, including increased corrosion, decreased catalyst life, process plugging, and/or increased usage of hydrogen during treatment. Thus, there is a significant economic and technical need for improved systems, methods, and/or catalysts for conversion of disadvantaged crudes, and other hydrocarbons into hydrocarbon products and crude products with properties that are more desirable.

SUMMARY OF THE TECHNOLOGY

[0011] A first embodiment of this disclosure relates generally to hydrocarbon product comprising at least 0.1 grams per gram of hydrocarbon product having a boiling point that is less than 739°C, at least 75 to 85 mass% carbon, at least 9 to 16 mass % hydrogen; and the hydrocarbon product exhibits an infrared spectroscopy reference peak, centered between approximately 1445 cm⁻¹ and 1465 cm⁻¹, a first infrared spectroscopy peak between approximately 1310cm⁻¹ and 1285cm⁻¹, and a second infrared spectroscopy peak between approximately 1135cm⁻¹ and 1110cm⁻¹, wherein a height or area of the first infrared spectroscopy peak is at least approximately 28% of a height or area of the infrared spectroscopy reference peak and a height or area of the second infrared spectroscopy peak is at least approximately 22% of the height or area of the infrared spectroscopy reference peak.

[0012] A second embodiment of this disclosure relates generally to a hydrocarbon product comprising at least 0.1 grams per gram of the hydrocarbon product has a boiling point greater than 738°C, up to 0.1 mass% of the hydrocarbon product is insoluble in pentane and the hydrocarbon product exhibits an infrared spectroscopy reference peak, centered between approximately 1445 cm⁻¹ and 1465 cm⁻¹, a first infrared spectroscopy peak between approximately 1310cm⁻¹ and 1285cm⁻¹, and a second infrared

spectroscopy peak between approximately 1135cm^{-1} and 1110cm^{-1} , wherein a height or area of the first infrared spectroscopy peak is at least approximately 28% of a height or area of the infrared spectroscopy reference peak and a height or area of the second infrared spectroscopy peak is at least approximately 22% of the height or area of the infrared spectroscopy reference peak.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Some of the embodiments will be described in detail, with reference to the following figures, wherein like designations denote like members, wherein:

[0014] Fig. 1a depicts a flowchart describing an embodiment of a method of oxidative desulfurization of a hydrocarbon feed.

[0015] Fig. 1b depicts a flowchart describing an embodiment of treating a sulfone and/or sulfoxide rich hydrocarbon feed.

[0016] Fig. 2 depicts how the selectivity of a reaction between a sulfone and/or sulfonate and caustic may be manipulated using an alcoholysis reaction to form more desirable products using a selectivity promoter.

[0017] Fig. 3 depicts multiple embodiments of an alcoholysis reaction between a sulfone, caustic and selectivity promoter and provides embodiments of the reaction products thereof.

[0018] Fig. 4 depicts an embodiment of a reaction mechanism for forming a sulfonate intermediate from a sulfone substrate.

[0019] Fig. 5a depicts an embodiment of a biphasic reaction mechanism for forming a hydrocarbon product and a sulfate salt.

[0020] Fig. 5b depicts an alternate embodiment of a biphasic reaction mechanism, forming a hydrocarbon product and a bisulfite salt.

[0021] Fig. 6a depicts a comparative graphical representation of multiple embodiments of a simulated distillation (SIMDIS) of multiple hydrocarbon feeds and their predicted boiling point distributions.

[0022] Fig. 6b depicts a graphical representation of a SIMDIS of the crude feed boiling point distribution provided in Fig. 6a.

[0023] Fig. 6c depicts a graphical representation of a SIMDIS of the sulfoxidized crude oil boiling point distribution provided in Fig. 6a.

[0024] Fig. 6d depicts a graphical representation of a SIMDIS of the hydrocarbon products of the low heteroatom removal boiling point distribution provided in Fig. 6a.

[0025] Fig. 6e depicts a graphical representation of a SIMDIS of the hydrocarbon products of the mild heteroatom removal boiling point distribution provided in Fig. 6a.

[0026] Fig. 6f depicts a graphical representation of a SIMDIS of the hydrocarbon products of the moderate heteroatom removal boiling point distribution provided in Fig. 6a.

[0027] Fig. 7a depicts a graphical representation of infrared spectroscopy of one embodiment of a hydrocarbon feed.

[0028] Fig. 7b depicts a graphical representation of an infrared spectroscopy of one embodiment of a sulfoxidized intermediate hydrocarbon stream.

[0029] Fig. 7c depicts a graphical representation of an infrared spectroscopy of one embodiment of a hydrocarbon product.

[0030] Fig. 7d depicts a graphical comparison of the infrared spectroscopies of Fig. 7a and Fig. 7b.

[0031] Fig. 7e depicts a graphical comparison of infrared spectroscopies of Fig. 7a and Fig. 7c.

[0032] Fig. 7f depicts a graphical comparison of infrared spectroscopies of Fig. 7b and Fig. 7c.

DETAILED DESCRIPTION OF THE DISCLOSURE

[0033] A detailed description of the hereinafter described embodiments of the disclosed apparatus and method are presented herein by way of exemplification and not limitation with reference to the Figures. Although certain embodiments are shown and described in detail, it should be understood that various changes and modifications may be made without departing from the scope of the appended claims. The scope of the present disclosure will in no way be limited to the number of constituting components, the materials thereof, the shapes thereof, the relative arrangement thereof, etc., and are disclosed simply as an example of embodiments of the present disclosure.

[0034] As a preface to the detailed description, it should be noted that, as used in this specification and the appended claims, the singular forms “a”, “an” and “the” include plural referents, unless the context clearly dictates otherwise.

[0035] Certain embodiments are described in detail below. Terms used herein may be defined as follows:

[0036] “ASTM” refers to American Standard Testing and Materials.

[0037] “API gravity” refers to American Petroleum Institute gravity (“API gravity”) at 15.5°C (approximately 60°F), unless stated otherwise. API gravity may be determined by ASTM Method D6822 or equivalent method. *API gravity*, is a measure of how heavy or light a petroleum liquid is compared to water. If its API gravity is greater than 10, it is lighter and floats on water; if less than 10, it is heavier and sinks. API gravity is thus an inverse measure of the relative density of a petroleum liquid and the density of water, but it is used to compare the relative densities of petroleum liquids. For example, if one petroleum liquid floats on another and is therefore less dense, it has a greater API gravity. Although mathematically, API gravity has no units, it is nevertheless referred to as being in “degrees” or according to the ASTM, API gravity may also be described in units of kg/m³. API gravity is typically gradated in degrees on a hydrometer instrument. Methods for determining API may be performed, using a glass thermohydrometer in conjunction with a series of calculations, of the density, relative density, or API gravity of crude petroleum, petroleum products, or mixtures of petroleum and nonpetroleum products which may be handled as liquids having a Reid vapor pressures of 101.325 kPa (14.696 psi) or less. Values are determined at the existing temperatures and may be corrected to 15°C or 60°F.

[0038] The ratio of atomic hydrogen to atomic carbon present in a hydrocarbon feed and the crude product may be determined by ASTM Method D5291 or equivalent method. In some embodiments, the test methods may be applicable to various hydrocarbons, including crude oils, fuel oils, additives, lubricants and residues. The hydrogen to carbon ratio may be tested in concentration ranges of at least 75 to 85 mass % for carbon and at least 9 to 16 mass % for hydrogen. Embodiments employing certain methods for identifying the hydrogen to carbon ratio may express the results as mass % carbon and mass % hydrogen.

[0039] Boiling range distributions for the hydrocarbon feed, the total product, and/or the crude product may be determined by ASTM Method D5307, ASTM Method D7169 or equivalent method thereof, unless otherwise mentioned.

[0040] “Biphasic” means a chemical system that contains two separate and distinct immiscible chemical phases. These phases may be any immiscible substances, including gas-liquid, gas-solid, liquid-liquid and liquid-solid phases.

[0041] Boiling range distributions for hydrocarbons and hydrocarbon containing material may be as determined by ASTM Method D5307, ASTM Method D7169 or equivalent method. Some methods testing the boiling range distribution of a water-free crude petroleum may determine the boiling range through approximately 538°C. In such an embodiment, materials that boil above 538°C may be reported as residue. In other embodiments of methods for identifying the boiling range distribution, the method may determine boiling point distribution and cut point intervals of hydrocarbons such as crude oils and residues by using high temperature gas chromatography. The method may extend the applicability of simulated distillation to samples that do not elute completely from chromatographic systems. In some methods, the range for diesel boiling points may be identified using a method that establishes a boiling point distribution range up through 720°C which may correspond to the elution of $C_n - C_{100}$ hydrocarbon compounds. In some embodiments of the methods, tests may use capillary columns with thin films, which results in the incomplete separation of $C_4 - C_8$ in the presence of large amounts of carbon disulfide, and thus yields an unreliable boiling point distribution corresponding to this elution interval. In addition, quenching of the response of the detector employed to hydrocarbons eluting during carbon disulfide elution, may result in unreliable quantitative analysis of the boiling distribution in the $C_4 - C_8$ region. Since the detector may not quantitatively measure the carbon disulfide, its subtraction from the sample using a solvent-only injection and corrections to this region via quenching factors, may result in an approximate determination of the net chromatographic area. A separate, higher resolution gas chromatograph (GC) analysis of the light end portion of the sample may be performed in order to obtain a more accurate description of the boiling point curve in the interval in question. Some testing methods may be designed to obtain the boiling point distribution of other incompletely eluting samples such as atmospheric residues, vacuum residues, etc., that are characterized by the fact that the sample components are resolved from the solvent. The content of a particular boiling range may be characterized by the grams of the hydrocarbon boiling within the specific range per 1 gram of the total hydrocarbon mixture of a hydrocarbon feed or hydrocarbon product. For example, if a hydrocarbon product produces 0.3g of

hydrocarbon having a boiling point within a range of 204 - 260°C, per gram of hydrocarbon product, means that for every gram of hydrocarbon product produced, 0.3g of the hydrocarbon product includes hydrocarbons that boil within the 204 - 260°C boiling point range.

[0042] "C₅ asphaltenes" refers to asphaltenes that are insoluble in n-pentane. C₅ asphaltene content may be determined by ASTM Method D2007 or equivalent thereof. Asphaltene compositions of oil and other hydrocarbons may be included in rubber compounds which may have a large effect on the characteristics and uses of the compounds. Methods for determining C₅ asphaltenes may also be useful in the determination of other components such as saturates, aromatics, and other polar compounds present in oil but insoluble in pentane. In some embodiments, C₅ asphaltenes and other components that are insoluble in pentane may comprise up to 0.1 mass % of the hydrocarbon being measured, including a hydrocarbon feed and hydrocarbon product.

[0043] "C₇ asphaltenes" refers to asphaltenes that are insoluble in n-heptane. C₇ asphaltene content may be determined by ASTM Method D3279. Some methods for quantifying C₇ asphaltenes may be applicable to all solid and semi-solid petroleum asphalts containing little or no mineral matter, gas oils, heavy fuel oils, and crude petroleum that has been topped to a cut-point of approximately 343°C or higher.

[0044] "Carbon to hydrogen ratio" (C/H ratio) refers to the ratio of the amount of atomic carbon present in a substance compared with the amount of atomic hydrogen present. For example a hydrocarbon product having a C/H ratio of 1.5 parts carbon for every one part hydrogen may have a C/H ratio of 1.5/1. Alternatively, the C/H ratio may reduce the fraction where applicable. Using the previous example, the C/H ratio may simply be referred to as a C/H ratio of 1.5, because 1.5 divided by 1 equals 1.5.

[0045] "Diesel" refers to hydrocarbons with a boiling range distribution from approximately 250°C up to approximately 350°C as determined in accordance with ASTM Method D5307, ASTM Method D7169 or equivalent method. Diesel content may be determined by the quantity of hydrocarbons having a boiling range between 250 - 350°C relative to the quantity of hydrocarbons as measured by the boiling range distribution.

[0046] "Distillate" refers to hydrocarbons with a boiling range distribution from approximately 200 - 350°C as determined by ASTM Method D5307, ASTM Method 7169, or an equivalent method thereof. Distillates may include diesel and kerosene.

[0047] "Gasolines" refers to hydrocarbons with a boiling range distribution from approximately 40 to 250°C in accordance with ASTM Method D5307, ASTM Method D7169 or equivalent method. Gasoline hydrocarbons may be short carbon chains having approximately 4 – 12 carbons per molecule. Gasoline content may be determined by the quantity of hydrocarbons having a boiling range between 40 to 250°C relative to the quantity of hydrocarbons as measured by the boiling range distribution.

[0048] "Hydrogen to carbon ratio" (H/C) ratio is the reciprocal of the C/H ratio. It refers to the amount of atomic hydrogen present compared with the amount of atomic carbon present in a substance.

For example, using the C/H ratio above, the H/C ratio would be 1/1.5. The H/C ratio may also be simplified by reducing the fraction to a decimal or whole number. For example, H/C ratio of 1/1.5 may simply be referred to as an H/C ratio of 0.67.

[0049] "Group X metal(s)" refers to one or more metals of a column of the Periodic Table of Elements in which X corresponds to a column number of the Periodic Table. For example, "group 4 metal(s)" refers to one or more metals from column 4 of the Periodic Table (ex. Ti, Zr, Hf, Rf). A "metal" may refer to any element of the periodic table residing in groups 1-12 (excluding hydrogen) of the periodic table of elements, plus aluminum, gallium, indium, thallium, tin, lead, bismuth and polonium.

[0050] "Group X element(s)" refers to one or more elements located in a column on the Periodic Table of Elements, wherein X corresponds to one or more column numbers recited (ex. columns 13-18). For example, a column 13 element may include B, Al, Ga, In, Tl, and Uut.

[0051] "Contaminated hydrocarbon stream" is a mixture of hydrocarbons containing heteroatom constituents.

[0052] "Content" refers to the weight of a component (for example heteroatom content) in a substrate. An example of a substrate may be a hydrocarbon feed, a reaction product and/or crude product. The content may be expressed as a weight fraction or weight % (wt%) which may be calculated as the $\frac{\text{weight of the component}}{\text{total weight of the substrate}} \times 100 = \text{wt\%}$. For example, "metal content" may be expressed as a weight percent (wt%) wherein the metal content may be determined using the formula :

$$\frac{\text{weight of the metal in substrate}}{\text{total weight of the substrate}} \times 100 = \text{wt\% of metal content.}$$

[0053] "Hydrocarbon(s)" refers to a substance that has primary components of hydrogen and carbon. Hydrocarbons may include, but are not limited to both saturate and unsaturated forms of aromatic hydrocarbons, alkanes, alkenes, alkynes, aryls and cycloalkanes.

[0054] "Hydrocarbon feed" refers to a feed that includes hydrocarbons. The hydrocarbon feed may include, but is not limited to, crudes, heavy or extra heavy crudes, crude oils containing significant quantities of residue or pitch, bitumen, disadvantaged crudes, contaminated hydrocarbon streams, hydrocarbons derived from tar sands, shale oil, crude atmospheric residues, asphalts, hydrocarbons derived from liquefying coal and hydrocarbons obtained from a refinery process or mixtures thereof. The hydrocarbon feed may include hydrocarbons and a mixture of one or more heteroatoms. Common sulfur containing contaminants to a hydrocarbon feed may be mercaptans, sulfides, disulfides, thiophenes, benzothiophenes, dibenzothiophenes and benzo-naphthothiophenes.

[0055] "Initial boiling point" (IBP) refers to the point where hydrocarbons or a mixture of hydrocarbons first begin to boil. The initial boiling point may vary depending on the composition of the mixture. Depending on the composition of hydrocarbons, the initial boiling point of the hydrocarbons may range from less than 30°C up to approximately 739°C. In some embodiments, the IBP may be less than 30°C, less than 50°C, less than 70°C, or less than 100°C. In other embodiments, the IBP may be between 30 - 50°C or 50 to 100°C. In alternative embodiments, the IBP may be less than 150°C, less than 200°C, less than 250°C, less than 350°C or less than 450°C. The IBP may be between 150 - 250°C, 250-

350°C or between 350 - 450°C. Other embodiments containing high quantities of hydrocarbons having longer chains, may have a IBP between 450 to 750°C. In some instances the IBP may be less than 450°C, less than 550°C, less than 650°C or less than 750°C. The IBP may be between 450-550°C, 550-650°C, 650-750°C or even greater than 750°C in some embodiments, for example those embodiments containing a higher quantity of bitumen or asphalt.

[0056] As the carbon chains of the crude oil fractions become longer, the boiling point of the fraction may become higher, thus as the composition contains short chained hydrocarbons, the initial boiling point may decrease, whereas in a composition having less short chained hydrocarbons, the initial boiling point may rise. For example, a mixture of hydrocarbons including petroleum gas fractions having a small alkanes between 1-4 carbon atoms per molecule may have an initial boiling point of 40°C or less. In a hydrocarbon mixture including naphtha, having a mixture of hydrocarbons between 5-9 carbon atoms per molecule, the naphtha portion may have a boiling point between 60 - 100°C, wherein the boiling point may be between 60-69°C, 70-79°C, 80-89°C and/or 90-100°C. In a hydrocarbon mixture including gasoline hydrocarbons, such as alkanes and cycloalkanes, having carbon chains between 4-12 atoms of carbon per molecule, the gasoline fraction may have an boiling point between approximately 30 - 250°C, wherein the boiling point may be between 40-59°C, 60-79°C, 80-99°C, 100-149°C, 150 -199°C and/or 200-250°C. In a hydrocarbon mixture including kerosene, the kerosene portion may include alkanes having a carbon chain length between 10-18 carbon atoms per molecule and/or aromatic hydrocarbons. The kerosene fractions may have a boiling point between approximately 175-325°C, wherein the boiling point may be 175-199°C, 200-249°C, 250-299°C and/or 300-325°C.

[0057] Some hydrocarbon mixture may include a gas oil fraction which may be used for diesel fuel and heating oil. The gas oil fraction may include alkanes having 12 or more carbon atoms per molecule. The gas oil fraction may have a boiling point between 250 - 350°C. In some embodiments, the boiling point may be 250-274°C, 275-299°C, 300-324°C and/or 325-350°C. Hydrocarbon products may include a lubricating oil fraction, having long hydrocarbons between 20 to 50 carbon atoms per molecule. The lubricating oil fraction may include alkanes, cycloalkanes and aromatics and the lubricating oil fractions may have a boiling point between 300 - 370°C, wherein the boiling point may be between 300-324°C, 325-349°C and/or 350-370°C. A hydrocarbon product may also include in its mixture of hydrocarbons a heavy gas or fuel oil fraction having long chains of carbon atoms between approximately 20-70 carbon atoms per molecule. The heavy gas or fuel oil fraction may have a boiling point between approximately 370 - 600°C, wherein the boiling point may be between 370 - 399°C, 400-449°C, 450-499°C, 500 - 549°C and/or 550 - 600°C.

[0058] "Kerosene" refers to hydrocarbons with a boiling point distribution between approximately 175° - 325°C at a pressure of 0.101 MPa. Kerosene content may be determined by the quantity of hydrocarbons having a boiling range from 204° C to 260° C at a pressure of 0.101 MPa relative to a total quantity of hydrocarbons as measured by boiling range distribution in accordance with ASTM Method D5307, ASTM Method D7169 or an equivalent method thereof.

[0059] "Naphtha" refers to hydrocarbon components with a boiling range distribution from approximately 38°C to 204°C at a pressure of 0.101MPa. Naphtha content may be determined by the quantity of hydrocarbons having a boiling range relative to a total quantity of hydrocarbons as measured by boiling range distribution in accordance with ASTM Method D5307, ASTM Method D7169 or equivalent method thereof.

[0060] The content of hydrocarbon components, for example paraffins, iso-paraffins, olefins, naphthenes and aromatics in naphtha may be determined by ASTM Method D6730 or equivalent method. Methods for identifying the hydrocarbon components may include chromatographic operating conditions and column tuning processes to provide and enhance the separation and subsequent determination of many individual components that may not be obtained with previous single-column analyses. The column temperature program profile may be selected to afford the maximum resolution of possible co-eluting components, for example, where there are of two different compound types (such as a paraffin and a naphthene). Some embodiments of methods determining hydrocarbon components may determine hydrocarbon components of spark-ignition engine fuels and their mixtures containing oxygenate blends (MTBE, ETBE, ethanol, and so forth) with boiling ranges up to 225°C. Other light liquid hydrocarbon mixtures typically encountered in petroleum refining operations, such as blending stocks (naphthas, reformates, alkylates, and so forth) may also be analyzed. Individual component concentrations and precision may be determined for hydrocarbon and hydrocarbon products having values in the range from 0.01 to approximately 30 mass % or higher. Some embodiments of methods for analyzing hydrocarbon components may be applicable to samples containing less than 25 mass % of olefins. However, some interfering co-elution with the olefins above C₇ may occur, particularly if blending hydrocarbon components or their higher boiling cuts. Embodiments of methods determining hydrocarbon components may further be applied to benzene, toluene and oxygenated hydrocarbons, including oxygenated aromatics. "n-Paraffin" refers to normal (straight chain) saturated hydrocarbons. Paraffins may be a mixture of hydrocarbons. Each of the hydrocarbons may contain between 10-16 carbons on average per molecule, however the general formula for a paraffin may be described as C_nH_{2n+2}, wherein n = 1 to 400. Constituents of paraffin may include n-dodecane, alkyl benzenes, and naphthalene and its derivatives. Paraffins may have a boiling point range between approximately 140 - 320°C or higher.

