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(54) Oxidative desulfurization of fuel oil

(57) A method for purifying a sulfur-containing fuel oil comprising (a) contacting in a first reaction mixture the sulfur-containing fuel oil with an exogenous binary catalyst, hydrogen peroxide, and a water-soluble acid at a temperature in a range of from about 25°C to about 150°C to provide a first oxidized mixture; and (b) separating at least one oxidized sulfur compound from the first oxidized mixture to provide a purified fuel oil. The first reaction mixture may further comprise a phase transfer catalyst. Furthermore, the sulfur-containing fuel oil may be deasphalted prior to contacting with the catalyst, hydrogen peroxide, and the water-soluble acid.

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Description

BACKGROUND

[0001] The invention includes embodiments that generally relate to a method for purifying sulfur-containing fuel oil using a catalyst, a water-soluble acid and a peroxide.

[0002] Raw/fossil fuels, such as fuel oil including a crude oil and oil distillates and refinery products like gasoline, kerosene, diesel fuel, naphtha, heavy fuel oil, natural gas, liquefied natural gas and liquefied petroleum gas, and like hydrocarbons, are useful for a number of different processes, particularly as a fuel source, and most particularly for use in a power plant. Virtually all of these fuels contain relatively high levels of naturally occurring, organic sulfur compounds, such as, but not limited to, sulfides, mercaptans and thiophenes. Hydrogen generated in the presence of such sulfur compounds has a poisoning effect on catalysts used in many chemical processes, particularly catalysts used in fuel cell processes, resulting in shortening the life expectancy of the catalysts. When present in a feed stream in a fuel cell process, sulfur compounds may also poison the fuel cell stack itself. Because of the relatively high levels of sulfur compounds that may be present in many crude fuel feed streams, it is necessary that these feed streams be desulfurized.

[0003] Furthermore, desulfurization of fuels has become an important problem due to the upcoming regulatory requirements that require a reduction in current sulfur emissions. Two major tasks in the sulfur removal from fuel include (i) the deep desulfurization of diesel fuel (reducing S content from ~500 parts per million to below 15 parts per million) and, (ii) sulfur removal from crude and heavy fuel oils used for energy production (reducing S content from 3-4 percent to less than 0.5 percent). Conventional hydrodesulfurization (HDS) method using hydrogen have not only been insufficient to effect the deep desulfurization of diesel fuels but are also relatively expensive for the direct sulfur removal from a crude and heavy fuel oils due to high cost of hydrogen and the use of high temperature and pressure. Alternatively oxidative desulfurization (ODS) methods using oxidants like hydrogen peroxide, molecular oxygen or ozone, require somewhat less demanding operating conditions when compared to the operating conditions employed in HDS methods. Further, where oxygen may be used as the stoichiometric oxidant, ODS methods may be cost competitive with HDS methods.

[0004] Thus, there exists a need for efficient and cost effective ODS methods for sulfur removal from fuel, to provide desulfurized fuels that meet modem engineering and regulatory standards.

BRIEF DESCRIPTION

[0005] In one embodiment, the present invention provides a method for purifying a sulfur-containing fuel oil comprising: (a) contacting in a first reaction mixture the sulfur-containing fuel oil with an exogenous binary catalyst, hydrogen peroxide, and a water-soluble acid at a temperature in a range of from about 25°C to about 120°C to provide a first oxidized mixture; and (b) separating at least one oxidized sulfur compound from the first oxidized mixture to provide a purified fuel oil.

[0006] In another embodiment, the present invention provides a method for purifying a sulfur-containing fuel oil comprising (a) contacting in a first reaction mixture the sulfur-containing fuel oil with a hydrocarbon diluent, an exogenous binary catalyst, hydrogen peroxide, and a water-soluble acid at a temperature in a range of from about 25°C to about 110°C to provide a first oxidized mixture; and (b) separating at least one oxidized sulfur compound from the first oxidized mixture; and (c) recovering the hydrocarbon diluent to provide a purified fuel oil.

[0007] In yet another embodiment, the present invention provides a method for purifying a sulfur-containing fuel oil comprising (a) contacting in a first reaction mixture the sulfur-containing fuel oil comprising benzothiophene, dibenzothiophene, alkyl substituted benzothiophenes, and alkyl substituted dibenzothiophenes with petroleum ether, an exogenous binary catalyst, hydrogen peroxide, and a water-soluble acid at a temperature in a range of from about 25°C to about 120°C to provide a first oxidized mixture comprising sulfoxides and sulfones of benzothiophene, dibenzothiophene, alkyl substituted benzothiophenes, and alkyl substituted dibenzothiophenes; (b) separating at least one oxidized sulfur compound from the first oxidized mixture; and (c) recovering petroleum ether to provide a purified fuel oil.