[0061] "Olefins" or "olefinic hydrocarbons" refer to hydrocarbon compounds with non-aromatic carbon-carbon double bonds (e.g. Alkene). Types of olefins may include, but are not limited to cis, trans, internal, terminal, branched and linear.

[0062] "Periodic Table" refers to the Periodic Table as specified by the International Union of Pure and Applied Chemistry (IUPAC).

[0063] "STP" as used herein refers to standard temperature and pressure, which is 25° C. and 0.101 MPa.

[0064] "Liquid mixture" refers to a composition that includes one or more compounds that are liquid at standard temperature and pressure (25° C., 0.101 MPa, hereinafter referred to as "STP"), or a

composition that includes a combination of one or more compounds that are liquid at STP with one or more compounds that are solids at STP.

[0065] "Organometallic" refers to compound that may include an organic compound bonded or complexed with a metal of the Periodic Table. "Organometallic content" refers to the total content of metal in the organometallic compounds.

[0066] "Promoted caustic visbreaker" refers to a heated reactor that contains a caustic and a selectivity promoter that react with oxidized heteroatoms to remove sulfur, nickel, vanadium, iron and other contaminants or heteroatoms, increase API gravity, decrease viscosity, and decreases total acid number.

[0067] "Residue" or residual refers to a hydrocarbon that has a boiling range distribution above 538° C. (1000° F.), as determined by ASTM Method D5307, ASTM Method D7169, or an equivalent method thereof. The residual portion of a hydrocarbon mixture of a hydrocarbon product may include coke, asphalt, tar and waxes. The hydrocarbon fraction may include multi-ringed structures having a carbon chain of approximately 70 or more carbon atoms per molecule. In some embodiments, residual portion of a hydrocarbon mixture may have a boiling point greater than 538°C, greater than 600°C, greater than 700°C, greater than 800°C, greater than 1000°C, greater than 1200°C, greater than 1500°C, and/or greater than 1800°C.

[0068] "Sulfoxidation" may refer to a reaction or conversion, whether or not catalytic, that produces organo-sulfoxide, organo-sulfone, organo-sulfonate, or organo-sulfonic acid compounds (and/or mixtures thereof) from organosulfur compounds.

[0069] "TAN" refers to a total acid number expressed as milligrams ("mg") of KOH per gram ("g") of sample. TAN may be determined by ASTM Method D664 or an equivalent method thereof. The TAN is a measurement of acidity that is determined by the amount of potassium hydroxide in milligrams that is needed to neutralize the acids in one gram of oil. It is an important quality measurement of crude oil. The TAN value indicates to the crude oil refinery the potential of corrosion problems. It is usually the naphthenic acids in the crude oil that causes corrosion problems. Methods for determining the TAN value may include titrating acidic constituents of hydrocarbons, and other petroleum products such as oxidation products. The acid number may be the measure of the amount of amount of an acidic substance in a hydrocarbon or hydrocarbon product. In one method for evaluating the TAN, the hydrocarbon products may be soluble or nearly soluble in mixtures of toluene and propan-2-ol. This method may be applicable for the determination of acids whose dissociation constants in water are larger than 10^{-9} . In this embodiment, salts may react if their hydrolysis constants are larger than 10^{-9} . The range of acid numbers of hydrocarbons and hydrocarbon products may range between 0.1 mg/g KOH to 150 mg/g KOH. Methods for calculating TAN may be used to indicate relative changes that occur in oil during use under oxidizing conditions regardless of the color or other properties of the resulting oil.

[0070] "Total base number (TBN)" is a measure of a petroleum product's reserve alkalinity. It is measured in milligrams of potassium hydroxide per gram (mg KOH/g). TBN determines how effective the control of acids formed will be during the combustion process. The higher the TBN, the more

effective it is in suspending wear-causing contaminants and reducing the corrosive effects of acids and acidic byproducts over an extended period of time. TBN may be determined using ASTM D2896 or an equivalent method thereof. Embodiments of methods for calculating TBN may make a determination of basic constituents in hydrocarbon products by titration with perchloric acid in glacial acetic acid. The constituents that may be considered to have basic characteristics include organic and inorganic bases, amino compounds, salts of weak acids (soaps), basic salts of polyacidic bases, and salts of heavy metals. In some methods of embodiments for determining TBN, embodiments of hydrocarbon and hydrocarbon products may be calculated to have a base number greater than 300mg KOH/g in some embodiments.

[0071] "Used catalyst" or "spent catalyst" refers to one or more catalysts that have been contacted with a hydrocarbon feed. In some embodiments, a used catalyst may be regenerated and re-contacted with the hydrocarbon feed.

[0072] "VGO" refers to hydrocarbons with a boiling range distribution between 343° C. (650° F.) and 538° C. (1000° F.) at 0.101 MPa. VGO content may be determined by ASTM Method D5307, ASTM Method D7169 or equivalent method thereof.

[0073] "Viscosity" refers to kinematic viscosity at 37.8° C. (100°F.), unless otherwise indicated. Viscosity may be determined using ASTM Methods D445, D2170, D2171 or equivalent methods thereof. Method for determining kinematic viscosity, ν , of liquid hydrocarbon products, which may be transparent or opaque, may be performed by measuring the time it takes for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. In some methods, the dynamic viscosity η may be calculated by multiplying the kinematic viscosity, ν , by the density ρ of the liquid hydrocarbon product. The value of a kinematic viscosity may range from approximately 0.2mm²/s to 300000 mm²/s. To calculate dynamic viscosity, the SI unit used may be mPa·s, wherein 1 mm²/s = 10⁻⁶ m²/s = 1 cSt and 1 mPa·s = 1 cP = 0.001 Pa·s. Crudes may be produced and/or retorted from hydrocarbon containing formations. Crudes may generally be a solid, semi-solid, and/or liquid. Crudes may include crude oil. A crude oil may be further stabilized. Stabilization of crudes may include the removal of non-condensable gases, water, salts, or combinations thereof from the crude. The resulting crude post-stabilization may be referred to as stabilized crude. Stabilization may occur at, or proximate to, the crude production site and/or at the site of retorting.

[0074] Stabilized crudes may or may not have been distilled and/or fractionally distilled in a treatment facility to produce multiple components with specific boiling range distributions (for example, naphtha, distillates, VGO, and/or lubricating oils). Distillation includes, but is not limited to, atmospheric distillation methods and/or vacuum distillation methods. Undistilled and/or unfractionated stabilized crudes may include components that have a carbon number above 4 in quantities of at least 0.5 grams of components per gram of crude. Examples of stabilized crudes include whole crudes, topped crudes, desalted crudes, desalted topped crudes, or combinations thereof. "Topped" refers to a crude that has been treated such that at least some of the components having a boiling point below 35° C. at 0.101 MPa (95° F. at 1 atm) have been removed. Typically, topped crudes will have a content of at most 0.1 grams, at most 0.05 grams, or at most 0.02 grams of such components per gram of the topped crude.

[0075] Some crudes may have one or more unsuitable properties that render the crudes disadvantaged. The properties of a disadvantaged crude may include a TAN of at least 0.1, at least 0.3, at least 0.5, at least 1.0 or at least 2.0; a viscosity of at least 10 centistokes (cSt); API gravity of at most 19, at most 15 or at most 10; a total heteroatom content of at least 0.005 grams of heteroatom per gram of crude; a residue content of at least 0.01 grams of residue per gram of crude; a content of metals in metal salts of organic acids of at least 0.0001 grams of metals per gram of crude; or a combination of properties thereof. In some embodiments the disadvantaged crude may also have an oxygen content of at least 0.005 grams of oxygen per gram of disadvantaged crude or a C₇ asphaltene content of at least 0.04 grams of C₇ per gram of the disadvantaged crude.

[0076] Embodiments of a disadvantaged crude may include at least 0.2 grams of residue, at least 0.3 grams of residue, at least 0.5 grams of residue, or at least 0.9 grams of residue per gram of disadvantaged crude. Embodiments of a disadvantaged crude may have a TAN in the range from 0.1 to 20, while in alternative embodiments, the TAN may range from 0.3 to 10 or 0.4 to 5. Disadvantaged crudes may also include a sulfur content of at least 0.005 grams per gram of disadvantaged crude.

[0077] Disadvantaged crudes may include at least 0.001 grams of hydrocarbons per grams of disadvantaged crudes having a boiling range distribution between 95° C and 200° C at 0.101 MPa; at least 0.001 grams of hydrocarbons per gram of disadvantaged crude with a boiling range distribution between 200° C. and 300° C at 0.101 MPa; at least 0.001 grams hydrocarbons per gram of crude with a boiling range distribution between 300° C and 400° C at 0.101 MPa; and at least 0.001 grams of hydrocarbons per gram of disadvantaged crude with a boiling range distribution between 400° C and 650° C at 0.101 MPa.

[0078] Examples of locations that may have disadvantaged crudes that might be treated using the processes described herein include, but are not limited to, crudes from the U.S. Gulf Coast and southern California, Canadian Oil sands, Brazil's Santos and Campos basins, Egyptian Gulf of Suez, Chad, United Kingdom North Sea, Angola Offshore, Chinese Bohai Bay, Venezuelan Zulia, Malaysia, and Indonesia Sumatra. Treatment of disadvantaged crudes using oxidative desulfurization and heteroatom removal may enhance the properties of the hydrocarbons present in crudes or disadvantaged crudes. The resulting hydrocarbon products from the methods described herein may make the crude products or disadvantaged crudes products easier and economically more viable to transport and or treat.

[0079] Referring to Fig. 1a, depicting an embodiment 100 of a system and method of oxidative desulfurization 100 of a hydrocarbon feed 101, hydrocarbon feed 101 may also be referred to as a heteroatom-containing hydrocarbon feed, or a contaminated hydrocarbon stream. Embodiments of the hydrocarbon feed 101 may include any element in addition to the carbon and hydrogen of the hydrocarbon. Heteroatoms contaminating the hydrocarbon feed may include, but is not limited to compounds containing sulfur, oxygen, nitrogen, nickel, vanadium, iron or other transition metals and combinations of compounds thereof. The heteroatom containing hydrocarbon feed may contain at least 15 weight parts per million (wppm) vanadium and at least 5 wppm nickel. The heteroatom containing hydrocarbon feed may also contain at least 0.20 Wt. % sulfur, or at least 2 Wt. % sulfur, or at least 4 Wt.

% sulfur; and the hydrocarbon-containing feedstock may contain at least 0.01 Wt. % nitrogen, or at least 0.4 Wt. % nitrogen.

[0080] In some embodiments, the content of the hydrocarbon feed may be characterized by infrared spectroscopy. Embodiments of a hydrocarbon feed tested using IR spectroscopy may exhibit one or more characteristics at a specific wavelength or wavenumber in comparison with a reference peak. Referring to embodiments depicted in Fig. 7a, the hydrocarbon feed reference peak was exhibited between approximately 1445cm^{-1} and 1465cm^{-1} . The reference peak may vary depending on the content of the hydrocarbon feed. In some embodiments, the hydrocarbon feed may exhibit an absorbance between 1310cm^{-1} and 1285cm^{-1} that is at most approximately 28% of the height of the reference peak. In alternative embodiments, the absorbance between 1310cm^{-1} and 1285cm^{-1} may be at most 25%, at most 20%, at most 15%, at most 10% or at most 5% of the peak of the reference peak.

[0081] Embodiments of the hydrocarbon feed may also exhibit specific characteristics under IR spectroscopy between the wavelengths or wavenumbers of approximately 1135cm^{-1} and 1110cm^{-1} . For example, the embodiments of the hydrocarbon feed may exhibit an absorbance peak between the wavelengths or wavenumbers of 1135cm^{-1} and 1110cm^{-1} that may be at most approximately 22% of the height of the reference peak. In alternative embodiments, the hydrocarbon feed 101 may exhibit a peak that is at approximately most 20%, at most 15%, at most 10% or at most 5% of the height of the reference peak.

[0082] Some embodiments of the hydrocarbon feed may also exhibit specific characteristics under IR spectroscopy between the wavelengths or wavenumbers of approximately 1040cm^{-1} and 1000cm^{-1} . For example, the embodiments of the hydrocarbon feed may exhibit an absorbance peak between the wavelengths or wavenumbers of 1040cm^{-1} and 1000cm^{-1} that may be at most approximately 22% of the height of the reference peak. In alternative embodiments, the hydrocarbon feed 101 may exhibit an IR absorbance peak that is at most approximately 20%, at most 15%, at most 10% or at most 5% of the height of the reference peak.

[0083] Referring again to Fig. 1a, the heteroatom-containing hydrocarbon feed 101 may be combined with an oxidant 104 and subjected to an oxidation reaction in a heteroatom oxidizer 102 or an oxidizer vessel.

[0084] Embodiments of the oxidation step may be carried out using at least one oxidant, optionally in the presence of a catalyst. Suitable oxidants 104 may include organic peroxides, hydroperoxides, hydrogen peroxide, O_2 , air, O_3 , peracetic acid, organic hydroperoxides may include benzyl hydroperoxide, ethylbenzene hydroperoxide, tert-butyl hydroperoxide, cumyl hydroperoxide and mixtures thereof, other suitable oxidants may include sodium hypochlorite, permanganate, biphasic hydrogen peroxide with formic acid, nitrogen containing oxides (e.g. nitrous oxide), and mixtures thereof, with or without additional inert organic solvents.

[0085] In an alternative embodiment, the step of oxidation may further include an acid treatment including at least one immiscible acid. The immiscible acid and oxidant treatment may remove a portion of the heteroatom contaminants from the feed, wherein upon being oxidized by the immiscible

acid and oxidant, the heteroatoms may become soluble in the acid phase, and be subsequently removed via a heteroatom containing by-product stream. The immiscible acid used may be any acid which is insoluble in the hydrocarbon oil phase. Suitable immiscible acids may include, but are not limited to, carboxylic acids, sulfuric acid, hydrochloric acid, and mixtures thereof, with or without varying amounts of water as a diluent. Suitable carboxylic acids may include, but are not limited to, formic acid, acetic acid, propionic acid, butyric acid, lactic acid, benzoic acid, and the like, and mixtures thereof, with or without varying amounts of water as a diluent.

[0086] In some embodiments, the oxidation reaction(s) may be carried out at a temperature of approximately 20°C to about 120°C, at a pressure of about 0.1 atmospheres to about 10 atmospheres, with a contact time of about 2 minutes to about 180 minutes.

[0087] A catalyst may be used in the presence of the oxidant 104. A suitable catalyst may include transition metals including but not limited to Ti(IV), V(V), Mo(VI), W(VI), transition metal oxides, including ZnO, Al₂O₃, CuO, layered double hydroxides such as ZnAl₂O₄·x(ZnO)_y(Al₂O₃), organometallic complexes such as Cu_xZn_{1-x} Al₂O₄, zeolite, Na₂WO₄, transition metal aluminates, metal alkoxides, such as those represented by the formula M_mO_m(OR)_n, and polymeric formulations thereof, where M is a transition metal such as, for example, titanium, rhenium, tungsten, copper, iron, zinc or other transition metals, R may be a carbon group having at least 3 carbon atoms, where at each occurrence R may individually be a substituted alkyl group containing at least one OH group, a substituted cycloalkyl group containing at least one OH group, a substituted cycloalkylalkyl group containing at least one OH group, a substituted heterocyclyl group containing at least one OH group, or a heterocyclylalkyl containing at least one OH group. The subscripts m and n may each independently be integers between about 1 and about 8. In some embodiments, R may be substituted with halogens such as F, Cl, Br, and I. For example, embodiments of the metal alkoxide catalyst may include bis(glycerol)oxotitanium(IV)), wherein M is Ti, m is 1, n is 2, and R is a glycerol group. Other examples of metal alkoxides include bis(ethyleneglycol)oxotitanium (IV), bis(erythritol)oxotitanium (IV), bis(sorbitol)oxotitanium (IV).

[0088] The sulfoxidation catalyst may further be bound to a support surface. The support surface may include an organic polymer or an inorganic oxide. Suitable inorganic oxides include, but are not limited to, oxides of elements of groups IB, II-A, II-B, III-A, III-B, IV-A, IV-B, V-A, V-B, VI-B, of the Periodic Table of the Elements. Examples of oxides that may be used as a support include copper oxides, silicon dioxide, aluminum oxide, and/or mixed oxides of copper, silicon and aluminum. Other suitable inorganic oxides which may be used alone or in combination with the abovementioned oxide supports may be, for example, MgO, ZrO₂, TiO₂, CaO and/or mixtures thereof. Other supports may include talc.

[0089] The support materials used may have a specific surface area in the range from 10 to 1000 m²/g, a pore volume in the range from 0.1 to 5 ml/g and a mean particle size of from 0.1 to 10 cm. Preference may be given to supports having a specific surface area in the range from 0.5 to 500 m²/g, a pore volume in the range from 0.5 to 3.5 ml/g and a mean particle size in the range from 0.5 to 3 cm.

Particular preference may be given to supports having a specific surface area in the range from 200 to 400 m²/g, and a pore volume in the range from 0.8 to 3.0 ml/g.

[0090] Referring still to Fig. 1a, after subjecting a hydrocarbon stream to oxidation conditions in the heteroatom oxidizer vessel 102, an intermediate stream 106 may be generated. A hydrocarbon feed 101 containing, for example sulfur-based heteroatom contaminants such as thiophenes, benzothiophenes, dibenzothiophenes and thioethers and others may be converted to a sulfone or sulfoxide rich intermediate stream 106. The intermediate hydrocarbon stream 106 may include oxidized heteroatom containing compounds and oxidant by-products. In some embodiments, the intermediate stream 106 may be subjected to distillation 107, for example in a distillation column. During distillation 107, the oxidized heteroatom containing compounds, may be separated from the oxidant by-products 109. The oxidant by-products may be recovered and recycled. As a result of the distillation 107, an oxidized hydrocarbon intermediate stream 111 may be formed including oxidized heteroatom compounds such as sulfones and sulfoxide rich hydrocarbons. The oxidized hydrocarbon intermediate stream 111 may also be referred to as a sulfoxidized intermediate hydrocarbon product. The sulfone and sulfoxide rich, sulfoxidized intermediate hydrocarbon product 111 may be sent to a reactor vessel 108 such as oil/caustic reactor vessel or promoted caustic visbreaker 108. In some embodiments, the reactor vessel 108 may be a sulfone management unit. Once inside the reactor vessel 108, the heteroatom rich stream 111, which may include sulfones and/or sulfoxides, may be subsequently reacted with a caustic treatment solution 110 in an alcoholysis reaction, under biphasic conditions to produce a hydrocarbon product and sulfate salts. The caustic treatment solution may comprise caustic, a selectivity promoter and/or a caustic selectivity promoter. Fig. 4 and Fig. 5 describe an embodiment of a reaction mechanism for producing a hydrocarbon product 120 and a sulfate salts 1040 under biphasic conditions 1000, 1010. In Fig. 4, the initial reaction may be a hydroxyl attack on the C-S bond of the sulfur containing compound present in the sulfone/sulfoxide rich oxidized heteroatom containing stream, such as in a dibenzothiophene sulfone depicted in Fig. 4. As a result of the hydroxyl attack, a hydrocarbon containing a sulfonate group may form as a reaction intermediate. Without being bound to any particular theory, Fig. 5 provides one possible explanation for the reaction mechanism.