[0008] These and other features, aspects, and advantages of the present invention may be understood more readily by reference to the following detailed description.

DETAILED DESCRIPTION

[0009] In the following specification and the claims, which follow, reference will be made to a number of terms, which shall be defined to have the following meanings.

[0010] The singular forms "a", "an", and "the" include plural referents unless the context clearly dictates otherwise. "Optional" or "optionally" means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where the event occurs and instances where it does not.

[0011] Approximating language, as used herein throughout the specification and claims, may be applied to modify any quantitative representation that could permissibly vary without resulting in a change in the basic function to which it is related. Accordingly, a value modified by a term or terms, such as "about" and "substantially", are not to be limited to the precise value specified. In at least some instances, the approximating language may correspond to the precision of an instrument for measuring the value. Here and throughout the specification and claims, range limitations may be combined and/or interchanged, such ranges are identified and include all the sub-ranges contained therein unless context or language indicates otherwise.

[0012] In one embodiment, the present invention provides a method for purifying a sulfur-containing fuel oil comprising, (a) contacting in a first reaction mixture the sulfur-containing fuel oil with an exogenous binary catalyst, hydrogen peroxide, and a water-soluble acid at a temperature in a range of from about 25°C to about 150°C to provide a first oxidized mixture; and (b) separating at least one oxidized sulfur compound from the first oxidized mixture to provide a purified fuel oil.

[0013] In one embodiment, the sulfur-containing fuel oil is a crude oil, for example Saudi sweet crude oil, West Texas Intermediate crude oil, Dubai crude oil, and Brent crude oil. In an alternate embodiment, the sulfur-containing fuel oil is a crude oil, which has been subjected to asphaltene removal. In one embodiment, the sulfur-containing fuel oil is a distillate or other refinery products of a crude oil like gasoline, kerosene, diesel fuel, naphtha, heavy fuel oil, natural gas, liquefied natural gas and liquefied petroleum gas. In one embodiment, the sulfur-containing fuel oil comprises dibenzothiophene, benzothiophene, alkyl substituted dibenzothiophenes, and alkyl substituted benzothiophenes.

[0014] In one embodiment, the sulfur-containing fuel oil comprises less than 5 weight percent sulfur based on the weight of sulfur-containing fuel oil. In another embodiment, the sulfur-containing fuel oil comprises less than 3 weight percent sulfur based on the weight of sulfur-containing fuel oil. In another embodiment, the sulfur-containing fuel oil comprises less than 2 weight percent sulfur based on the weight of sulfur-containing fuel oil.

[0015] As used herein the phrase "exogenous binary catalyst" means an "external binary catalyst" that is combined in a first reaction mixture with a sulfur-containing fuel oil. In one embodiment, the exogenous binary catalyst comprises a first component, a catalyst and a second component, a promoter. In one embodiment, the binary catalyst comprises a first component selected from the group consisting of phosphate salts, and oxides, acids and salts of molybdenum, tungsten, manganese, and combinations thereof; and the second component is selected from the group consisting of oxides and salts of cerium, iron, vanadium, titanium, manganese, cobalt, nickel, copper and combinations thereof. In another embodiment, the first component comprises an oxide or a salt of molybdenum. In another embodiment, the molybdenum containing first component is a molybdenum isopolyacid or heteropolyacid or its salt with different cations, for example, ammonium or alkali metal. The isopolyacid means a polyacid having a polynuclear structure wherein a single oxo-acid is condensed. The heteropolyacid means a polyacid having a polynuclear structure wherein two or more kinds of oxo-acids may be condensed. The heteropolyacid has a structure comprising a condensed structure of an acid forming the skeleton (skeleton acid) and a small number of other kinds of atoms (hetero atom) contained in the center thereof and the like. In yet another embodiment, the first component comprises an oxide or a salt of manganese. In another embodiment, the second component comprises an oxide or a salt of cobalt. In yet another embodiment, the second component comprises an oxide or a salt of cerium. In still yet another embodiment, the second component comprises an oxide or a salt of iron.