[0091] Referring to Fig. 5, under the biphasic conditions of the oil/caustic reactor vessel or promoted caustic visbreaker 108, one of the phases may be a polar phase 1010 such as an organic alcohol, other selectivity promoter or phase transfer agent. The other phase may be a non-polar phase 1000, which may include non-polar oil or hydrocarbon rich molecules. The boundary between the two phases is delineated by a phase boundary 1020. The phase boundary may further be a liquid-solid phase boundary. The intermediate sulfonate 1030, may align its polar sulfonate group into the more preferable polar phase 1010 while the aromatic hydrocarbon portion of the intermediate 1030 prefers the non-polar phase 1000. Subsequently, a hydroxyl group or other nucleophile present in the polar phase may perform a nucleophilic attack on the Sulfur of the sulfonate group. As a result of the nucleophilic attack, the sulfonate portion may form a sulfate 1040, a good leaving group. The sulfate 1040 may remain in the polar phase 1010 and the hydrocarbon left behind may remain in the non-polar phase of an intermediate

stream 114. The separate phases allow for the hydrocarbon products 120 of the non-polar phase to be removed and separated from the heteroatom containing byproducts 116 such as sulfates in separating vessel 115. Without being bound to any particular mechanism, referring again to figure 5, another possible mechanism may involve the conversion of the starting sulfone to a sulfinate salt 1130, which may also be aligned at a phase boundary 1020, between non-polar phase 1000 and polar phase 1010. This may be followed by hydrolysis of the sulfinate salt to form a bisulfite salt 1140 and a hydrocarbon product.

[0092] In some instances, undesired side reactions may occur. Referring to Fig. 2, it can be seen that in situations wherein the sulfonate intermediate B may be attacked by the hydroxyl nucleophile in the polar phase, the hydroxyl may perform a carbon selective attack on the carbon, forming the C-O bond instead of forming an S-O bond. In that instance, reaction (2) may occur resulting in phenolic hydrocarbon products and a sulfite, instead of the formation of the biphenyl and sulfate depicted by reaction (3). Other oxide salts of sulfur may also be present (e.g. thiosulfate, thiosulfite, etc).

[0093] Referring again to Fig. 1a, in some embodiments, the reactor vessel 108 such as the oil/caustic reactor vessel or promoted caustic visbreaker may be heated to an elevated temperature between 100°C and 500°C with a pressure between 0 and 1000psi. Suitable caustic compounds 110 that may be used for the alcoholysis reaction may be compounds which may exhibit basic properties. Caustic compounds may include inorganic oxides having group IA and IIA metals, inorganic hydroxides including group IA and IIA elements, alkali metal sulfides, alkali earth metal sulfides, mixtures and molten mixtures thereof. Non-limiting examples include, but are not limited to, Li_2O , Na_2O , K_2O , Rb_2O , Cs_2O , Fr_2O , BeO , MgO , CaO , SrO , BaO , Na_2S , K_2S , LiOH , NaOH , KOH , RbOH , CsOH , FrOH , $\text{Be}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Sr}(\text{OH})_2$, $\text{Ba}(\text{OH})_2$.

[0094] Caustic compounds may also include carbonate salts, such as alkali metal carbonates and alkali earth metal carbonates including Na_2CO_3 , K_2CO_3 , CaCO_3 , MgCO_3 and BaCO_3 ; phosphate salts, including alkali metal phosphates, such as sodium pyrophosphate, potassium pyrophosphate, sodium tripolyphosphate and potassium tripolyphosphate; and alkali earth metal phosphates, such as calcium pyrophosphate, magnesium pyrophosphate, barium pyrophosphate, calcium tripolyphosphate, magnesium tripolyphosphate and barium tripolyphosphate; silicate salts, such as, alkali metal silicates, such as sodium silicate and potassium silicate, and alkali earth metal silicates, such as calcium silicate, magnesium silicate and barium silicate, organic alkali compounds expressed by the general formula: $\text{R-E}^n\text{M}^m\text{Q}^{m-1}$, where R is hydrogen or an organic compound (which may be further substituted) including, but not limited to, straight, branched and cyclic alkyl groups; straight, branched and cyclic alkenyl groups; and aromatic or polycyclic aromatic groups. Further substituents where R is an organic may include hydroxide groups, carbonyl groups, aldehyde groups, ether groups, carboxylic acid and carboxylate groups, phenol or phenolate groups, alkoxide groups, amine groups, imine groups, cyano groups, thiol or thiolate groups, thioether groups, disulfide groups, sulfate groups, and phosphate groups. E^n represents an atom with a negative charge (where $n = -1, -2, -3, -4$ etc.) such as oxygen, sulfur, selenium, tellurium, nitrogen, phosphorus, and carbon; and M^m is any cation ($m = +1, +2, +3, +4$ etc.),

such as a metal ion, including, but not limited to, alkali metals, such as Li, Na, and K, alkali earth metals, such as Mg and Ca, and transition metals, such as Zn, and Cu. When $m > +1$, Q may be the same as E^n-R or an atom with a negative charge such as Br-, Cl-, I-, or an anionic group that supports the charge balance of the cation M^m including but not limited to, hydroxide, cyanide, cyanate, and carboxylates.

[0095] In one embodiment of the present invention, the caustic may also be in the molten phase. Molten phase caustics may include previously mentioned caustics as well as eutectic mixtures thereof of two or more caustics. The eutectic mixtures of molten caustics may have a melting point less than 350°C, such as, for example, a 51 mole % NaOH / 49 mole % KOH eutectic mixture which may melt at about 170°C.

[0096] Referring still to Fig. 1a, a selectivity promoter may be introduced to the reactor vessel as part of the caustic treatment solution 110. The selectivity promoter may be any compound capable of being used in the alcoholysis reaction between the caustic and an oxidized heteroatom containing hydrocarbon to generate biphasic conditions that may promote the formation of non-oxygenated hydrocarbon products 120 and sulfate salts. In some embodiments, the selectivity promoter may also be referred to as a phase transfer agent. Examples of heteroatom products may include non-oxygenated hydrocarbon products 120 including, but not limited to, unsubstituted biphenyl compounds, and aromatic hydrocarbons shown in Fig. 3. The alcoholysis reaction examples provided in Fig. 3, disclose multiple embodiments wherein a caustic mixture of NaOH and KOH may be used with an Na_2S desulfonation catalyst nucleophile and ethylene glycol selectivity promoter. In the exemplary embodiment, the reaction may take place over 60 minutes at a pressure of 300psi, at a temperature of approximately 275°C. In other embodiments, other hydrocarbon distillates and fractions that are non-oxygenated, may include, but not limited to, non-oxygenated crude oils or crude oil derived products such as gasolines, naphthas, paraffins, olefins, asphaltenes/bitumens, diesel and gas oils. The non-oxygenated products may depend on the carbon groups of the heteroatom containing compounds present.

[0097] Fig. 2 further illustrates how the selectivity promoter and the biphasic conditions may improve the alcoholysis reaction to form more valuable products. Dibenzothiophene sulfone was chosen as an exemplary sulfur compound because most of the challenging sulfur to treat in diesel fuel is in the form of substituted or unsubstituted dibenzothiophene. Equation (1) illustrates how hydroxide attacks the sulfur atom of dibenzothiophene sulfone (A), forming biphenyl-2-sulfonate (B). Equation (2) illustrates how hydroxide may attack (B) at the carbon atom adjacent to the sulfur atom, forming biphenyl-2-ol (C) and sulfite salts (D). Compound C may ionize in basic media, and may dissolve in the aqueous or molten salt layer. Equation (3) illustrates how hydroxide may attack the sulfur atom of (B) to form biphenyl (E) and sulfate salts (F). Equation (4) illustrates how, in the presence of a primary alcohol, including, but not limited to, methanol, methoxide ions generated in-situ may attack the carbon atom, forming ether compounds, such as 2-methoxybiphenyl (G). Equation (5) illustrates the reaction of dibenzothiophene sulfone with alkoxides alone, not in the presence of hydroxide to form biphenyl-2-methoxy-2'-sulfinate salt (H), which may be substantially soluble in the polar caustic phase.

[0098] Using aqueous or molten caustic without the presently disclosed selectivity promoter may cause reaction (1) to occur, followed predominantly by reaction (2). When a selectivity promoter disclosed herein is used, reaction (1) occurs, followed predominantly by reaction (3). Without being confined to any particular theory, it is believed that the biphasic conditions may assist in promoting the selective nucleophilic attack at the Sulfur. When the selectivity promoter (such as an alcohol) disclosed herein is used, reaction (1) occurs, followed predominantly by reaction (3) under biphasic conditions. It can be seen that the hydrogen atoms that become attached to biphenyl may come from hydroxide. When water is used in the regeneration of the caustic, the ultimate source of the hydrogen atoms added to the biphenyl may be water.

[0099] In some embodiments, the selectivity promoter may be referred to by other names including polar protic solvent, desulfonylation catalyst or phase transfer catalyst. Compounds suitable for promoting substantially non-oxygenated hydrocarbon reaction products may include organic alcohols, morpholine, dioxane, dimethylethanolamine, methyldiethanolamine, mono ethanolamine, diethanolamine, triethanolamine, crown ethers (18-crown-6, 15-crown-5), piperazine, choline hydroxide, benzyltrimethylammonium hydroxide, ethylene glycol, propylene glycol, glycerin, sugars, starches, cellulose, diethylene glycol, triethylene glycol, polyethylene glycol, sulfides, hydrosulfides, polysulfides, hydroxide, cyanide, ammonia, anionic amides, halides, acetates, naphthenates, alkoxides, selenides, hydroselenides, tellurides, hydrotellurides, carboranes, phosphorous oxyanions, nitrogen oxyanions, aluminates, borates, carbonates, chromates, silicates, vanadates and titanates. Embodiments may include introducing an excess molar ratio of selectivity promoters to caustic cations for increased conversion and selectivity.

[0100] Referring again to Figure 1a., in one embodiment the caustic treatment solution 110 may include at least one caustic and the at least one selectivity promoter. The at least one caustic and at least one selectivity promoters may be different components. In another embodiment, the at least one caustic and the at least one selectivity promoter may be the same component. When the at least one caustic and the at least one selectivity promoter are the same component they may be referred to as a caustic selectivity promoter. Moreover, a suitable caustic selectivity promoter may possess the properties of both the at least one caustic and the at least one selectivity promoter. That is, combinations of caustics with selectivity promoters may react (*in situ* or *a priori*) to form a caustic selectivity promoter which has the properties of both a caustic and a selectivity promoter.

[0101] The molar ratio of caustic to selectivity promoter in the caustic treatment solution 110 may be in the range of from about 100:1 to about 1:100. In some embodiments, the mole ratio of caustic to selectivity promoter is in the range of from about 70:1 – 1:70, 50:1 – 1:50, 25:1 – 1:25, 1:10, 10:1, 1-5 – 5:1, 3:1 to about 1:3 or from about 2:1 to about 1:2.

[0102] Generally, the molar ratio of caustic and selectivity promoter to heteroatom in the heteroatom-containing hydrocarbon feed oil 111 may be in the range of from about 100:1 to about 1:1. In some embodiments, the molar ratio of caustic and selectivity promoter to heteroatom in the heteroatom-containing hydrocarbon feed oil may be in the range of about 10:1 to about 1:1, and in alternative

embodiments, the molar ratio of caustic and selectivity promoter to heteroatom in the heteroatom-containing hydrocarbon feed oil may be from about 3:1 to about 1:1.

[00103] Referring still to embodiment 100 in Fig. 1a, the phases resulting from the contact of the caustic treatment solution 110 with the oxidized heteroatom feed 111, may be separated into a light phase containing the hydrocarbon products 120 and a dense phase consisting of the caustic containing byproducts. The intermediate 114 comprises a biphasic, caustic treated hydrocarbon intermediate stream that may be transferred to a separating vessel 115, such as a gravity settler in some embodiments to separate the hydrocarbon products 120 from the caustic by-products 116. The hydrocarbon products 120 may be further washed, refined or utilized for gas, oil, fuel, lubricants or other hydrocarbon based products and further treated using known refinery processes. Separation of the heavy caustic phase from the light oil phase may be performed using gravity or other suitable separation methods. The hydrocarbon product 120 may further be washed to remove traces of by-product 116 with known methods including, but not limited to, solvent extraction or by washing with water, centrifugation, distillation, vortex separation, and membrane separation and/or combinations thereof. Trace quantities of caustic and selectivity promoter may be removed using electrostatic desalting and dewater techniques according to known methods by those skilled in the art.

[00104] Referring to alternative embodiment 200 in Fig. 1b, the hydrocarbon feed 211 may already be rich in sulfones or sulfoxides without having to oxidize the hydrocarbon feed or the hydrocarbon feed may be pre-oxidized using other known methods in the art. The hydrocarbon feed 211 may have properties similar to the sulfone or sulfoxide rich intermediate stream 111 shown in Fig. 1a. In this alternative embodiment, the steps of oxidation 102 may not be needed. Instead, the sulfone or sulfoxide rich oil may be sent directly from the source of the hydrocarbon feed 211 into the oil/caustic reactor vessel 108. From the reactor vessel 108, a caustic treatment solution 110 may be provided into reactor 108 to form a biphasic mixture 114 of substantially non-oxygenated hydrocarbon products 120 and caustic byproducts 116. The hydrocarbon products 120 may settle in the light phase, while the denser phase may contain caustic byproducts. The mixture 114 may be separated in a settler vessel 115 or other vessel capable of separating the light phase from the dense phase. Once separated, the hydrocarbon products 120 may be used directly or transported, refined or fractionally distilled into one or more distillate fractions. The distillate fractions may be further processed to produce hydrocarbon products such as gasoline, fuel oil, heating oil, lubricants or other hydrocarbon based products.

[00105] The hydrocarbon product 120 may be a liquid at standard temperature and pressure (STP). In some embodiments, the resulting hydrocarbon product 120 may be a crude product wherein the crude product is a liquid mixture at approximately 25°C and 0.101 MPa. In some embodiments the hydrocarbon product 120 may have a TAN of at most 90% of the TAN of the hydrocarbon feed 101. In other embodiments, the TAN of the hydrocarbon product 120 may have a TAN of at most 80%, at most 60%, at most 50%, at most 40%, at most 30% at most 20% or at most 10% of the hydrocarbon feed. In certain embodiments, the hydrocarbon products may have a TAN of at most 1, while in other embodiments, the TAN may range from at most 0.5, at most 0.3, at most 0.2 or at most 0.1 mg of KOH

equivalent per gram of oil. Embodiments of the hydrocarbon product 120 may have a TAN that ranges. For example, the hydrocarbon may have a TAN ranging from 0.001 to 0.5, 0.004 to 0.4 or from 0.01 to 0.2. In certain embodiments, the hydrocarbon products may have a TAN measuring less than 0.5mg KOH equivalent per gram of the hydrocarbon product.

[00106] In some embodiments, the hydrocarbon product 120 may include a content of trace metallic heteroatoms such as Ni, V and Fe wherein the content of the metallic heteroatoms may be at most 90% of the metallic heteroatom content of the hydrocarbon feed. In other embodiments, the metallic heteroatom content may be at most 80%, at most 70%, at most 60%, at most 50%, at most 30%, at most 10%, or at most 5% of the metallic heteroatom content of the hydrocarbon feed 101. In certain embodiments, the hydrocarbon product 120 may have a metallic heteroatom content per gram of hydrocarbon product ranging from 1×10^{-7} g to 5×10^{-4} g or approximately 0.1ppm to approximately 50ppm.

[00107] In some embodiments, the crude product may have a total content of metals in metal salts of organic acids of at most 90% of the total content of metals in metal salts in organic acids of the hydrocarbon feed. In other embodiments, the content of metals in metal salts of organic acids may range from at most 50% to at most 5% of the content found in the hydrocarbon feed. Organic acids that may form metal salts may include carboxylic acids such as naphthenic acids, phenanthrenic acids and benzoic acid. Other organic acids that might form metal salts may include thiols, imides, sulfonic acids and sulfonates. Metals that may form metal salts in organic acids may include alkali metals, alkali earth metals, and transition metals from groups 3-12 of the periodic table including Ti, Zr, Zn, Cu, Ni and cadmium. Other metals that may form metal salts may include metalloids (also called semi-metals) found in group 13-16 of the periodic table include for example aluminum, arsenic, boron and selenium. In one or more embodiments, the hydrocarbon product 120 may have a total content of metals in metal salts of organic acids, in the range from 0.0000001g to 0.0005g per gram of hydrocarbon product.

[00108] In certain embodiments, the API gravity of the hydrocarbon product 120 produced from the caustic treatment may be between 10 and 30. In other embodiments, the API gravity of the hydrocarbon product may be increased by at least 3 units over the API gravity of the hydrocarbon feed 101, at least 10 units over the API gravity of the hydrocarbon feed or at least 15 units over the API gravity of the hydrocarbon feed 101. In yet another embodiment, the API gravity of the hydrocarbon product may be at least 12, at least 15, at least 20 or at least 25.

[00109] Embodiments of the hydrocarbon products 120 may have a viscosity less than the viscosity of the hydrocarbon feed. For example, in some embodiments, the viscosity may be at most 90% of the viscosity of the hydrocarbon feed 101. In other embodiments, the viscosity of the hydrocarbon product may be at most 80% or at most 70% of the hydrocarbon feed. Embodiments of the hydrocarbon product 120 may also have a total heteroatom content that is at most 90% of the total heteroatom content of the hydrocarbon feed. In certain embodiments, the hydrocarbon products may contain at most 50%, at most 10% or at most 5% of the heteroatom content of the hydrocarbon feed 101. In some embodiments, the viscosity of the hydrocarbon composition may be measured by a stabinger viscometer.

[00110] Embodiments of the hydrocarbon product 120 may have a sulfur content that may be at most 95% of the hydrocarbon feed. In other embodiments, the sulfur content may be at most 50%, at most 10% or at most 5% of the sulfur content of the hydrocarbon feed. In one or more embodiments, the sulfur content of the hydrocarbon product 120 may be less than approximately 4.0wt% of the hydrocarbon product. The wt% of the sulfur content may be measured by ASTM D4294 or equivalent methods. Methods for measuring the wt% of sulfur content may provide a rapid and precise measurement of total sulfur in the hydrocarbon feed or hydrocarbon product and it may be performed in an analysis time between 1 to 5 minutes per sample. Methods for identifying the total sulfur may be applied to hydrocarbons, including diesel, jet fuel, kerosene, distillates, naphtha, residues, lubricating oil, crude oil, gasoline, gasohol and biodiesel, wherein the hydrocarbons may be liquid at an ambient condition, liquefiable with moderate heat, or soluble in hydrocarbon solvents. Methods identifying sulfur content may further be applied to oxygenated fuels with high oxygen content (>3%) by diluting the samples. In some embodiments, the method may be performed on hydrocarbon or hydrocarbon product samples having 17 mg/kg to 4.6 mass % sulfur present. Embodiments of the method for determining sulfur content may have a pooled limit of quantitation (PLOQ) is 16.0 mg/kg as calculated in accordance with ASTM D6259 or an equivalent method. In some embodiments, samples of the hydrocarbon feed or hydrocarbon product containing a mass % of sulfur greater than 4.6 mass % may be diluted to less than 4.6 mass %.

[00111] In some embodiments the hydrocarbon products may contain per gram of hydrocarbon product, at least 0.0005 gram of sulfur or at least 0.001 gram of sulfur. The sulfur content of the hydrocarbon composition may be determined in accordance with ASTM Method D4294. A substantial portion of the sulfur in the hydrocarbon composition may be contained in hydrocarbons having a carbon number of 17 or less, Where at least 40 Wt. %, or at least 50 Wt. %, or at least 60 Wt. %, or at least 70 Wt. % of the sulfur may be contained in hydrocarbons having a carbon number of 17 or less, Where at least 60 Wt. %, or at least 70 Wt. %, or at least 75 Wt. % of the sulfur contained in hydrocarbons having a carbon number of 17 or less may be contained in benzothiophenic compounds. The amount of sulfur in hydrocarbons having a carbon number of 17 or less and the amount of sulfur in benzothiophenic compounds in the hydrocarbon composition relative to all sulfur containing compounds in the hydrocarbon composition may be determined by two dimensional gas chromatography (GCxGC-SCD).

[00112] In some embodiments, the total of the hydrocarbon product 120 may be at most 90% of the hydrocarbon feed. In other embodiments, the nitrogen content may be at most 50%, at most 10% or at most 5% of the nitrogen content of the hydrocarbon feed 101. In one or more embodiments, the nitrogen content of the hydrocarbon product 120 may be less than approximately 0.2 wt% of the hydrocarbon product. The wt% of nitrogen content may be measured by ASTM D5291 or equivalent methods. Embodiments of the method for measuring the total nitrogen content may be performed on a hydrocarbon feed or hydrocarbon product having a concentration of approximately <0.1 to 2 mass % nitrogen.

[00113] In some embodiments, the nitrogen content may contain, per gram of hydrocarbon product, at least 0.0005 gram or at least 0.001 gram of nitrogen as determined in accordance with ASTM Method D5762. Embodiments of hydrocarbons and hydrocarbon products may be tested and

demonstrated to include a nitrogen concentration per gram of liquid hydrocarbon. In some embodiments, the nitrogen content of hydrocarbon streams or feeds and hydrocarbon products may be in the concentration range of 40 to 10,000 $\mu\text{g/g}$ nitrogen. The hydrocarbon product may have a relatively low ratio of basic nitrogen compounds to other nitrogen containing compounds. In some embodiments, at least 30 Wt. % of the nitrogen is contained in hydrocarbon compounds having a carbon number of 17 or less, and at least 35 Wt. % or at least 40 Wt. % of the nitrogen may be contained in hydrocarbon compounds having a carbon number of 17 or less.

[00114] In some embodiments, the oxygen content of the hydrocarbon product may be at most 90% of the hydrocarbon feed. In other embodiments, the oxygen content may be at most 50%, at most 30%, at most 10% or at most 5% of the oxygen content of the hydrocarbon feed. In certain embodiments, the oxygen content may be less than approximately 1.2 wt% of the hydrocarbon product.

[00115] In some embodiments, the hydrocarbon product may include from approximately 0.05 – 0.15 grams of hydrogen per gram of hydrocarbon product 120. The hydrocarbon product may include in its molecular structure 0.8 to 0.9 grams of carbon per gram of hydrocarbon product. The hydrocarbon product may have a ratio of atomic carbon to atomic hydrogen (C/H) within 70-130% of the hydrocarbon feed. In an exemplary embodiment, the C/H ratio of the hydrocarbon product may be $\geq 90\%$ of the hydrocarbon feed. Embodiments of a hydrocarbon product may have a hydrogen to carbon ratio of the hydrocarbon less than or equal to 1.7:1 in some embodiments. In other embodiments, the H/C ratio may be between approximately 0.01:1 to 0.09:1, between 0.1: 1 to 0.49:1, between 0.50:1 to 1:1 and/or between 1:1 to 1.7:1. Accordingly, in some embodiments, the H/C ratio may be less than 1:100, less than 1:75, less than 1:50, less than 1:30, less than 1:20 or less than 1:10.

[00116] In some embodiments, the hydrocarbon product 120 may be amenable to additional refinery operations and treatments, including but not limited to distillation, hydrotreating, alkylation, hydrocracking, fluid catalytic cracking, coking, and visbreaking.

[00117] In some embodiments, the hydrocarbon products may be hydro-treated to adjust the H/C or C/H ratio of the hydrocarbon products and/or decrease the sulfur content of the hydrocarbon products. A hydrocarbon product with a C/H ratio within 10-30% of the hydrocarbon feed may indicate that the uptake or consumption of hydrogen was relatively small and/or that the hydrogen was produced in situ. In some embodiments, the hydrocarbon product with a low C/H ratio may be sent to a refinery for further processing wherein the refinery may modify the C/H ratio by increasing the hydrogen content as needed in the formation of the refined product. In such an embodiment, the oil producers may save money by avoiding the addition of costly hydrogen processing, while still being able to economically transport the oxidized hydrocarbon products.

[00118] Referring to Fig. 6a-6f, which depicts various boiling point distributions for hydrocarbon feeds such as crude bitumen, sulfoxidized intermediates 111 of the hydrocarbon feed and the boiling point of distributions of various hydrocarbon products based on the amount of heteroatom removal that has occurred. For example, the hydrocarbon products 120 may contain VGO hydrocarbons, distillate hydrocarbons (kerosene and diesel), naphtha hydrocarbons and residual hydrocarbons (asphalt

and bitumen). The hydrocarbon composition may contain, per gram of hydrocarbon composition, at least 0.1 grams of hydrocarbons having a boiling point from the initial boiling point (IBP) of the hydrocarbon composition up to 204° C. (400° F.). The hydrocarbon composition may also contain, per gram of hydrocarbon composition, at least 0.15 grams of hydrocarbons having a boiling point from 204° C up to 260° C. The hydrocarbon composition may also contain, per gram of hydrocarbon composition, at least 0.3 grams, or at least 0.35 grams of hydrocarbons having a boiling point of from 260° C up to 343° C. The hydrocarbon composition may also contain, per gram of hydrocarbon composition, at least 0.35 grams, or at least 0.4 grams, or at least 0.45 grams of hydrocarbons having a boiling point of from 343° C up to 538° C. The relative amounts of hydrocarbons within each boiling range and the boiling range distribution of the hydrocarbons may be determined in accordance with ASTM Method D5307, ASTM Method D7169 or an equivalent method thereof.

[00119] Referring still to Fig. 6a-6f, the hydrocarbon product 120 may include hydrocarbons within one or more ranges of boiling points. In some embodiments, the hydrocarbon product may include at least 0.1g of hydrocarbons per gram of hydrocarbon product having a boiling range distribution between the initial boiling point and 739°C. In other embodiments, the hydrocarbon product may have approximately at least 0.2g, at least 0.3g, at least 0.4g, at least 0.5g, at least 0.8g, at least 0.9g of hydrocarbons per gram of hydrocarbon product having a boiling range distribution between the IBP and the 739°C.

[00120] In some embodiments, the hydrocarbon product may include at least 0.05grams of hydrocarbons per gram of hydrocarbon product 120 having a boiling range distribution from the initial boiling point of the hydrocarbon product to 67°C. The initial boiling point may be the temperature wherein a hydrocarbon or mixture of hydrocarbons first begins to boil. The IBP may vary depending on the composition of hydrocarbons present. For example, a hydrocarbon product including a high gasoline hydrocarbon content having short chain hydrocarbons between 4-12 carbons per molecule will begin to boil at a much lower temperature than a mixture of hydrocarbons lacking gasoline. For example, a hydrocarbon product with a high concentration of gasolines may have an initial boiling point of less than 70°C, whereas a hydrocarbon product including a higher concentration of gas oil or diesel and a lower concentration of gasolines may have a higher initial boiling point around 120 - 150°C. In an embodiment including few gasolines and a lower concentration of gas oil or diesel, and instead having a higher concentration of lubricating oils, the hydrocarbon product may have an IBP of approximately 150 - 300°C. In comparison, a hydrocarbon product having a high concentration of fuel oil fractions but still having a fair amount of naphtha and gasoline may still have a lower IBP because the naphtha and gasoline may begin to boil at temperature between 40 - 200°C. In a hydrocarbon product that is predominantly lubricating oil, heavy gas and residual products, the hydrocarbon mixture may have a much higher IBP than the previous examples, for instance between 275°C - 450°C.

[00121] In some embodiments, the hydrocarbon product 120 may include 0.01 to 0.25 grams of hydrocarbon per gram of hydrocarbon product having a boiling range distribution between the IBP of the hydrocarbon products and 204°C. In another embodiment, the hydrocarbon product may include at least

0.1 gram of hydrocarbons per gram of hydrocarbon product having a boiling range distribution from the IBP to 253°C. In other embodiments, the hydrocarbon product may include at least 0.4g of hydrocarbons per gram of hydrocarbon product having a boiling range distribution between IBP of the hydrocarbon product to approximately 538°C.

[00122] Additional embodiments of the hydrocarbon product 120 may include at least .05g of hydrocarbons per gram of hydrocarbon products having a boiling point distribution between 204°C and 260°C. Embodiments of the hydrocarbon product 120 may further include at least 0.1 grams of hydrocarbons per gram of hydrocarbon product 120 having a boiling point distribution between 260°C to 343°C. Embodiments of the hydrocarbon products may also include at least 0.2 grams of hydrocarbons per gram of the hydrocarbon product 120 with a boiling range distribution between 343°C and 510°C. In certain embodiments, of the hydrocarbon products, the hydrocarbon products may contain at least 0.75 grams of hydrocarbons per gram of hydrocarbon product having a boiling range distribution from the IBP of the hydrocarbon products 120 up to 739°C. In other embodiments, the hydrocarbon products 120 may include at most 0.3grams of hydrocarbons per gram of hydrocarbon products having a boiling range distribution greater than 738°C.

[00123] In some embodiments, the hydrocarbon products 120 may have at least 0.05g of gasolines per gram of hydrocarbon product. The gasoline fraction may have a boiling range distribution between the IBP of the hydrocarbon product and approximately 67°C. In other embodiments, the hydrocarbon product may have at most 0.6 grams of gasolines per gram of hydrocarbon product.

[00124] In some embodiments, the hydrocarbon product may have less than 0.001 g of olefinic hydrocarbons per gram of hydrocarbon product. In some embodiments, the hydrocarbon product may have at least 0.001g of olefinic hydrocarbons per gram of the hydrocarbon product. In one or more embodiments, the hydrocarbon product may contain less than 0.02g of olefins per gram hydrocarbon product. The amount of olefinic hydrocarbons measured per gram of the hydrocarbon product may be measured using the Canadian Crude Quality Technical Association (CCQTA) – Olefins in Crude Oil by ¹H-NMR method. The olefinic hydrocarbon fractions may have a boiling range distribution between the IBP of the hydrocarbon product and 253°C. Non-limiting examples of olefins may include for example, styrene, 1-hexene, cyclohexene, limonene, and trans-stilbene.

[00125] In some embodiments, the hydrocarbon product may have between 0.01g and 0.30g of gasolines, naphtha, and/or paraffin, per gram of hydrocarbon product. The gasolines, naphtha and/or paraffin fractions may have a boiling point range distribution between the IBP and approximately 204°C.

[00126] In one or more embodiments, the hydrocarbon product may contain at least 0.05g of diesel oil per gram hydrocarbon products. In other embodiments, the hydrocarbon product may contain at most 0.8g of diesel oil per gram of hydrocarbon product. The diesel oil fraction may have boiling range distribution between approximately 204°C and 260°C.

[00127] In some embodiments, the hydrocarbon products may contain at least 0.1g of lubricating oils per gram of hydrocarbon products. In other embodiments, the lubricating oils may be at most 0.8g per gram of hydrocarbon product. The lubricating oil fraction may have a boiling range

distribution between approximately 260°C and 343°C.

[00128] Embodiments of the hydrocarbon products may contain at least 0.2g of fuel oils, greases, waxes and/or some bitumens per gram hydrocarbon product. In other embodiments, the hydrocarbon product may contain at most 0.8g of fuel oils, greases, waxes and/or some bitumens per gram hydrocarbon product. The fuel oils, greases, waxes and/or some bitumens may have a boiling range distribution between approximately 343°C and 510°C.

[00129] Embodiments of the hydrocarbon products may contain at most 0.3g of bitumen per gram of hydrocarbon product wherein the bitumen has a boiling point range distribution greater than 738°C.

[00130] The hydrocarbon products 120 of the present invention may contain significant quantities of aromatic hydrocarbon compounds. The hydrocarbon product may contain, per gram of hydrocarbon product, at least 0.3 gram, or at least 0.35gram, or at least 0.4 gram, or at least 0.45 gram, or at least 0.5 gram of aromatic hydrocarbon compounds.

[00131] In some embodiments, the hydrocarbon product may have a distillate content between 50-150% of the distillate content of the hydrocarbon feed. The distillate content of the distillate hydrocarbons per gram of hydrocarbon product may be in a range from 0.00001 - 0.8g. In certain embodiments, the hydrocarbon product may have VGO content of 50-150% of the VGO content of the hydrocarbon feed. In some embodiments, the VGO content may range from 0.0001 – 0.8g per gram of hydrocarbon product.

[00132] Embodiments of the hydrocarbon product may have a residue content of at most 90% of the hydrocarbon feed. In other embodiments, the residue content may be at most 80%, at most 50%, at most 30%, at most 20%, at most 10% or at most 3% of the residue content of the hydrocarbon feed. In certain embodiments, the hydrocarbon products may have a residue content between 70-130% of the residue content of the hydrocarbon feed.

[00133] Embodiments of the hydrocarbon product may have a total C₅ and C₇ asphaltene content of at most 90% of the total C₅ and C₇ asphaltene content of the hydrocarbon feed. In other embodiments, the asphaltene content may be at most 50%, at most 30% or at most 10% of the hydrocarbon feed. In certain embodiments, the hydrocarbon feed may have a total C₅ and C₇ asphaltene content of at least 0.01g per gram of hydrocarbon product. In other embodiments, the asphaltene content may be at most 0.5g per gram of hydrocarbon product. In some embodiments, the asphalt content of the hydrocarbon product may be the content of C₅ and/or the content of C₇ asphaltene. The asphalt content may be measured using ASTM D3279-2 or an equivalent method thereof. The asphalt content may be the measurement of the grams of asphaltene insoluble n-heptane per gram of hydrocarbon product containing asphalt. In one embodiment, the asphalt content may be at least 0.3g of asphaltene may be insoluble in n-heptane, per gram of hydrocarbon product. A hydrocarbon product containing asphalt or asphaltenes may have a hydrogen to carbon ratio of less than 1.5:1 in some embodiments.

[00134] Embodiments of methods for quantifying C₅ or C₇ asphaltene content may include the determination of the mass percent of asphaltene defined by their insolubility in an n-heptane solvent.

Embodiments of methods characterizing the insolubility of the asphaltene in n-heptane may be applicable to all solid, and semi-solid asphalts, gas oils, heavy fuel oils and crude petroleum that may be topped to a cut-point of approximately 343°C or higher.

[00135] The H/C ratio of hydrogen to carbon may be determined by ASTM D5291 or equivalent method. In some embodiments, the H/C ratio may be between approximately 0.01:1 to 0.09:1, between 0.1:1 to 0.49:1, between 0.50:1 to 1:1 and/or between 1:1 to 1.5:1. Accordingly, in other embodiments, the H/C ratio may be less than 1:100, less than 1:75, less than 1:50, less than 1:30, less than 1:20 or less than 1:10. The methods for testing test the carbon and hydrogen content of various hydrocarbons and hydrocarbon products, including crude oils, fuel oils, additives, lubricants and residues may include concentration ranges of at least 75 to 85 mass % of carbon and at least 9 to 16 mass % for hydrogen in some embodiments. Embodiments employing certain methods for identifying the hydrogen to carbon ratio may express the results as mass % carbon and mass % hydrogen.

[00136] A hydrocarbon product containing asphalt or asphaltenes may be the product of a crude asphalt hydrocarbon feed. In embodiments where a crude asphalt hydrocarbon feed is used for hydrocarbon feed 101, the total acid number of the asphalt hydrocarbon product 120 may be less than the total acid number of the crude asphalt hydrocarbon feed. In some embodiments, the TAN of asphalt hydrocarbon products may be between 5 to 90% of the TAN of the asphalt hydrocarbon feed. Embodiments of an asphalt hydrocarbon product may have a TAN less than 0.5mg KOH per gram of asphalt containing hydrocarbon product.

[00137] A hydrocarbon product containing asphalt or derived from a crude asphalt hydrocarbon feed subjected to oxidative desulfurization treatment may have a viscosity of hydrocarbon product that is less than the viscosity of the hydrocarbon feed. For instance, in some embodiments, the viscosity of the asphalt containing hydrocarbon product may have a viscosity less than the hydrocarbon feed measured at 15°C, 80°C, 100°C, 120°C using ASTM D7042 to measure the viscosity. In some embodiments, methods for determining viscosity may include measurements of both the dynamic viscosity, η , and the density, ρ , of hydrocarbons and hydrocarbon products and, both transparent and opaque. The kinematic viscosity, ν , can be obtained by dividing the dynamic viscosity, η , by the density, ρ , obtained at the same test temperature. Embodiments of the methods may include determining the density or relative density of hydrocarbons and hydrocarbon products for the conversion of measured volumes to volumes at the standard temperature of 15°C. The results obtained from testing methods may be dependent upon the behavior of the sample in some embodiments, and it's intended application to liquids for which primarily the shear stress and shear rate are proportional (Newtonian flow behavior).

[00138] In other embodiments, ASTM D7042 methods may be used to measure the density of the hydrocarbon product and hydrocarbon feeds containing asphalts and crude asphalts. The density of the hydrocarbon feed may be 1.05grams/cubic centimeter (g/cc) or greater when measured at 15°C. In other embodiments, the density of the hydrocarbon product may be measured at intervals above 15°C, such as 80°C, 100°C and 120°C then extrapolated back to 15°C to determine that the density of the hydrocarbon product is greater than 1.05g/cc.

[00139] In some embodiments, as a result from removing heteroatoms from the hydrocarbon feed, the light oil phase containing the hydrocarbon products 120, may have a lower density and viscosity than the untreated, contaminated feed. The heavy caustic phase density may be in the range from about 1.0 to about 3.0 g/cc and the light product oil phase may have density generally in the range of from about 0.7 to about 1.1 g/cc as measured at 15°C.

[00140] In some embodiments, the composition of the crude asphalt hydrocarbon product may have some residual or remaining metals after oxidative desulfurization. The metal content of the hydrocarbon product may be less than the crude asphalt hydrocarbon feed. In some embodiments, the hydrocarbon product may have a total metal content that is less than 90% of the metal content of the hydrocarbon feed. In other embodiments, the hydrocarbon product may be less than 50%, less than 20% or less than 10% of the metal content of the hydrocarbon feed. The product may be further treated by other well-known refinery operations including, but not limited to: hydrotreating, hydrocracking, fluidized catalytic cracking, coking, distillation, etc.

[00141] In some embodiments, the hydrocarbon feed 101, hydrocarbon products 120 and the intermediate products 111 may be characterized using infrared (IR) spectroscopy to identify the characteristics and properties of the hydrocarbons. The IR spectra may be used to measure the absorbance (A) at each wavelength or wavenumber and then the peaks may be plotted along the spectrum, wherein the location along the spectrum may signify the functional class (such as sulfoxide or sulfone) and the height or area of the peak may be proportional to the amount (for example weight %) of the functional class present. A non-limiting list of examples of functional classes are provided in Table 1 and Table 2 below.

[00142] The hydrocarbon feed, hydrocarbon products and intermediate products may be measured by any known infrared spectroscopy techniques. For example, each of the hydrocarbons may be measured using attenuated total reflectance Fourier Transform Infrared Spectroscopy. Embodiments measuring the content of the hydrocarbon feed 101, the sulfoxidized intermediate stream 111 and the hydrocarbon product may be measured “neat” in some embodiments (without the addition of solvents or additives).

[00143] The IR spectra provided in Fig. 7a to Fig. 7e demonstrate an example of using IR to characterize, compare and contrast the compositions and content of the hydrocarbon feed 101, hydrocarbon product 120 and intermediate stream 111. In some embodiments, the infrared spectroscopy peaks or areas of interest in classifying the signature compositions of the intermediate stream and the hydrocarbon products may be those peaks or areas corresponding to sulfone and sulfoxide functional groups. Table 1 provides an example of typical infrared absorption frequencies and some sample characteristics describing the vibrations, range and intensity of the bands. Table 2 below provides example absorption ranges for IR spectroscopy for various functional classes including classes of compositions that may be present in hydrocarbon feeds, sulfoxidized intermediate streams and the hydrocarbon product such as sulfones, sulfoxides and sulfates.

TABLE 1

Functional Class	Stretching Vibrations			Bending Vibrations		
	Range (cm ⁻¹)	Intensity	Assignment	Range (cm ⁻¹)	Intensity	Assignment
Alkanes	2850-3000	str	CH ₃ , CH ₂ & CH 2 or 3 bands	1350-1470 1370-1390 720-725	med med wk	CH ₂ & CH ₃ deformation CH ₃ deformation CH ₂ rocking
Alkenes	3020-3100 1630-1680 1900-2000	med var str	=C-H & =CH ₂ (usually sharp) C=C (symmetry reduces intensity) C=C asymmetric stretch	880-995 780-850 675-730	str med med	=C-H & =CH ₂ (out-of-plane bending) cis-RCH=CHR
Alkynes	3300 2100-2250	str var	C-H (usually sharp) C≡C (symmetry reduces intensity)	600-700	str	C-H deformation
Arenes	3030 1600 & 1500	var med-wk	C-H (may be several bands) C=C (in ring) (2 bands) (3 if conjugated)	690-900	str-med	C-H bending & ring puckering
Alcohols & Phenols	3580-3650 3200-3550 970-1250	var str str	O-H (free), usually sharp O-H (H-bonded), usually broad C-O	1330-1430 650-770	med var-wk	O-H bending (in-plane) O-H bend (out-of-plane)

TABLE 2

Functional Class	Characteristic Absorptions
Sulfur Functions	
S-H thiols	2550-2600 cm^{-1} (wk & shp)
S-OR esters	700-900 (str)
S-S disulfide	500-540 (wk)
C=S thiocarbonyl	1050-1200 (str)
S=O sulfoxide	1030-1060 (str)
sulfone	1325 $\pm$ 25 (as) & 1140 $\pm$ 20 (s) (both str)
sulfonic acid	1345 (str)
sulfonyl chloride	1365 $\pm$ 5 (as) & 1180 $\pm$ 10 (s) (both str)
sulfate	1350-1450 (str)
Phosphorous Functions	
P-H phosphine	2280-2440 cm^{-1} (med & shp) 950-1250 (wk) P-H bending
(O=)PO-H phosphonic acid	2550-2700 (med)
P-OR esters	900-1050 (str)
P=O phosphine oxide	1100-1200 (str)
phosphonate	1230-1260 (str)
phosphate	1100-1200 (str)
phosphoramidate	1200-1275 (str)
Silicon Functions	
Si-H silane	2100-2360 cm^{-1} (str)
Si-OR	1000-11000 (str & brd)
Si-CH₃	1250 $\pm$ 10 (str & shp)
Oxidized Nitrogen Functions	
=NOH oxime	
O-H (stretch)	3550-3600 cm^{-1} (str)
C=N	1665 $\pm$ 15
N-O	945 $\pm$ 15
N-O amine oxide	
aliphatic	960 $\pm$ 20
aromatic	1250 $\pm$ 50
N=O nitroso	1550 $\pm$ 50 (str)
nitro	1530 $\pm$ 20 (as) & 1350 $\pm$ 30 (s)

[00144] Referring to Fig. 7a to 7e as an example of an IR spectra, an infrared spectroscopy reference peak may be established between approximately 1445 cm^{-1} and 1465 cm^{-1} for the hydrocarbon product 120, intermediate product 111 and the hydrocarbon feed 101. In some embodiments, the peak height or area of the reference peak may be at approximately 1455 cm^{-1} . In the embodiments depicted in Fig. 7a to Fig. 7e, the height or area of the reference peak may be normalized so that the peak height or

area of the reference peak may be approximately 1.0 absorbance (A). In an alternative embodiment, the reference peak may be measured by absolute absorbance rather than normalizing the curve.