[0016] In one embodiment, the exogenous binary catalyst may comprise oxides or salts of molybdenum as the first component and oxides or salts of cerium as the second component. In another embodiment, the binary catalyst may comprise oxides or salts of manganese as the first component and oxides or salts of iron, cobalt, or nickel as the second component. In yet another embodiment, the binary catalyst may comprise a phosphate salt, for example ammonium hydrophosphate as the first component and oxides or salts of iron, cobalt, or nickel as the second component.

[0017] In one embodiment, the total amount of the first component and the second component used in the first reaction mixture is in a range of from about 0.5 weight percent to about 10 weight percent based on the amount of sulfur-containing fuel oil. In another embodiment, the total amount of the first component and the second component used in the first reaction mixture is in a range of from about 0.5 weight percent to about 5 weight percent based on the amount of sulfur-containing fuel oil. In yet another embodiment, the total amount of the first component and the second component used in the first reaction mixture is in a range of from about 1 weight percent to about 3 weight percent based on the amount of sulfur-containing fuel oil.

[0018] In one embodiment, the atomic ratio of the first component to the second component is 6:1. In another embodiment, the atomic ratio of the first component is 9:1. In yet another embodiment, the atomic ratio of the first component to the second component is 12:1. In one embodiment, a physical mixture of the first and the second components may be used as the binary catalyst. In another embodiment, a pre-synthesized complex compound comprising the first and the second components, for example a heteropolyanion salt may be used as the exogenous binary catalyst.

[0019] In one embodiment, the water-soluble acid may be selected from the group consisting of formic acid, acetic acid, propionic acid, butyric acid, sulfuric cid, phosphoric acid, and mixtures of two or more of the foregoing acids. In one embodiment, the acid is acetic acid. In another embodiment, the acid is formic acid. In yet another embodiment, the acid is sulfuric acid. In one embodiment, acetic acid anhydride may be used to generate acetic acid in situ in the first reaction mixture.

[0020] In one embodiment, the amount of water-soluble acid employed in the oxidation reaction is in a range of from about 15 volume percent to about 40 volume percent based on the amount of the sulfur-containing fuel oil. In another embodiment, the amount of water-soluble acid employed in the oxidation reaction is in a range of from about 20 volume percent to about 35 volume percent based on the amount of the sulfur-containing fuel oil. In another embodiment, the amount of water-soluble acid employed in the oxidation reaction is in a range of from about 25 volume percent to about 30 volume percent based on the amount of the sulfur-containing fuel oil.

[0021] In one embodiment, the amount of hydrogen peroxide (calculated as 100 percent) employed in the oxidation reaction is in a range of from about 4 weight percent to about 20 weight percent based on the amount of the sulfur-containing fuel oil. In another embodiment, the amount of hydrogen peroxide employed in the oxidation reaction is in a range of from about 5 weight percent to about 15 weight percent based on the amount of the sulfur-containing fuel oil. In yet another embodiment, the amount of hydrogen peroxide employed in the oxidation reaction is in a range of from about 6 weight percent to about 10 weight percent based on the amount of the sulfur-containing fuel oil. In one embodiment, hydrogen peroxide may be added as an aqueous solution having a concentration in a range of from about 15 weight percent to about 30 weight percent. In various embodiments, hydrogen peroxide may be added to the first reaction mixture using methods known to one skilled in the art, such as for example, in a continuous manner or in portions.

[0022] In one embodiment, the at least one oxidized sulfur compound may be separated from the first oxidized mixture using a solid-liquid extraction process, for example an adsorption process, to provide the purified fuel oil. In one embodiment, the at least one oxidized sulfur compound may be separated from the first oxidized mixture using a liquid-liquid extraction process, to provide the purified fuel oil. One skilled in the art can easily determine the process and the conditions required to achieve satisfactory separation.

[0023] In one embodiment, the method for purifying the sulfur-containing fuel oil further comprises a step of recovering the binary catalyst. In one embodiment, the binary catalyst is recovered from the first oxidized mixture by filtration or centrifuging/decantation, using methods known to one skilled in the art.

[0024] In one embodiment, the first oxidized mixture is contacted with a porous silica adsorbent material, wherein the adsorbent material is characterized by a Brunauer-Emmett-Teller (BET) surface area value (total) of at least about 15 m^2/g; and a Barrett-Joyner-Halenda (BJH) pore volume (total) of at least about 0.5 cc/g. Such porous adsorbent materials and their use are described in copending US Patent Application Serial No. 11/934298 filed November 2, 2007 which is incorporated herein by reference in its entirety. In instances wherein the sulfur-containing fuel oil comprises other metallic impurities such as vanadium compounds, such contact results in removal of these other metallic impurities or their oxidation products from the first oxidized mixture.