[00145] As shown in Fig. 7b and Fig. 7d, intermediate products 111 may be characterized by the presence of infrared spectroscopy peaks identified by one or more peaks recorded using IR spectroscopy. The peaks may be referred to as a first, second, third, fourth or fifth peak, etc., however name of the peak denotes the order in which the peak is discussed. The location and identifying nature of the peak may be based on the wavelength or wavenumber where the peak may be located during IR spectroscopy, not the designation of the peak as the first, second or third, etc. For example, a peak that may be described as a first peak in one embodiment because it resides at a lower wavenumber, may also be referred to as a second peak, or a third peak in another embodiment when the peak appears subsequent to another peak. Likewise, a peak that may be present in an IR spec as a “second peak” in a first embodiment may be referred to as a first peak in a second embodiment wherein the “first peak” of the first embodiment is not present in the second embodiment.

[00146] A first peak that may characterize the contents of the intermediate products 111 may be present on the IR spectrum between the wavelengths or wavenumbers of approximately 1310 cm^{-1} to 1285 cm^{-1} . This first peak may have a height or area that is at least approximately 28% of the height or area of the reference peak. In some embodiments, the first peak may have a height or area that is approximately at least 30%, at least 35%, at least 40%, at least 50%, at least 70%, at least 85%, at least 100% or greater than 100% of the height or area of the reference peak.

[00147] Embodiments of the intermediate products 111 may also be classified using IR spectroscopy by the presence of another peak. This second peak may appear on an IR spectroscopy readout at a wavelength or wavenumber between approximately 1135 cm^{-1} and 1110 cm^{-1} . The peak height or area of this second peak may be present at a wavelength or wavenumber of approximately 1125 cm^{-1} . Embodiments of the intermediate product 111, may exhibit this second peak with height or area that is approximately at least 22% of the height or area of the reference peak. In some embodiments, this second peak may have a height or area that is at least 25%, at least 30%, at least 40%, at least 50%, at least 70%, at least 85%, at least 100% or greater than 100% of the height or area of the reference peak.

[00148] In some embodiments of the intermediate products 111, the intermediate products may be characterized by the presence of yet a third peak identified using IR spectroscopy. This third peak may appear on an IR spectroscopy readout at a wavelength or wave number between approximately 1040 cm^{-1} and 1000 cm^{-1} . The peak height or area of the third peak may be present at a wavelength or wavenumber of approximately 1031 cm^{-1} . Embodiments of the intermediate product 111, may exhibit a third peak having a height or area that is approximately at least 22% of the height or area of the reference peak. In some embodiments, the second peak may have a height or area that is at least 25%, at least 30%, at least 40%, at least 50%, at least 70%, at least 85%, at least 100% or greater than 100% of the height or area of the reference peak.

[00149] Embodiments of the hydrocarbon product 120 may also be characterized by IR spectroscopy in a manner similar to the intermediate products 111. For example, the hydrocarbon

products may be characterized by the presence of peaks identified by one or more peaks recorded using IR spectroscopy. For example, in one embodiment, a first peak that may characterize the contents of the hydrocarbon products 120 may be present on the IR spectrum between the wavelengths or wavenumbers of approximately 1310 cm^{-1} to 1285 cm^{-1} . This first peak may have a height or area that is at least approximately 28% of the height or area of the reference peak. In some embodiments, the first peak may have a height or area that is approximately at least 30%, at least 35%, at least 40%, at least 50%, at least 70%, at least 85%, at least 100% or greater than 100% of the height or area of the reference peak.

[00150] Embodiments of the hydrocarbon product may also be classified using IR spectroscopy by the presence of other peaks. A second peak that may appear on an IR spectroscopy readout may be at a wavelength or wavenumber between approximately 1135 cm^{-1} and 1110 cm^{-1} . The peak height or area of this second peak may be present at a wavelength or wave number of approximately 1125 cm^{-1} .

Embodiments of the hydrocarbon products 120, may exhibit a second peak with height or area that is approximately at least 22% of the height or area of the reference peak. In some embodiments, the second peak may vary in height or area, for example, the height or area of the second peak may be at least 25%, at least 30%, at least 40%, at least 50%, at least 70%, at least 85%, at least 100% or greater than 100% of the height or area of the reference peak.

[00151] In some embodiments of the hydrocarbon products 120, the hydrocarbon products may be characterized by the presence of a third signature peak identified using IR spectroscopy. The third peak may appear on an IR spectroscopy readout at a wavelength or wavenumber between approximately 1040 cm^{-1} and 1000 cm^{-1} . The peak height or area of the third peak may be present at a wavelength or wavenumber of approximately 1031 cm^{-1} . Embodiments of the hydrocarbon product 120, may exhibit a third peak having a height or area that is approximately at least 22% of the height or area of the reference peak. In some embodiments, the second peak may have a height or area that is at least 25%, at least 30%, at least 40%, at least 50%, at least 70%, at least 85%, at least 100% or greater than 100% of the height or area of the reference peak.

[00152] In the embodiments of the intermediate product 111 and the hydrocarbon product 120, having a reference peak, a first peak, a second peak or a third peak, the wavelength or wavenumber classifying the location of the peaks may vary between +/- 10% of the value of the upper and lower bounds of the peak's range described herein. Distillates derived from intermediate product 111 or hydrocarbon product 120 having a reference peak and a plurality of peaks such as a first peak, a second peak or a third peak, the peak heights or areas in relation to the reference peak may vary between +/- 60% of those described herein. The following non-limiting examples illustrate certain aspects of the present invention:

[00153] Example 1

[00154] Preparation of Catalyst

[00155] Bis(glycerol)oxo titanium(IV) is prepared according to the method of US Patent 8,394,261 B2 which is hereby incorporated by reference. Titanium oxychloride (2 kilograms (kg), Millenium Chemicals) is diluted with de-ionized water (2 kg) and then added to a 20 liter (l) round

bottom flask containing glycerine (2 kg). The mixture is allowed to stir until a straw color is attained. The 20 liter round bottom flask is then heated to 50° C. under vacuum (–25 inches Hg) in a rotary evaporator to remove excess water and hydrochloric acid. When no further liquid condensate is noted, the flask is recharged with water (0.65 l) and rotary evaporated to further remove excess water and hydrochloric acid. This is repeated two additional times. After the final evaporation, the viscous, straw colored liquid is weighed (2.64 kg) and diluted with methoxypropanol (0.85 kg) to reduce the viscosity. This is then neutralized with triethylamine (3.3 kg, 33% weight/weight in ethanol). The combined neutralized solution is then chilled for several hours producing rod-like needles of triethylamine hydrochloride. The crystalline triethylamine hydrochloride is removed by vacuum filtration. The filtrate is added slowly to acetone (70 L) causing the product to precipitate as a white solid. The acetone is then decanted and an off-white solid residue is obtained. The off-white solid residue is then washed vigorously with hexanes (20 L) to afford a fine white powder. The powder is collected by filtration (>63% yield based upon Ti). % Ti Calculated: 16.98. Analysis: 16.7; mp DSC (dec) 273° C.; ESI-MS (positive mode) 245 amu; ¹H-NMR (DMSO-d₆) 4.25 (br s, 4H), 3.45 (m, 2H), 3.38 (m, 4H), 3.31 (m, 4H).

[00156] Example 2

[00157] General Method for Adsorption of Catalyst onto Support

[00158] A 2% by weight solution of the catalyst from example 1 is prepared by mixing with methanol. The solution is added to a silica support until the solids are fully immersed at ambient temperature. The solids are allowed to soak for approximately 30 minutes, or until all air is displaced. The liquid is decanted from the solids and the solids are dried in vacuo (50°C) until the weight of the solids no longer changes. A 40% solution of t-butyl hydroperoxide in xylene is added to the dried catalyst-coated support until the solids are fully immersed. The suspension is allowed to gently mix at 95°C for 90 minutes. Afterwards, the liquid is decanted from the solids. Then the solids are washed with sufficient hexanes until residual peroxide content in the hexanes is less than 0.5%. The solids are then dried in vacuo at 50°C until the solid weight no longer changes.

[00159] Example 3

[00160] Preparation of Caustic Treatment Mixture.

[00161] A solution containing 79.1% w/w sodium sulfide nonahydrate and 20.9% w/w propylene glycol is prepared. The mixture is heated to 50°C to insure complete dissolution. The solution is stored in a warm water bath to prevent sulfide precipitation before further use.

[00162] Examples 4A and 4B

[00163] Continuous Catalytic Heteroatom Oxidation

[00164] A water-jacketed plug flow reactor with an aspect ratio (length/diameter) of 20 is filled with 171 grams of supported catalyst prepared according to the method of example 2 containing about 0.4% w/w Ti. The reactor temperature is stabilized at 95°C. An Athabasca bitumen feed is warmed to 80°C under nitrogen in a stainless steel drum to facilitate pumping into the reactor. The bitumen is combined with an excess of tert-butylhydroperoxide solution in xylenes (40% w/w) to obtain a 6:1 molar ratio of peroxide to sulfur at the reactor inlet.

[00165] The solution is pumped into the reactor at a sufficient flow rate to obtain a liquid residence time of 90 minutes in the reactor. Samples are collected periodically at the reactor outlet to measure peroxide concentration. The reactor effluent is continuously distilled under vacuum to remove all residual peroxide, tert-butanol, and xylenes and to obtain an oxidized heteroatom bitumen stream.

[00166] Example 4B is the same as 4A except that the reactor temperature is increased to 115°C.

[00167] Example 5A and 5B

[00168] Caustic treatment of Example 4 Output

[00169] The oxidized heteroatom bitumen stream of Example 4A and 4B are independently co-fed with the mixture of Example 3 into a continuously stirred tank reactor (CSTR) so as to obtain a liquid residence time of 90 minutes at 275°C under 300 psig. The reactor effluent flows into a gravity settler producing an oil phase and a spent caustic phase. The oil product is separated from the spent caustic phase. The properties of the products of 4A, 4B, 5A, 5B and the hydrocarbon feed may be compared and characterized by the IR spectroscopy printout depicted in Fig. 7a to Fig. 7e.

[00170] While this disclosure has been described in conjunction with the specific embodiments outlined above, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art. Accordingly, the preferred embodiments of the present disclosure as set forth above are intended to be illustrative, not limiting. Various changes may be made without departing from the spirit and scope of the invention, as required by the following claims. The claims provide the scope of the coverage of the invention and should not be limited to the specific examples provided herein.

CLAIMS

What is claimed is:

1. A hydrocarbon product comprising:
at least 0.1 grams per gram of hydrocarbon product having a boiling point that is less than 739°C;
at least 75 to 85 mass% carbon;
at least 9 to 16 mass % hydrogen; and
the hydrocarbon product exhibits an infrared spectroscopy reference peak, centered between approximately 1445 cm⁻¹ and 1465 cm⁻¹, a first infrared spectroscopy peak between approximately 1310cm⁻¹ and 1285cm⁻¹, and a second infrared spectroscopy peak between approximately 1135cm⁻¹ and 1110cm⁻¹, wherein a height or area of the first infrared spectroscopy peak is at least approximately 28% of a height or area of the infrared spectroscopy reference peak and a height or area of the second infrared spectroscopy peak is at least approximately 22% of the height or area of the infrared spectroscopy reference peak.
2. The hydrocarbon product of claim 1, having a sulfur content measure between 17mg/kg of the hydrocarbon product and 4.6 mass % of the hydrocarbon product.
3. The hydrocarbon product of claim 1, having a nitrogen concentration between approximately < 0.1 to 2 mass % of the hydrocarbon product.
4. The hydrocarbon product of claim 1, having a nitrogen concentration per gram of hydrocarbon product between 40 to 10,000µg/g nitrogen.
5. The hydrocarbon product of claim 1, wherein the hydrocarbon product has an acid dissociation constant in water larger than 1x10⁻⁹.
6. The hydrocarbon product of claim 1, wherein the hydrocarbon product has a total acid number (TAN) between 0.1mg/g KOH and 150 mg/g KOH.
7. The hydrocarbon product of claim 1, wherein the hydrocarbon product has a total base number (TBN) greater than 300mg KOH/g.
8. The hydrocarbon product of claim 1 further comprising a hydrocarbon component accounting for approximately 0.01 to 30 mass % of the hydrocarbon product.
9. The hydrocarbon product of claim 8, wherein the hydrocarbon component has a boiling point range up to 225°C and is a parafin, iso-parafin, olefin, naphthanene, aromatic in naphtha or a blending stock.

10. The hydrocarbon product of claim 1, wherein the hydrocarbon product has an olefin content less comprising than 25 mass% of the hydrocarbon product.
11. The hydrocarbon product of claim 1, having a kinematic viscosity between 0.2mm²/s and 300000mm²/s.
12. The hydrocarbon product of claim 1, wherein the hydrocarbon product further exhibits a third infrared spectroscopy peak between approximately 1040cm⁻¹ and 1000cm⁻¹, wherein a height or area of the third infrared spectroscopy peak is at least approximately 22% of the height or area of the infrared spectroscopy reference peak.
13. A hydrocarbon product comprising:
 - at least 0.1 grams per gram of the hydrocarbon product has a boiling point greater than 738°C;
 - up to 0.1 mass% of the hydrocarbon product is insoluble in pentane; and
 - the hydrocarbon product exhibits an infrared spectroscopy reference peak, centered between approximately 1445 cm⁻¹ and 1465 cm⁻¹, a first infrared spectroscopy peak between approximately 1310cm⁻¹ and 1285cm⁻¹, and a second infrared spectroscopy peak between approximately 1135cm⁻¹ and 1110cm⁻¹, wherein a height or area of the first infrared spectroscopy peak is at least approximately 28% of a height or area of the infrared spectroscopy reference peak and a height or area of the second infrared spectroscopy peak is at least approximately 22% of the height or area of the infrared spectroscopy reference peak.
14. The hydrocarbon product of claim 13, wherein the hydrocarbon product is a liquid having a Reid vapor pressure of 101.325 kPa and an API gravity greater than 10.
15. The hydrocarbon product of claim 13 further comprising a carbon to hydrogen to sulfur ratio, having a carbon concentration of at least 75 to 85 mass%, a hydrogen concentration of at least 9 to 16 mass% and a sulfur concentration of 17mg/kg to 4.6 mass%.
16. The hydrocarbon product of claim 13, further comprises a nitrogen concentration of approximately <0.1 to 2 mass%.
17. The hydrocarbon product of claim 13, further comprises a nitrogen concentration range between 40 to 10,000 µg/g nitrogen.
18. The hydrocarbon product of claim 13, wherein the hydrocarbon product has a kinematic viscosity at 37.8°C between 0.2mm²/s and 300,000 mm²/s.

19. The hydrocarbon product of claim 13, wherein the hydrocarbon product has an acid dissociation constant in water larger than 1×10^{-9} .
20. The hydrocarbon product of claim 13, wherein the hydrocarbon product has a total acid number (TAN) between 0.1mg/g KOH and 150 mg/g KOH.
21. The hydrocarbon product of claim 13, wherein the hydrocarbon product has a total base number (TBN) greater than 300mg KOH/g.
22. The hydrocarbon product of claim 13 further comprising a hydrocarbon component accounting for approximately 0.01 to 30 mass % of the hydrocarbon product.
23. The hydrocarbon product of claim 22, wherein the hydrocarbon component has a boiling point range up to 225°C and is a parafin, iso-parafin, olefin, naphthanene, aromatic in naphtha or a blending stock.
24. The hydrocarbon product of claim 13, wherein the hydrocarbon product has an olefin content less comprising than 25 mass% of the hydrocarbon product.
25. The hydrocarbon product of claim 13, having a kinematic viscosity between 0.2mm²/s and 300,000mm²/s.
26. The hydrocarbon product of claim 13, wherein the hydrocarbon product further exhibits a third infrared spectroscopy peak between approximately 1040cm⁻¹ and 1000cm⁻¹, wherein a height or area of the third infrared spectroscopy peak is at least approximately 22% of the height or area of the infrared spectroscopy reference peak.