[0025] In another embodiment, the first reaction mixture further comprises a phase transfer catalyst. In one embodiment, the phase transfer catalyst comprises a quaternary ammonium salt or a phosphonium salt. Non-limiting examples of suitable phase transfer catalysts may be selected from the group consisting of methyltrioctylammonium chloride (Aliquat 336 ™), tetraalkylammonium bromide, trialkylmethylammonium bromide, and hexaethylguanidium bromide. In another embodiment, the phase transfer catalyst comprises a quaternary ammonium or a phosphonium salt comprising an heteropolyanion $M^1{}_nM^2mO^q{}_p$, wherein M^1 is selected from the group consisting of phosphorus, cerium, vanadium, manganese, iron, and cobalt, M^2 is selected from the group consisting of molybdenum, tungsten and vanadium or their mixture, "n" is an integer having a value 1 to 2, "m" is an integer having a value 6 to 18, "p" is an integer having a value 24 to 62, and "q" is an integer having a value 3 to 6.

[0026] In one embodiment, the amount of phase transfer catalyst used is in a range of from about 0.1 weight percent to about 10 weight percent based on the amount of sulfur-containing fuel oil. In another embodiment, the amount of phase transfer catalyst used is in a range of from about 0.5 weight percent to about 1 weight percent based on the amount of sulfur-containing fuel oil. In yet another embodiment, the amount of phase transfer catalyst used is in a range of from about 1 weight percent to about 3 weight percent based on the amount of sulfur-containing fuel oil.

[0027] In one embodiment, the temperature at which the oxidation (also referred to as contacting the fuel oil with an exogenous binary catalyst, hydrogen peroxide, and an acid at a temperature in a range of from about 25°C to about 120°C, to provide a first oxidized mixture) is carried out is in a range of from about 25°C to about 110°C. In another embodiment, the temperature at which the oxidation is carried out is in a range of from about 55°C to about 95°C. In yet another embodiment, the temperature at which the oxidation is carried out is in a range of from about 60°C to about 90°C.

[0028] In another embodiment, the sulfur-containing fuel oil is deasphalted prior to contacting the sulfur-containing fuel oil with the binary catalyst and oxygen. Deasphalting of the sulfur-containing fuel oil may be carried out by methods known to one skilled in the art. Typically, deasphalting is carried out by contacting the sulfur-containing fuel oil with an inert diluent and filtering or centrifuging the resultant mixture to separate the fuel oil from the insoluble asphaltenes to provide a deasphalted fuel oil. In one embodiment, the inert diluent is selected from the group consisting of liquid saturated hydrocarbons, liquid cyclic hydrocarbons, and mixtures of at least two of the foregoing inert diluents. Suitable non-limiting examples of liquid cyclic hydrocarbons include cyclohexane, cycloheptane, and decalin. Suitable non-limiting examples of liquid saturated hydrocarbons include propane, butane, and petroleum ether. In one embodiment, the method for purifying the sulfur-containing fuel oil further comprises a step of recovering the inert diluent. In one embodiment, the inert diluent is recovered from the first oxidized mixture by distillation, using methods known to one skilled in the art.

[0029] In another embodiment, the present invention provides a method for purifying a sulfur-containing fuel oil comprising (a) contacting in a first reaction mixture the sulfur-containing fuel oil with a hydrocarbon diluent, an exogenous binary catalyst, hydrogen peroxide, and a water-soluble acid at a temperature in a range of from about 25°C to about 110°C to provide a first oxidized mixture; and (b) separating at least one oxidized sulfur compound from the first oxidized mixture; and (c) recovering the hydrocarbon diluent to provide a purified fuel oil.

[0030] In yet another embodiment, the present invention provides a method for purifying a sulfur-containing fuel oil comprising (a) contacting in a first reaction mixture the sulfur-containing fuel oil comprising benzothiophene, dibenzothiophene, alkyl substituted benzothiophenes, and alkyl substituted dibenzothiophenes with petroleum-ether, an exogenous binary catalyst, hydrogen peroxide, and a water-soluble acid at a temperature in a range of from about 25°C to about 120°C to provide a first oxidized mixture comprising sulfoxides and sulfones of benzothiophene, dibenzothiophene, alkyl substituted benzothiophene, and alkyl substituted dibenzothiophene; (b) separating at least one oxidized sulfur compound from the first oxidized mixture; and (c) recovering petroleum-ether to provide a purified fuel oil.

[0031] The following examples are intended only to illustrate methods and embodiments in accordance with the invention, and as such should not be construed as imposing limitations upon the claims.

EXAMPLES

[0032] Reagents and catalysts employed herein were obtained from Aldrich Chemical Company.

[0033] Examples 1 to 21 and Comparative Examples CE-1 to CE-11 : Effect Of Oxidative Desulfurization On A Sulfur-Containing Fuel Oil Model Mixture.

[0034] Two model mixtures were prepared as described below. The first model mixture was prepared from tetralin and benzothiophene (BT), and dibenzothiophene (DBT) wherein the sulfur-containing compounds were present in a 1:2 weight ratio (mixture #1). The second model mixture was prepared from tetralin and dioctylsulfide (DOS), BT, and DBT wherein the sulfur-containing compounds were present in a 2:2:3 weight ratio (mixture #2). The mixture #1 was used in Examples 1 to 16 and Comparative examples 1 to 7. The mixture #2 was used in Examples 17 to 19 and Comparative examples 8 to 9. The model mixtures were shown to comprise about 3 weight percent sulfur, when tested using a Varian Saturn 2000 GCMS.

[0035] 5 milliliters (ml) of a model mixture, sulfuric acid 0.6 grams (g), a catalyst 50 milligrams (mg) and a co-catalyst 5 to 25 mg; or a combination of 5 ml of model mixture, acetic acid 0.6 g, a cataylst 50 mg, and a co-catalyst 5 to 25 mg; or a combination of 5 ml of model mixure, an acid 0.6 g, a catalyst 50 mg, a co-catalyst 5 to 25 mg, and 100 mg of a phase transfer catalyst Aliquat 336™ were placed in two-dram vials equipped with magnetic cross-like stirbars. Hydrogen peroxide (30 weight percent, 2 ml) was then added to each of the vials and the vials were placed in a Thermoline dry block heater and stirrer. The reaction mixture was stirred for about 30 minutes. The vials were removed and cooled in an ice bath. The cooled mixture was filtered through a filter device (Whatman autovial 0.45 micron PTFE). The filtrate was collected in a fresh vial. On standing, the filtrate separated into a top oil layer and a bottom aqueous layer. For analysis, the top oil layer 0.25 ml was diluted with 2.25 ml of acetonitrile containing 0.35 weight percent of biphenyl (internal standard). The diluted oil layer was analyzed on the Varian Saturn 2000 GCMS. The results are provided in Table 1, Table 2, and Table 3 below.

Table 1. Conversion of BT and DBT in the reaction of oxidation with hydrogen peroxide in the presence of exogenous binary calaysts and sulfuric acid.

Example	Catalyst	Co-Catalyst		Catalyst -Co-Catalyst molar ratio	Conversion Percentage	
		Formula	mg		DBT	DOS
1	Na_2WO_4	$Ce(NO_3)_3$	7	11.9	43.2	82.0
2	Na_2WO_4	$(NH_4)Fe(SO_4)_2$	12	6.1	40.9	65.9
3	Na_2WO_4	$NiSO_4$	7	5.7	47.7	81.4
4	Na_2WO_4	$Co(OAc)_2$	8	4.7	44.8	80.5
5	$(NH_4)_6Mo_7O_{24}$	$Ce(NO_3)_3$	13	11.9	65.0	92.9

(continued)

Example	Catalyst	Co-Catalyst		Catalyst -Co-Catalyst molar ratio	Conversion Percentage	
		Formula	mg		DBT	DOS
6	$(NH_4)_6Mo_7O_{24}$	CoSO4	7	6.3	30.2	98.1
7	$MnSO_4$	$(NH_4)Fe(SO_4)_2$	24	5.9	80.0	73.7
8	$MnSO_4$	$NiSO_4$	9	8.6	40.4	24.3
9	$MnSO_4$	$Co(OAc)_2$	15	4.9	87.6	70.7
10	$MnSO_4$	$Ce(NO_3)_3$	14	11.6	87.5	38.4
11	$MnSO_4$	$KMnO_4$	5	9.3	47.3	43.6
12	$NH_4H_2PO_4$	$CoSO_4$	7	4.8	40.3	55.8
CE-1	Na_2WO_4	None	-	-	35.0	55.7
CE-2	$(NH_4)_6Mo_7O_{24}$	None	-	-	56.3	98.6
CE-3	$MnSO_4$	None	-	-	21.6	27.3
CE-4	$NH_4H_2PO_4$	None	-	-	19.4	15.4

Table 2. Conversion of BT and DBT in the reaction of oxidation with hydrogen peroxide in the presence of exogenous binary catalysts and acetic acid.