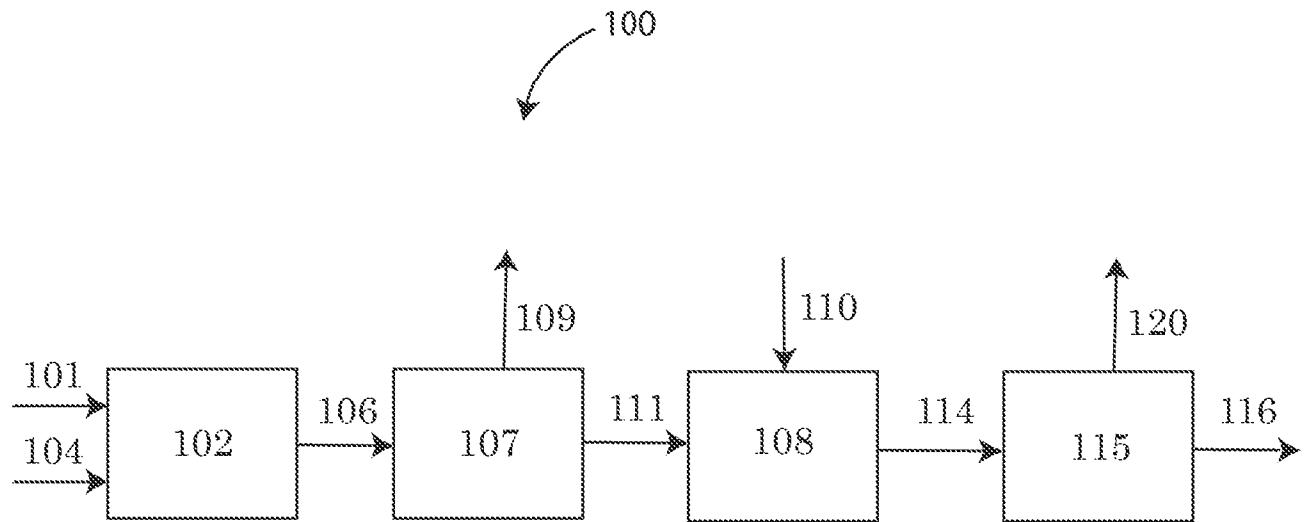


Fig. 1a

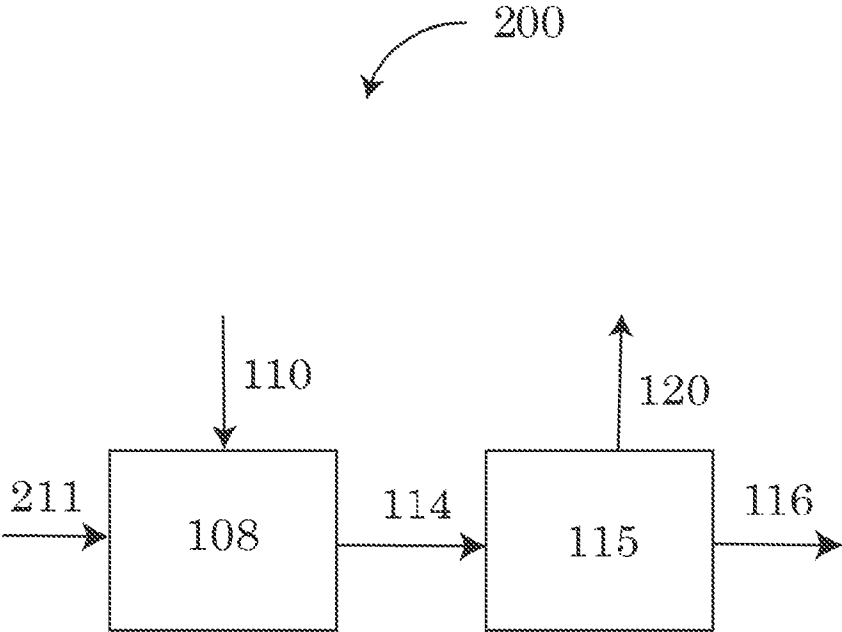


Fig. 1b

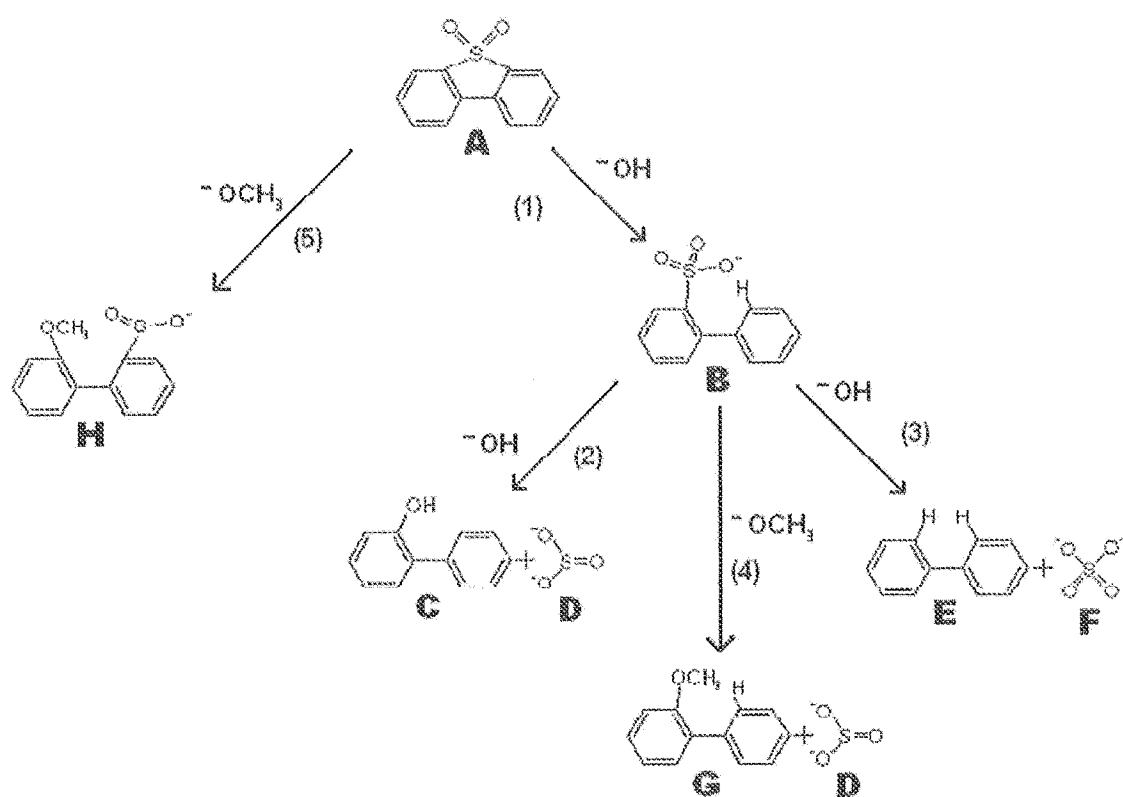


Fig. 2

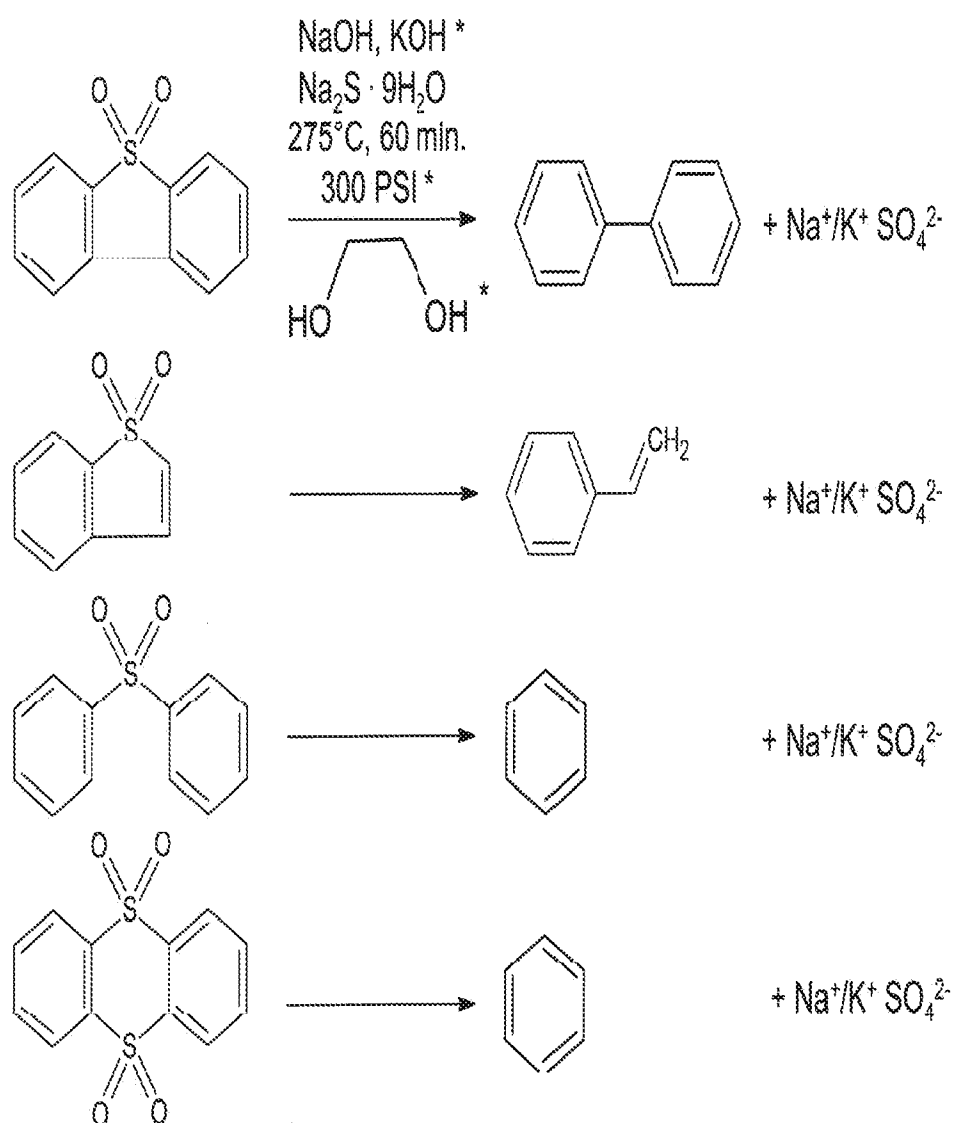


Fig. 3

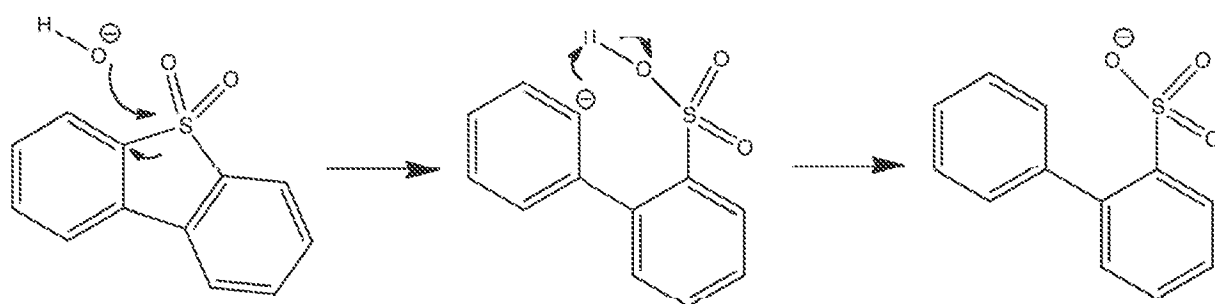


Fig. 4

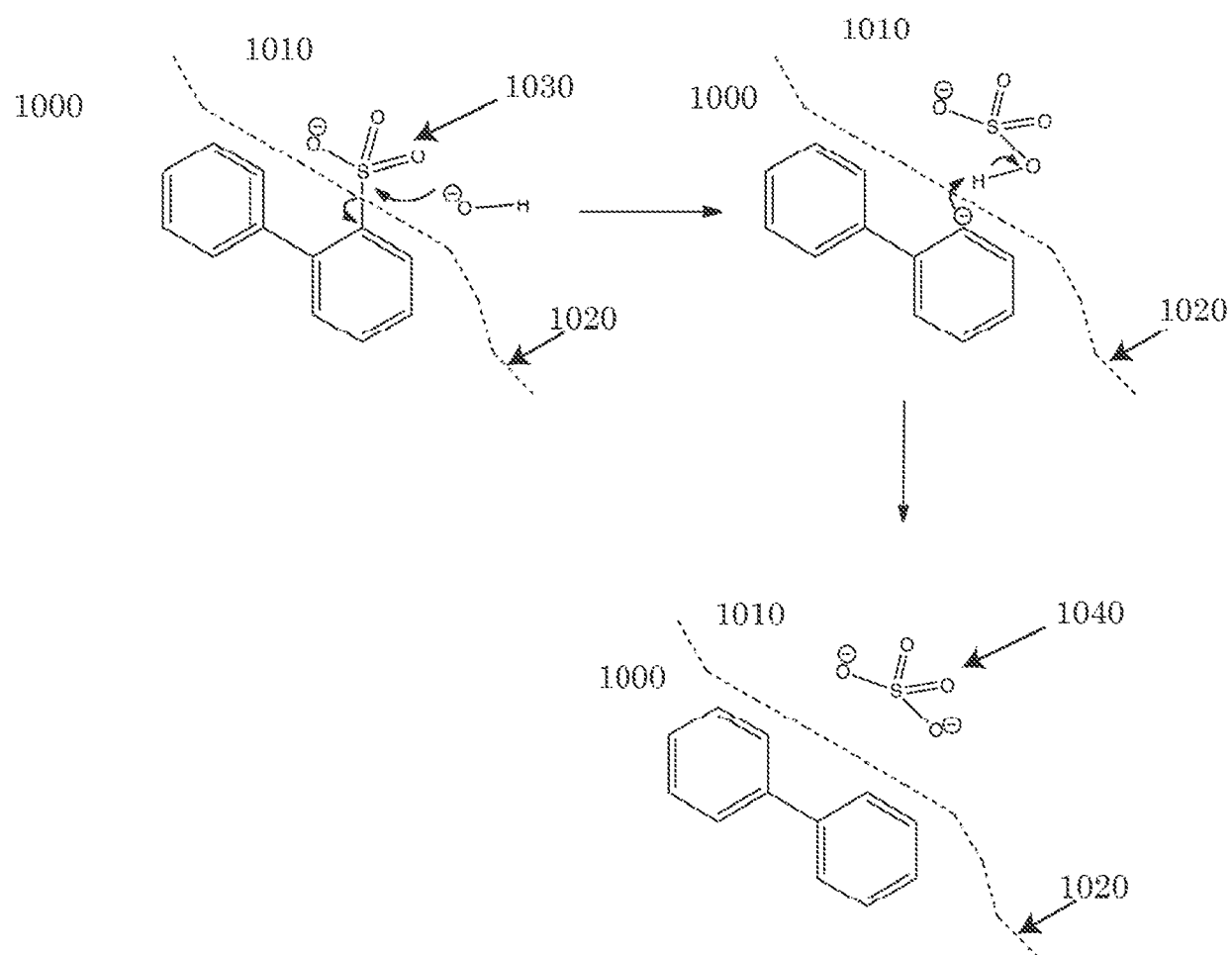


Fig. 5a

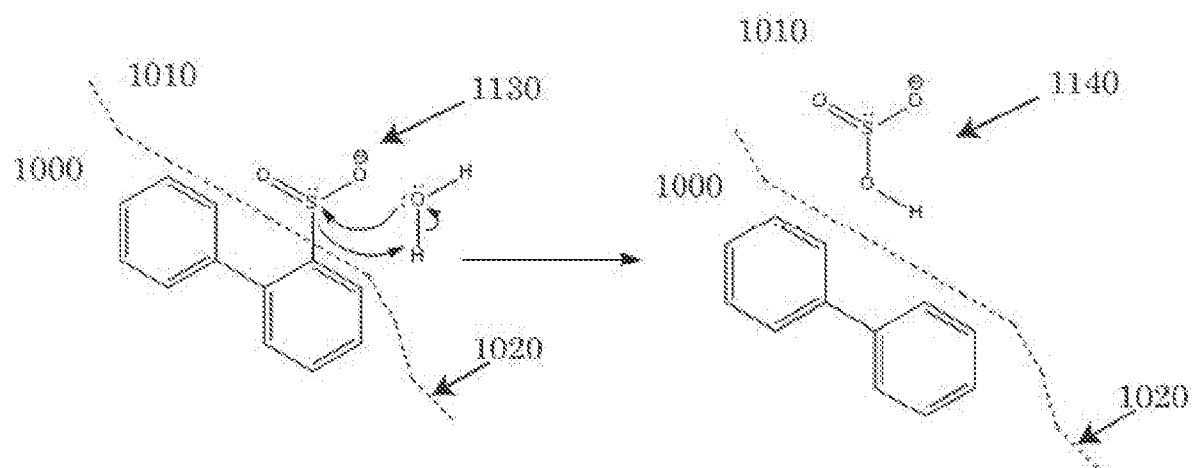


Fig. 5b

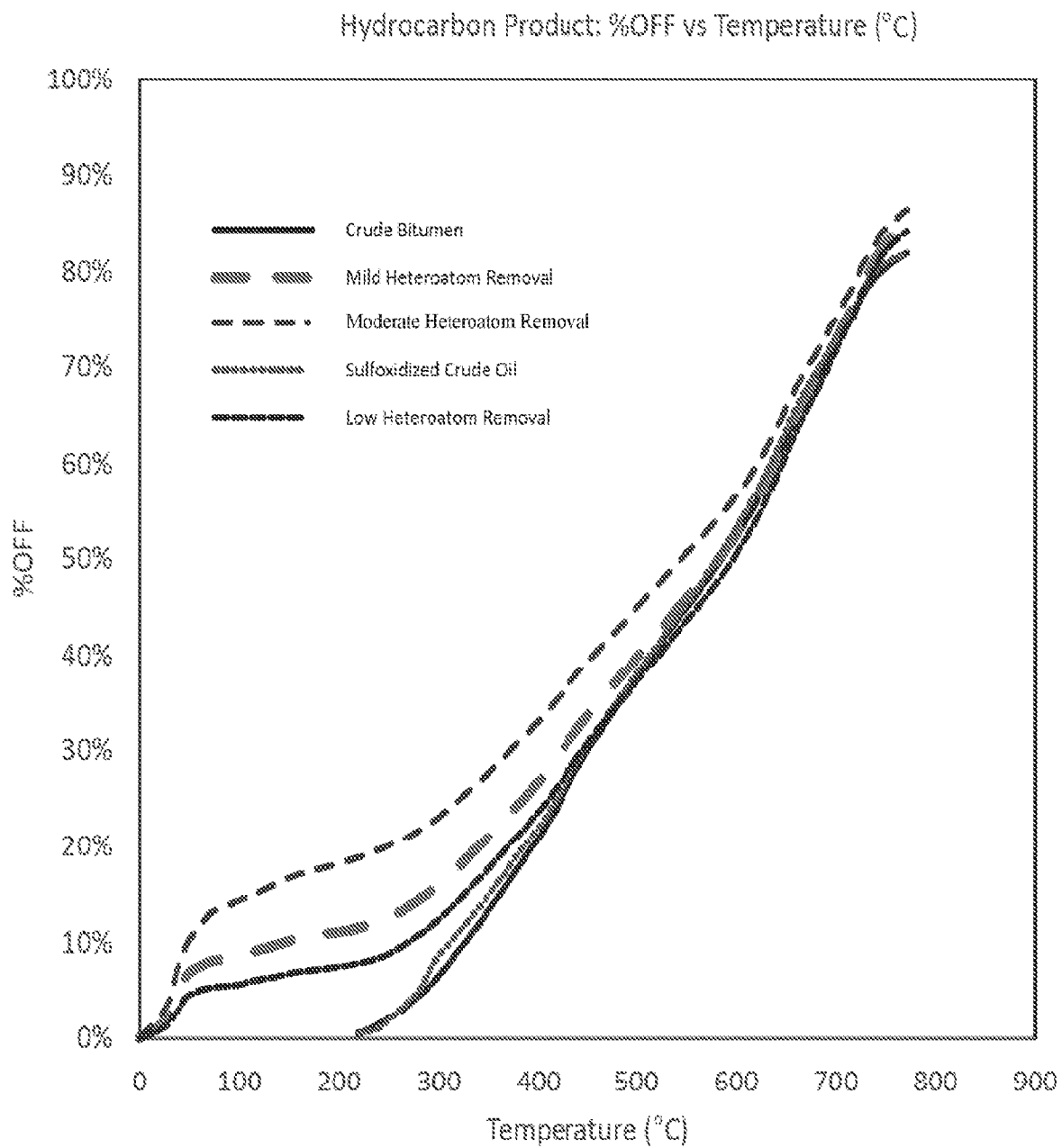


Fig. 6a

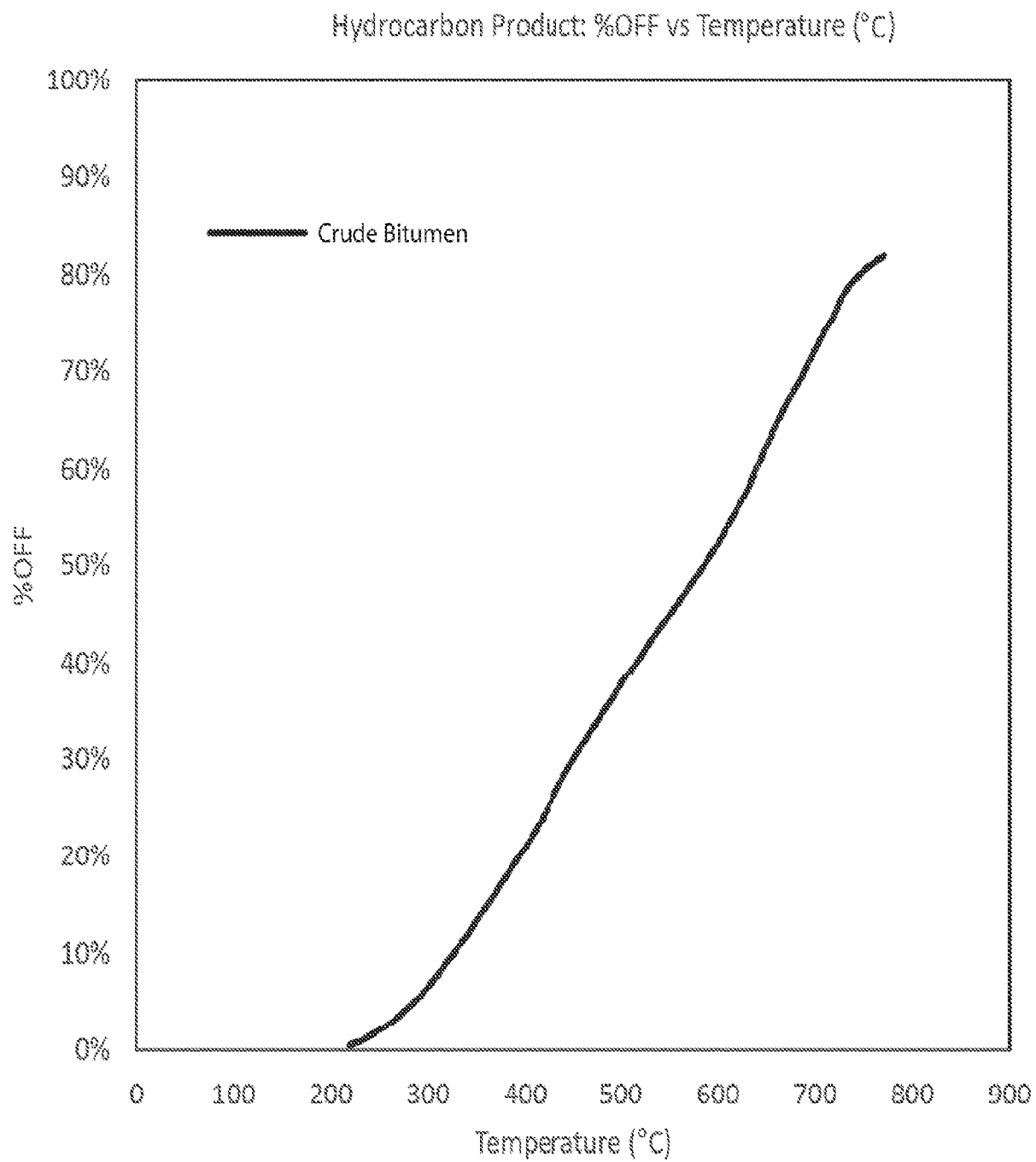


Fig. 6b

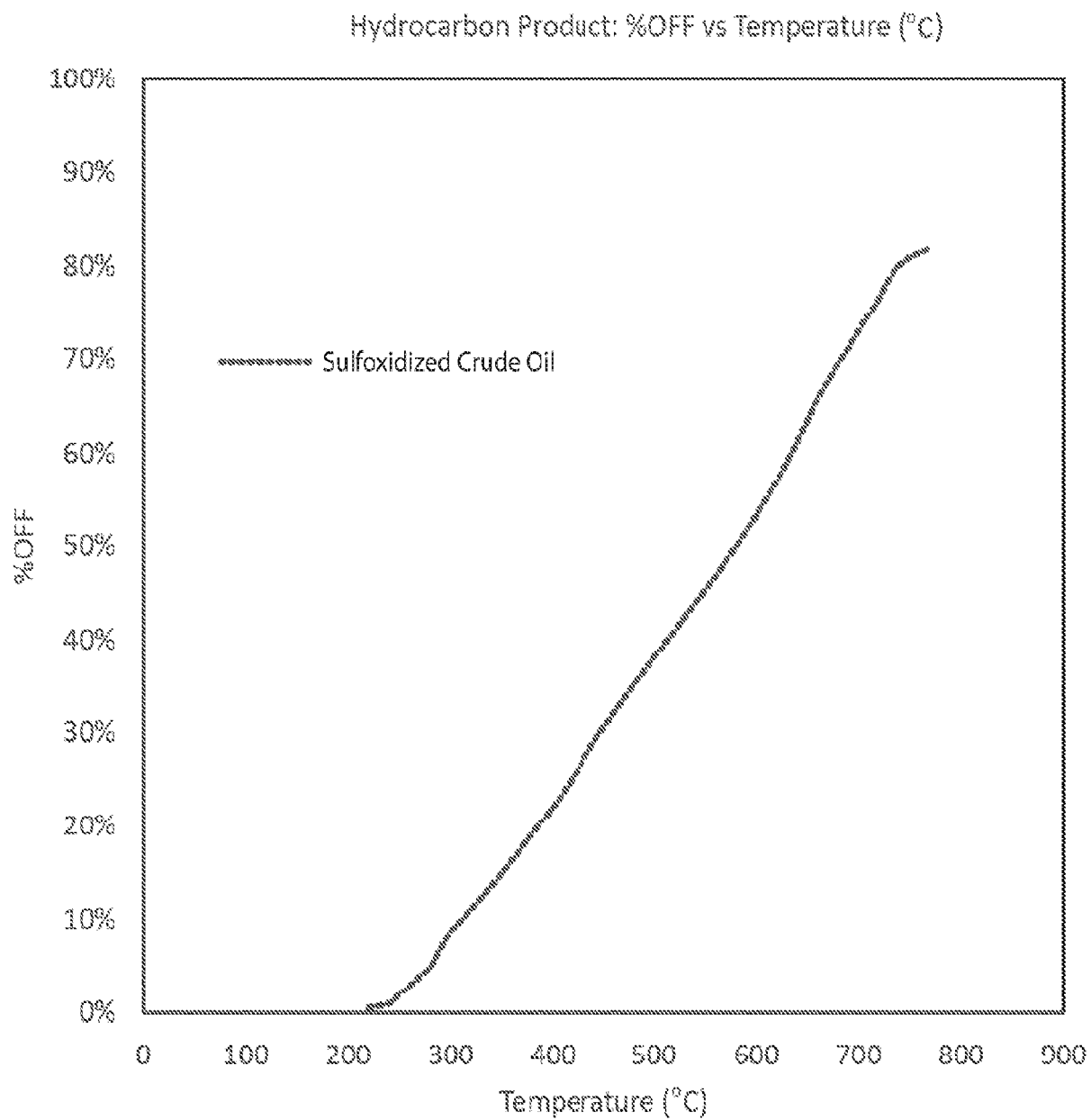


Fig. 6c

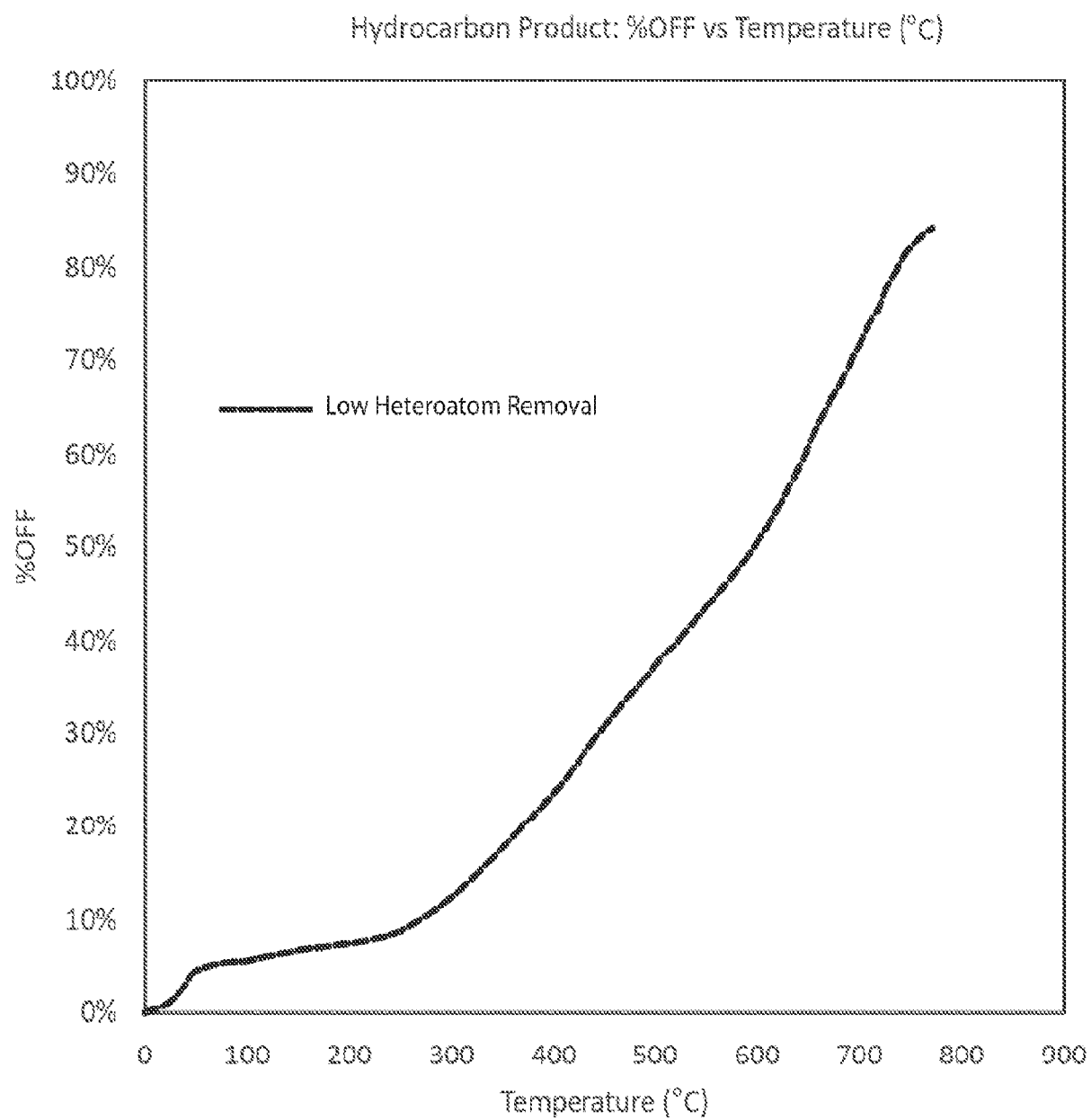


Fig. 6d

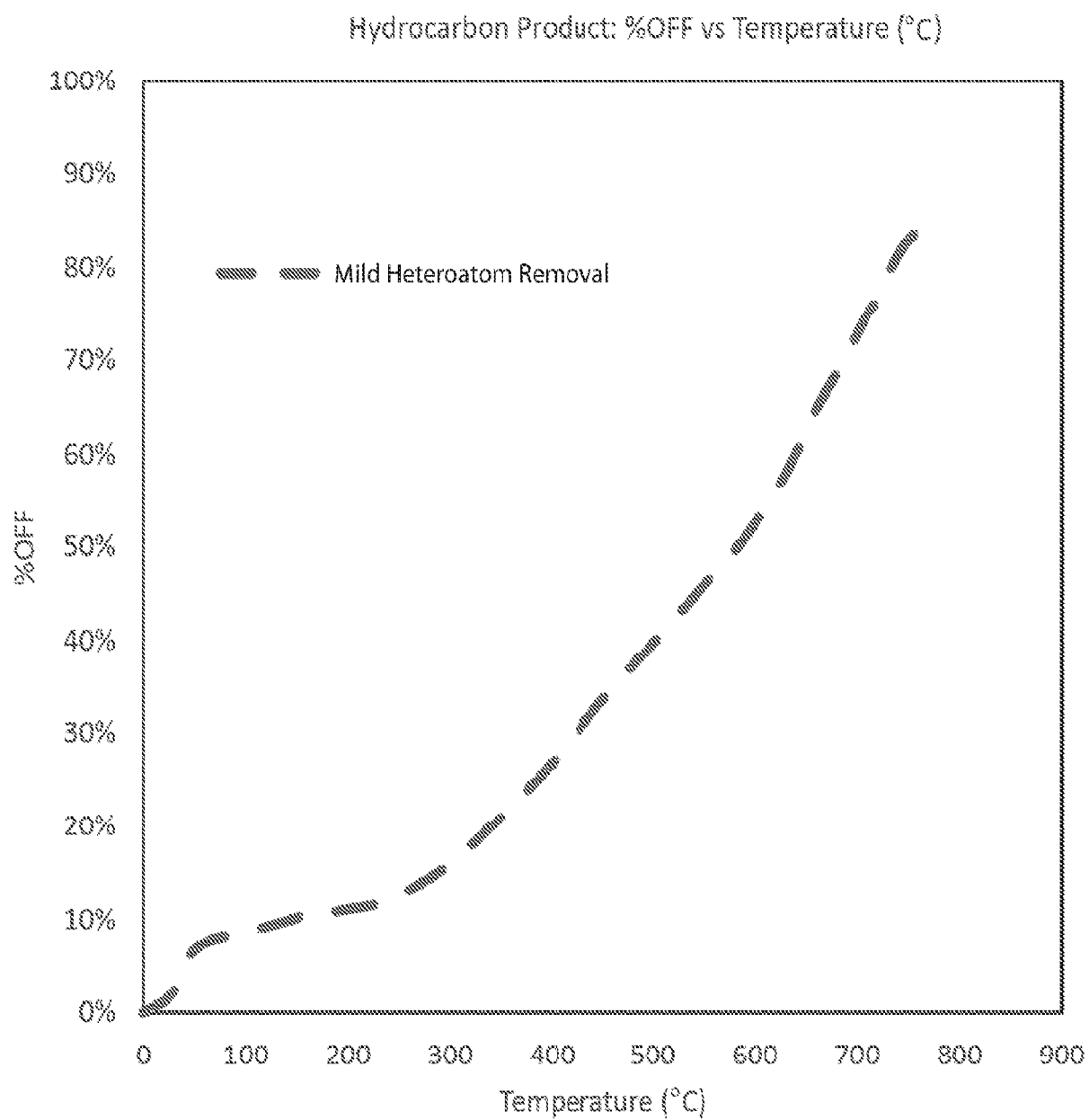


Fig. 6e

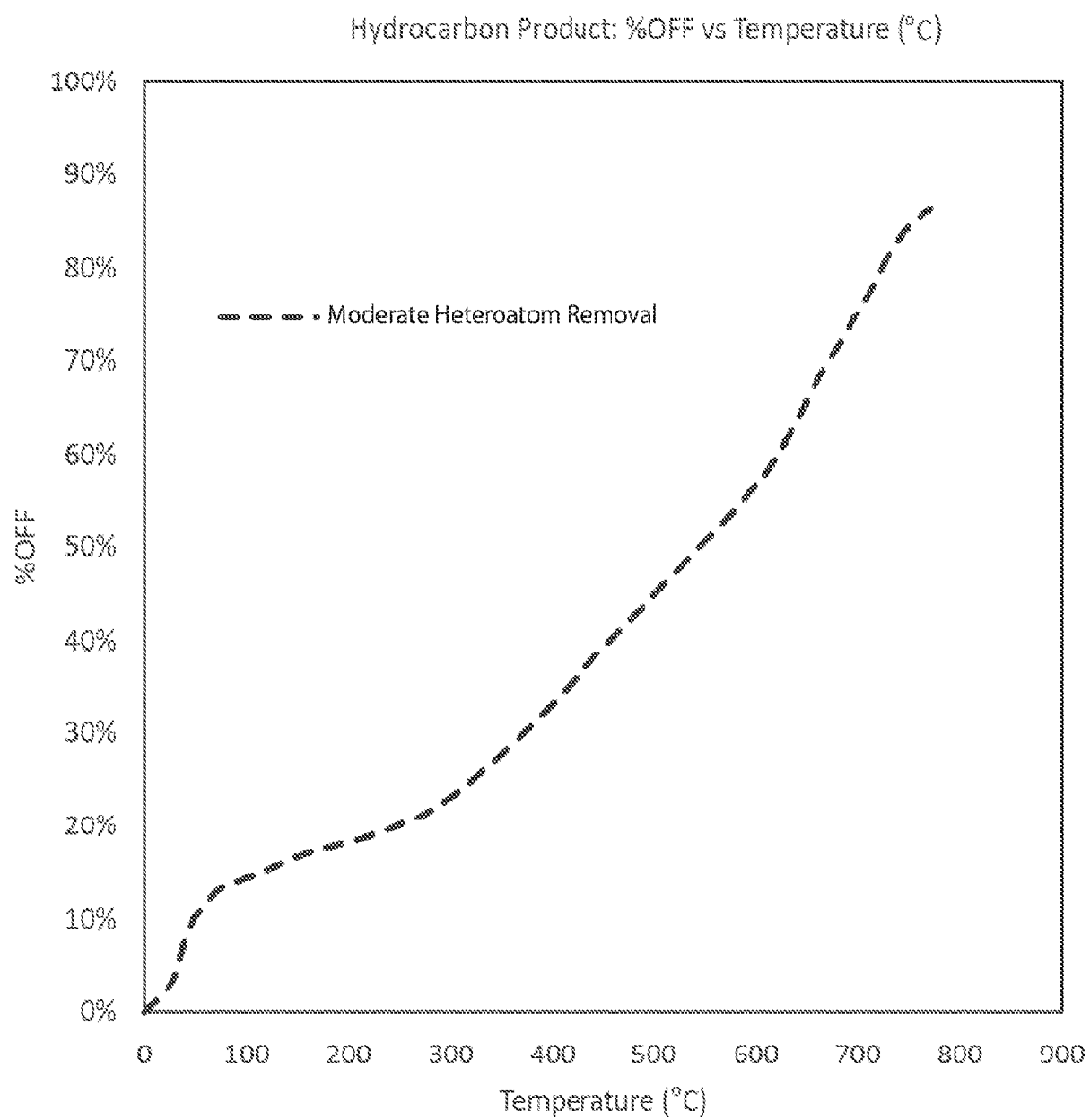


Fig. 6f

IR SPECTROSCOPY HYDROCARBON FEED

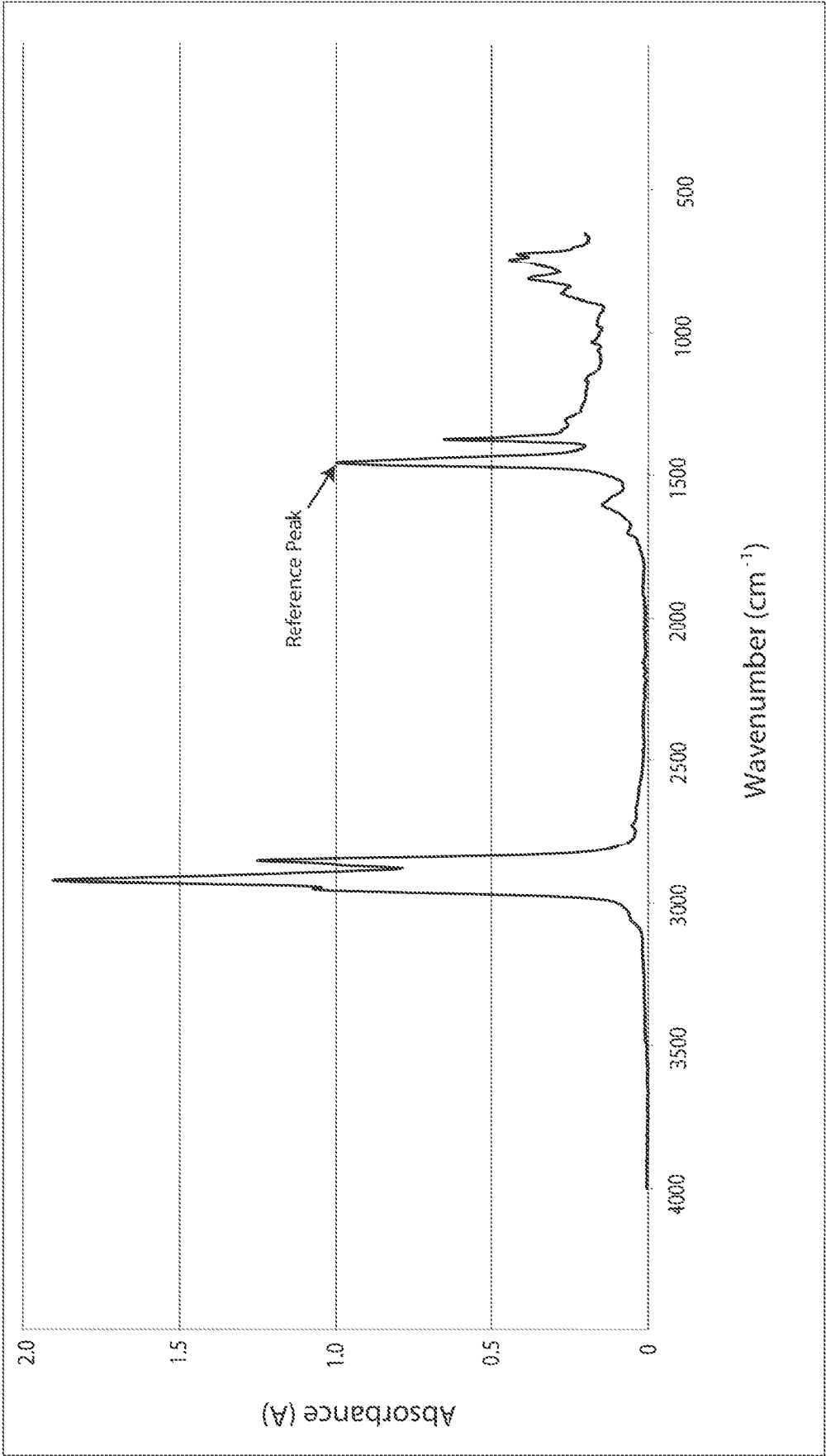


Fig. 7a

IR SPECTROSCOPY SULFOXIDIZED INTERMEDIATE FEED

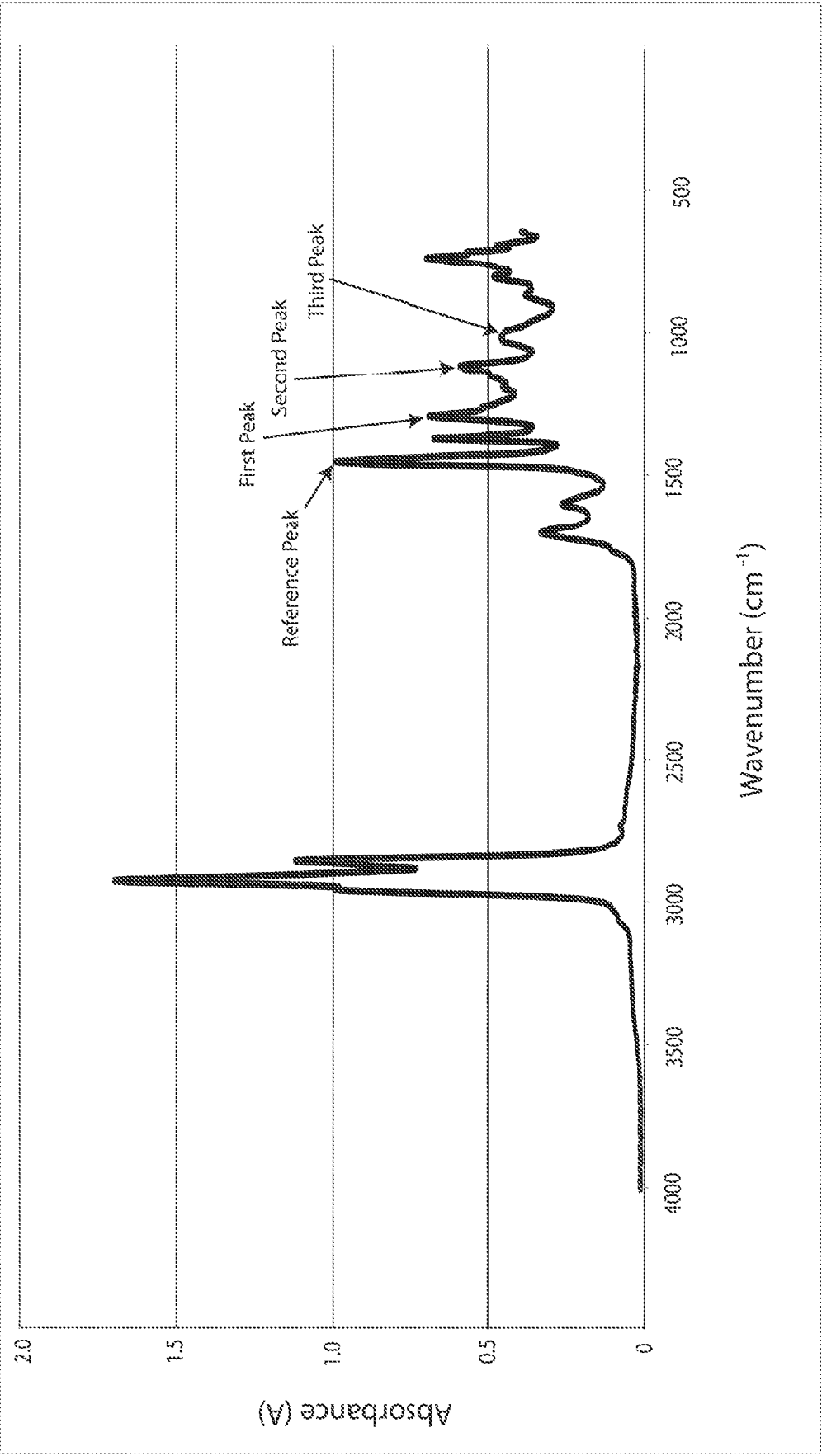


Fig. 7b

IR SPECTROSCOPY HYDROCARBON PRODUCT

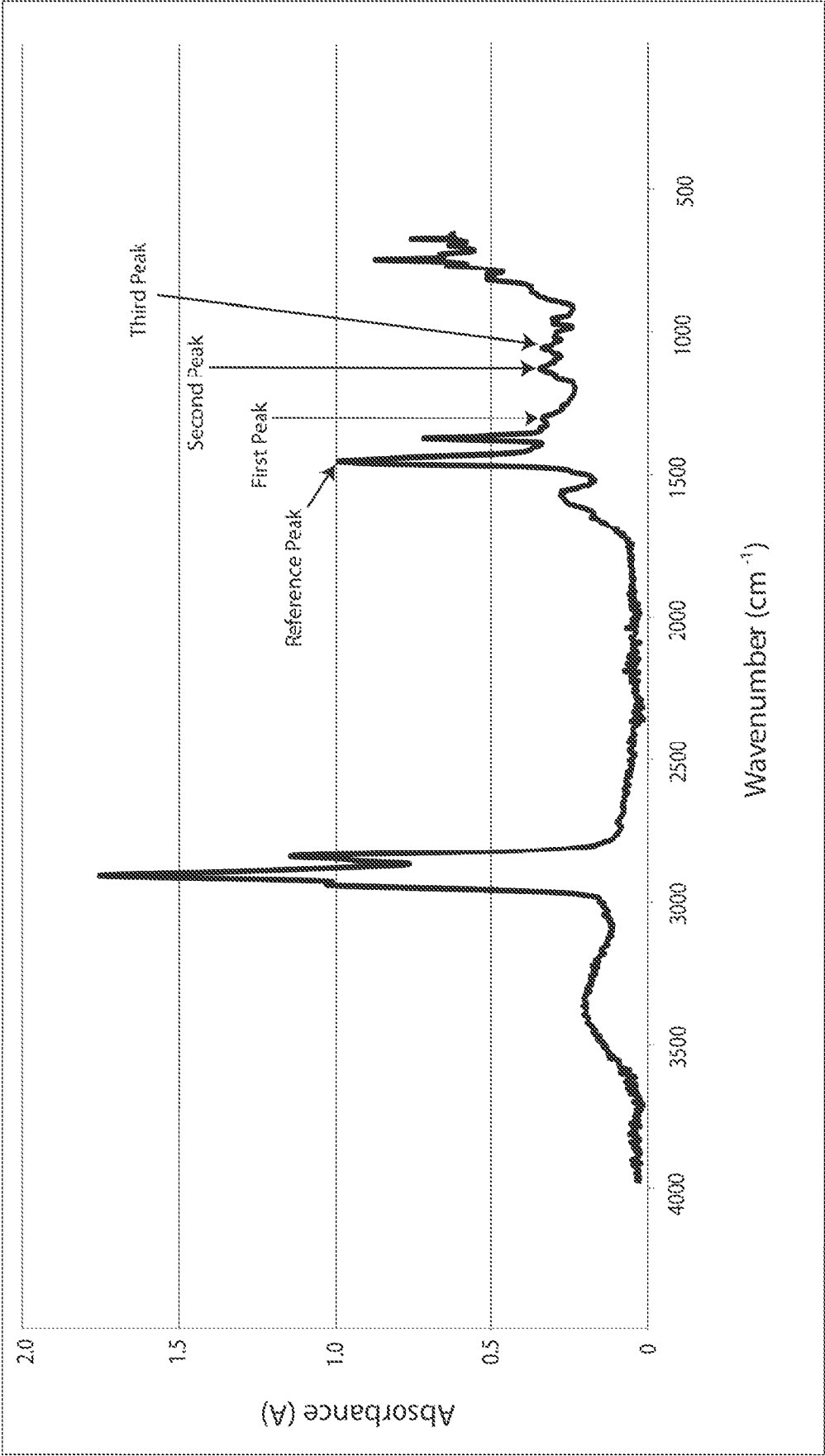


Fig. 7c