Example	Catalyst	Co-Catalyst		Catalyst -Co-Catalyst molar ratio	Conversion Percentage	
		Formula	mg		DBT	DOS
13	MoO_3	$(NH_4)Fe(SO_4)_2$	5	33.1	69.8	67.8
14	$NH_4H_2PO_4$	$CoSO_4$	5	13.5	87.9	17.2
15	$NH_4H_2PO_4$	$NiSO_4$	12	9.5	88.4	25.3
16	$(NH_4)_6Mo_7O_{24}$	$Ce(NO_3)_3$	13	11.9	48.5	54.4
CE-5	MoO_3	None	-	-	13.9	16.2
CE-6	$NH_4H_2PO_4$	None	-	-	10.8	8.0
CE-7	$(NH_4)_6Mo_7O_{24}$	None	-	-	34.2	45.6

Table 3. Conversion of BT and DBT in the reaction of the oxidation with hydrogen peroxide in the presence of binary catalysts, an acid, and a phase transfer catalyst.

Example	Catalyst	Co-Catalyst		Acid	Phase transfer catalyst	Conversion Percentage		
		Formula	mg			BT	DBT	DOS
17	$(NH_4)_6Mo_7O_{24}$	$KMnO_4$	5	Sulfuric	Yes	69.8	67.8	100
18	$(NH_4)_6Mo_7O_{24}$	$KMnO_4$	5	Acetic	Yes	87.9	17.2	100

(continued)

Example	Catalyst	Co-Catalyst		Acid	Phase transfer catalyst	Conversion Percentage		
		Formula	mg			BT	DBT	DOS
19	$(NH_4)_6Mo_7O_{24}$	$MnSO_4$	6	Sulfuric	Yes	83.0	99.7	100
20	$(NH_4)_6Mo_7O_{24}$	$MnSO_4$	6	Acetic	Yes	81.0	99.8	100
21	$(NH_4)Fe(SO_4)_2$	$CoSO_4$	9	Acetic	Yes	88.4	25.3	87.5
CE-8	$(NH_4)_6Mo_7O_{24}$	$KMnO_4$	5	Sulfuric	No	48.5	54.4	14.6
CE-9	$(NH_4)_6Mo_7O_{24}$	$KMnO_4$	5	Acetic	No	16.0	4.4	8.3
CE-10	$(NH_4)_6Mo_7O_{24}$	$MnSO_4$	6	Sulfuric	No	56.4	86.9	99.8
CE-11	$(NH_4)_6Mo_7O_{24}$	$MnSO_4$	6	Acetic	No	30.0	50.1	99.7

[0036] Examples 1 to 21 demonstrate that the process disclosed herein, generally affords satisfactory sulfur removal of greater than about 85 percent. Further, catalyst activity appears to be dependent on the molecular structure of the catalyst. On comparing the conversion efficiency of catalysts in Tables 1 and 2, it can be seen that the binary catalysts having the following combinations Mo/Fe, P/Co, and P/Ni demonstrate good catalytic activity in the presence of acetic acid, while binary catalysts having the following combinations Mo/Ce, Mo/Ni, and Mn/Co demonstrate good catalytic activity in the presence of sulfuric acid. Furthermore, at least as seen in Examples 9 and 10 and Comparative examples CE-2 the use of binary catalysts significantly improves the conversion of the most difficult to oxidize sulfur-containing compound BT from about 56 percent in the absence of the catalyst to about 87 percent in the presence of the catalyst. Also, as seen in Table 3, Examples 17 to 21, use of a phase transfer catalyst demonstrates significant improvement in the conversion of all the sulfur compounds used to prepare the model fuel mixtures.

[0037] Examples 22 to 26 and Comparative Examples CE-12 to CE-13: Effect Of Oxidative Desulfurization On A Sulfur-Containing Distillate Fuel Oil.

[0038] 25 ml of Saudi Crude atmospheric distillate fraction 600 - 700 °F (315 - 370 °C), containing 2.255 weight percent sulfur, is first mixed with sulfuric or acetic acid and a binary catalyst consisting of about 250 mg of the first component and about 50 mg of the second component and placed into a reaction flask. Hydrogen peroxide (30 weight percent) is then added sequentially in three portions by 3 ml to the flask under stirring. The reaction mixture is stirred for about 30 minutes. The mixture is centrifuged and the oil layer is separated from the aqueous one. The oil layer is washed with 10 ml of acetonitrile to remove oxidized products. The oil layer is analyzed on the Spectro Phoenix II XRF analyzer. The results are provided in Table 4 below. In general, the oxidized sulfur compounds may be separated from the crude oil containing reaction mixture (first oxidized mixture) using any of the techniques disclosed herein as being effective for that purpose.

Table 4. Sulfur removal from distillate fuel oil and oil yield in the reaction of the oxidation with hydrogen peroxide in the presence of binary catalyst, an acid, and a phase transfer catalyst.

Example	Catalyst	Co-Catalyst		Acid	Phase transfer catalyst	Sulfur in treated oil, perent	Sulfur removal, percent	Oil yield, percent
		Formula	mg					
22	$MnSO_4$	$Co(OAc)_2$	53	Sulfuric	No	0.49	78.2	59.1
23	$(NH_4)_6Mo_7O_{24}$	$Ce(NO_3)_3$	51	Sulfuric	No	0.40	82.3	83.5
24	$(NH_4)_6Mo_7O_{24}$	$MnSO_4$	52	Acetic	No	1.47	34.8	86.0
25	$(NH_4)_6Mo_7O_{24}$	$MnSO_4$	52	Acetic	Yes	1.29	42.8	84.0
CE-12	$MnSO_4$	None	-	Sulfuric	No	1.03	54.3	85.1
CE-13	$(NH_4)_6Mo_7O_{24}$	None	-	Sulfuric	No	0.41	81.8	50.4

[0039] Examples 22 to 25 also demonstrate that the process disclosed herein, generally applicable to real oil distillates and affords satisfactory sulfur removal of greater than about 80 percent at satisfactory fuel oil yield. On comparing the ODS process efficiency of binary catalysts in examples 22 and 23 and single component catalysts in comparative examples CE-12 and CE-13, it can be seen that the binary catalyst having the combination Mn/Co demonstrates noticeable improvement in sulfur removal, while binary catalyst having the combination Mo/Ce demonstrates significant improvement of the process selectivity and the fuel oil yield. Furthermore, as seen in comparing Examples 24 and 25, the use of a phase transfer catalyst significantly improves the sulfur removal from a fuel oil at about the same oil yield in that is obtained in the presence of acetic acid. It should be noted that the experiments conducted as part of this study were not optimized in all cases. Thus it is believed that much higher conversion of sulfur compounds that those shown in Table 1, 2, 3 and 4 are achievable, by adjusting various reaction parameters which are known to those skilled in the art. Such optimization falls within the scope of the instant invention.

[0040] In each of Examples 1 to 25 the oxidized sulfur compounds may be separated from the reaction mixture (first oxidized mixture) using any of the techniques disclosed herein as being effective for that purpose. In one embodiment, the reaction mixture of Example 1 is filtered through a pad of silica gel to remove both the oxidized sulfur compounds and the exogenous binary catalyst which may be recovered therefrom.

[0041] The foregoing examples are merely illustrative, serving to illustrate only some of the features of the invention. The appended claims are intended to claim the invention as broadly as it has been conceived and the examples herein presented are illustrative of selected embodiments from a manifold of all possible embodiments. Accordingly, it is Applicants' intention that the appended claims are not to be limited by the choice of examples utilized to illustrate features of the present invention. As used in the claims, the word "comprises" and its grammatical variants logically also subtend and include phrases of varying and differing extent such as for example, but not limited thereto, "consisting essentially of" and "consisting of." Where necessary, ranges have been supplied, those ranges are inclusive of all sub-ranges there between. It is to be expected that variations in these ranges will suggest themselves to a practitioner having ordinary skill in the art and where not already dedicated to the public, those variations should where possible be construed to be covered by the appended claims. It is also anticipated that advances in science and technology will make equivalents and substitutions possible that are not now contemplated by reason of the imprecision of language and these variations should also be construed where possible to be covered by the appended claims.