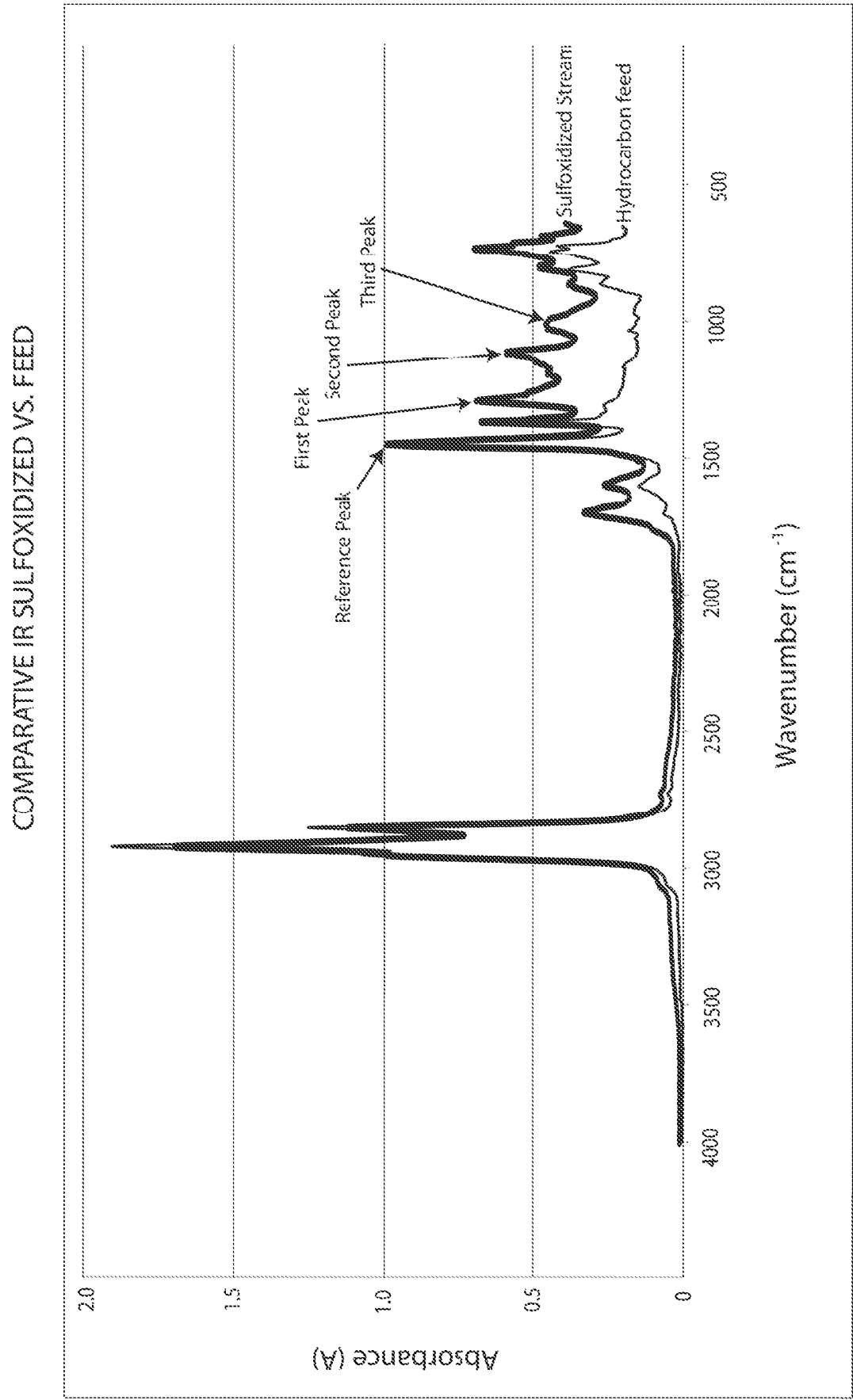


Fig. 7d

COMPARATIVE IR HYDROCARBON PRODUCT VS. FEED

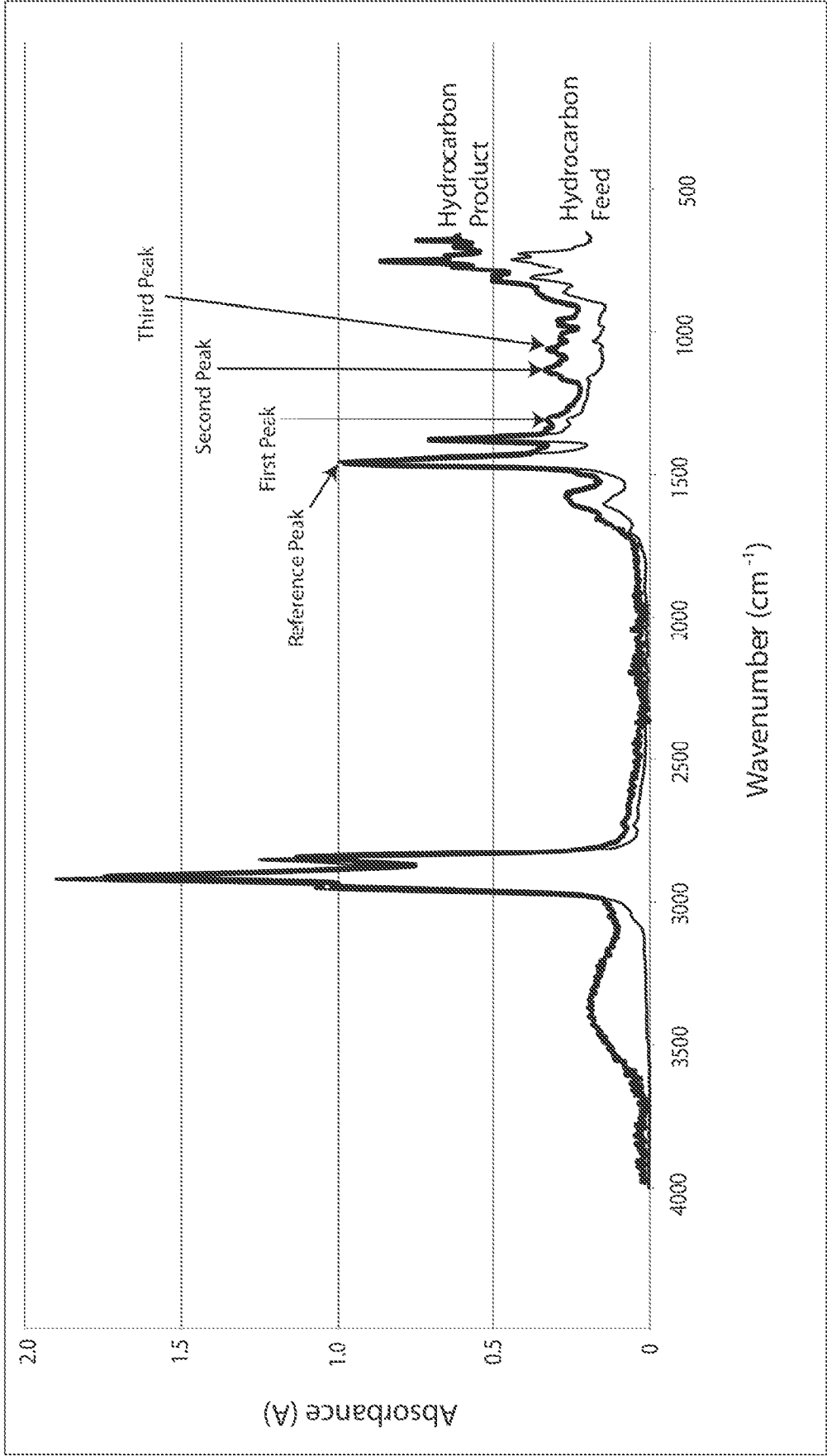


Fig. 7e

COMPARATIVE IR HYDROCARBON PRODUCT VS. SULFOXIDIZED STREAM

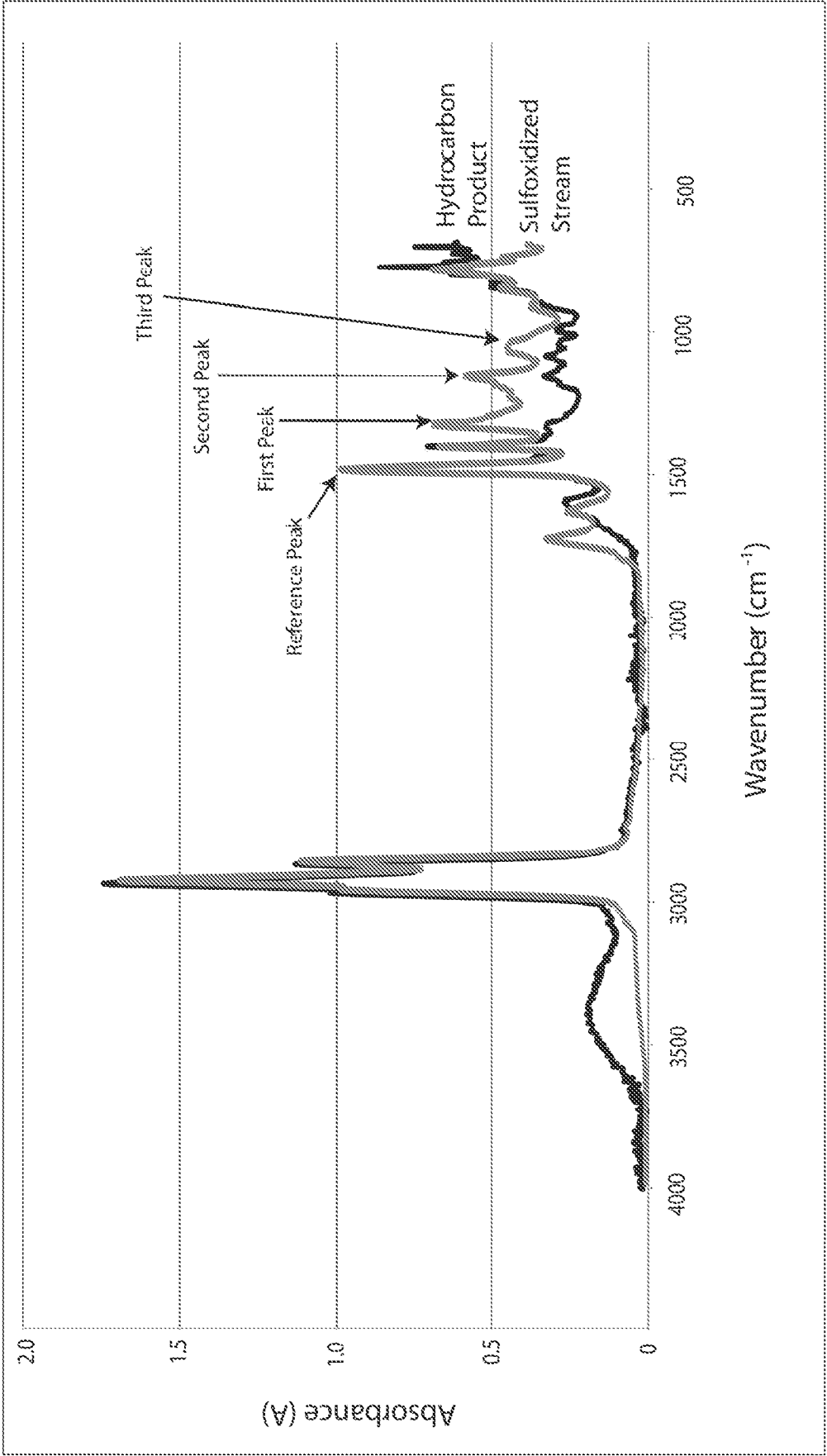


Fig. 7f

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2015/064587

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C10L 1/04 (2016.01)

CPC - C10L 1/04 (2016.01)

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)

IPC(8) - C10G 1/04, 27/12; C10L 1/04 (2016.01)

CPC - C10G 1/04, 27/12; C10L 1/04 (2016.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 208/14; 585/2; IPC(8) - C10G 1/04, 27/12; C10L 1/04; CPC - C10G 1/04, 27/12; C10L 1/04 (keyword delimited)

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

Orbit, Google Patents, Google Scholar.
Search terms used: hydrocarbon, mass.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 2011/0210043 A1 (WELLINGTON et al) 01 September 2011 (01.09.2011) entire document	1-4, 6, 8-10, 12 ----- 5, 7, 11, 14-17, 20, 22-24
X --- Y	WO 2014/095813 A1 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ BV) 26 June 2014 (26.06.2014) entire document	13, 26 ----- 14-25
Y	US 2,789,134 A (NELSON et al) 16 April 1957 (16.04.1957) entire document	5, 19
Y	US 2014/0024569 A1 (BERA et al) 23 January 2014 (23.01.2014) entire document	7, 21
Y	US 2011/0178346 A1 (MILAM et al) 21 July 2011 (21.07.2011) entire document	11, 18, 25
A	US 6,087,662 A (WILT et al) 11 July 2000 (11.07.2000) entire document	1-26
P, X	US 2015/0337208 A1 (AUTERRA INC et al) 26 November 2015 (26.11.2015) entire document	1-26

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

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"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

29 January 2016

Date of mailing of the international search report

16 FEB 2016

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