Claims

1. A method for purifying a sulfur-containing fuel oil, the method comprising:

(a) contacting in a first reaction mixture the sulfur-containing fuel oil with an exogenous binary catalyst, hydrogen peroxide and a water-soluble acid, at a temperature in a range of from about 25°C to about 120°C to provide a first oxidized mixture; and
(b) separating at least one oxidized sulfur compound from the first oxidized mixture to provide a purified fuel oil.

2. The method according to claim 1, wherein the exogenous binary catalyst comprises a first component selected from the group consisting of phosphate salts, and oxides, acids and salts of molybdenum, tungsten, manganese, and combinations thereof; and a second component selected from the group consisting of oxides and salts of cerium, iron, vanadium, titanium, manganese, cobalt, nickel, copper and combinations thereof.

3. The method according to claim 2, wherein the first component comprises an oxide, an acid or a salt of manganese.

4. The method according to claim 3, wherein the first component comprises a molybdenum ispolyacid or its salt.

5. The method according to claim 2, wherein the exogenous binary catalyst comprises oxides, acids or salts of molybdenum as the first component and oxides or salts of cerium as the second component; oxides or salts of manganese as the first component and oxides or salts of iron, cobalt, or nickel as the second component; or phosphate salts as the first component and oxides or salts of iron, cobalt, or nickel as the second component.

6. The method according to claim 1, wherein the sulfur-containing fuel oil is deasphalted prior to contacting the sulfur-containing fuel oil with the binary catalyst, hydrogen peroxide and the water-soluble acid by contacting the sulfur-containing fuel with an inert diluent.

7. The method according to claim 1, wherein the water-soluble acid is selected from the group consisting of formic acid, acetic acid, propionic acid, butyric acid, sulfuric acid, phosphoric acid, and mixtures of two or more of the foregoing acids.

8. The method according to claim 1, wherein the separating is carried out using solid-liquid extraction or liquid-liquid extraction.

9. The method according to claim 1, wherein the sulfur-containing fuel oil comprises benzothiophene, dibenzothiophene, alkyl substituted benzothiophenes, and alkyl substituted dibenzothiophenes.

10. The method according to claim 1, further comprising a step of recovering the binary catalyst.

11. The method according to claim 1, wherein the first reaction mixture further comprises a phase transfer catalyst.

12. The method according to claim 12, wherein the phase transfer catalyst comprises a quaternary ammonium salt or a quaternary phosphonium salt.

13. A method for purifying a sulfur-containing fuel oil, the method comprising:

(a) contacting in a first reaction mixture the sulfur-containing fuel oil with a hydrocarbon diluent, an exogenous binary catalyst, hydrogen peroxide, and a water-soluble acid at a temperature in a range of from about 25°C to about 110°C to provide a first oxidized mixture;
(b) separating at least one oxidized sulfur compound from the first oxidized mixture; and
(c) recovering the hydrocarbon diluent to provide a purified fuel oil.

14. A method for purifying a sulfur-containing fuel oil, the method comprising:

(a) contacting a sulfur-containing fuel oil comprising benzothiophene, dibenzothiophene, alkyl substituted benzothiophenes, and alkyl substituted dibenzothiophenes with petroleum-ether, a exogenous binary catalyst hydrogen peroxide and a water soluble acid at a temperature in a range of from about 25°C to about 120°C, and at a pressure in a range of from about 1 atmosphere to about 150 atmospheres to provide a first oxidized mixture comprising sulfoxides and sulfones of benzothiophene, dibenzothiophene, alkyl substituted benzothiophenes, and alkyl substituted dibenzothiophenes;
(b) separating at least one oxidized sulfur compound from the first oxidized mixture; and
(c) recovering petroleum-ether to provide a purified fuel oil.

15. The method according to claim 13 or claim 14, wherein the exogenous binary catalyst a first component selected from the group consisting of phosphate salts, and oxides, acids and salts of molybdenum, tungsten, manganese, and combinations thereof; and a second component selected from the group consisting of oxides and salts of cerium, iron, vanadium, titanium, manganese, cobalt, nickel, copper and combinations thereof.

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EUROPEAN SEARCH REPORT

Application Number
EP 09 15 6238

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The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	4 August 2009	Harf, Julien

CATEGORY OF CITED DOCUMENTS

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EUROPEAN SEARCH REPORT

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EP 09 15 6238

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Munich	4 August 2009	Harf, Julien

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