

PROCESS FOR REMOVING SULFUR-CONTAINING COMPOUNDS FROM A FUEL

Cross-Reference to Related Application

[0001] This application claims the benefit of priority of United States Provisional Patent Application No. 61/333,404, filed 11 May 2010, the contents of which being hereby incorporated by reference in its entirety for all purposes.

Technical Field

[0002] The invention relates to a process for removing sulfur-containing compounds from fuels, and in particular, to a process for removing compounds containing sulfur in oxidized forms from fuels.

Background

[0003] Desulfurization of transportation fuels such as diesel has increasingly gained importance due to more stringent legislation for vehicular emissions and fuel quality coupled with an increasing need to process low-quality oil feedstocks. Developed countries now require that the sulfur level in diesel be brought down from about 400-500 ppm (parts per million on weight basis) to 15-10 ppm. Near zero sulfur (NZZ) diesel fuel of 15 ppm sulfur or less allows advanced post-engine exhaust clean up devices to effectively remove emissions and particulate materials. Due to the need for an additional desulfurization process required for such fuel refining, there has been a growing concern to the long term economics of petroleum refineries.

[0004] Ultra low sulfur diesel (ULSD) fuel of less than 50 ppm became the specification in both the European Union and Japan in 2005. The European Commission

further adopted a 10 ppm sulfur specification for road diesel fuel beginning 1 January 2005 with full conversion by the year 2010. An U.S. EPA rule of 15 ppm sulfur highway diesel fuel was implemented on 1 June 2006. U.S. pipelines are anticipated to include a plan to deliver a sulfur level of below 10 ppm fuel. In Japan, 10 ppm sulfur fuel in 2007 was proposed. Countries in other regions of the world are also working to reduce the sulfur content in diesel fuel. Although most of the developing countries are still using 500 ppm sulfur diesel, the ULSD specification (i.e. below 50 ppm sulfur) will soon be adopted as well.

[0005] Conventional hydrodesulphurization (HDS) processes have been employed extensively by refineries to remove organic sulphur compounds from fuels for several decades and the lowest sulphur content achieved by such processes has been at levels of about 500 ppm. However, it has been found that HDS is less effective in removing certain residual sulfur-containing compounds present in petroleum distillates, particularly heterocyclic sulfur-containing compounds such as thiophenes, benzothiophenes (BT), dibenzothiophenes (DBT), especially DBTs having alkyl substituents on their 4 and/or 6 positions, as well as higher homologs of these compounds. One possible reason is that the sulfur atom is sterically hindered by the bulky benzyl groups, thereby making the sulfur atom less accessible to oxidative attack. In various attempts to meet the challenges of producing ultra-clean fuels, especially with sulfur content lower than 15 ppm, both capital investment and operational costs would be rather high due to applications of more severe operating conditions during the HDS process. Consequently, several alternative options such as selective adsorption and oxidative desulfurization (ODS) have been developed.

[0006] Despite the developments that have taken place, alternative technologies need to be developed in order to reduce sulfur content in fuels while maintaining fuel quality without significantly increasing the capital and processing costs.

Summary

[0007] Various embodiments of the the present process provide the advantage of using cheap and commercially available activated carbon as an adsorbent material for adsorbing sulfur-containing compounds in a fuel. In addition to obtaining ultra-low sulfur content fuels (≤ 10 ppm sulfur), the contents of polycyclic aromatic hydrocarbons (PAH) are simultaneously reduced. Furthermore, various embodiments provide technically feasible and economically viable processes to regenerate the spent activated carbon as well as to recover mono- and di-aromatic hydrocarbons to minimize the yield loss.

[0008] Various embodiments provide for a process for removing sulfur-containing compounds from a fuel. The process may include contacting the fuel with an adsorbent which adsorbs the sulfur-containing compounds in the fuel. The adsorbent may comprise, consist essentially of or consist of activated carbon derived from biomass.

[0009] Various embodiments provide for a system for removing sulfur-containing compounds from a fuel. The system may include a first tank for storing the fuel. The system may further include an adsorbing unit containing an adsorbent for adsorbing the sulfur-containing compounds. The adsorbing unit may be configured to receive the fuel from the first tank. The adsorbent may comprise, consist essentially of or consist of activated carbon derived from biomass.

[0010] Various embodiments provide for an adsorbing unit for containing an adsorbent for adsorbing the sulfur-containing compounds. The adsorbent may comprise, consist essentially of or consist of activated carbon derived from biomass.

Brief Description of the Drawings

[0011] In the drawings, like reference characters generally refer to the same parts throughout the different views. The drawings are not necessarily drawn to scale, emphasis instead generally being placed upon illustrating the principles of various embodiments. In the following description, various embodiments of the invention are described with reference to the following drawings.

[0012] **FIG. 1** illustrates a schematic flow-diagram of the present process for removing sulfur-containing compounds from a fuel.

[0013] **FIG. 2(a)** shows breakthrough curves of total sulfur using real diesel SRC300 as feedstock and the activated carbons reported in Example 4. The sulfur analysis data are obtained from total sulfur analyzer (TS-100).

[0014] **FIG. 2(b)** shows the adsorption capacity as a function of the sulfur concentration of the treated diesel using real diesel SRC 300 as feedstock and the activated carbons reported in Example 4.

[0015] **FIG. 3(a)** shows breakthrough curves of total sulfur using real diesel SRC400 as feedstock and the activated carbons reported in Example 5. The sulfur analysis data are obtained from total sulfur analyzer (TS-100).

[0016] **FIG. 3(b)** shows adsorption capacity as a function of the sulfur concentration of the treated diesel using real diesel SRC 400 as feedstock and the activated carbons reported in Example 5.

[0017] FIG. 4 shows adsorption capacity as a function of the volume of meso-pores for various activated carbons used in Example 4 and 5.

[0018] FIG. 5(a) shows GC-AED chromatograms of sulfur compounds before and after oxidizing real diesel SRC 300 as described in Example 6.

[0019] FIG. 5(b) shows breakthrough curves of total sulfur using activated carbon PQR-01 as adsorbent and both real diesel SRC 300 and oxidized real diesel ORD 300 feedstocks as described in Example 6.

[0020] FIG. 5(c) shows adsorption capacity as a function of the sulfur concentration of the treated diesel using activated carbon PQR-01 as adsorbent and both real diesel SRC 300 and oxidized real diesel ORD 300 feedstocks as described in Example 6.

[0021] FIG. 6(a) shows breakthrough curves of total sulfur using activated carbon PQR-01 as adsorbent and oxidized real diesel ORD 400 feedstock as described in Example 7.

[0022] FIG. 6(b) shows adsorption capacity as a function of the sulfur concentration of the treated diesel using activated carbon PQR-01 as adsorbent and oxidized real diesel ORD 400 feedstock as described in Example 7.

[0023] FIG. 7 shows adsorption capacity of activated carbon PRQ-01 before and after regeneration using hexane/acid washing as described in Example 8.

[0024] FIG. 8 shows a hexane washing step where remaining amounts of aromatic hydrocarbons and sulfur-containing compounds on the adsorbent are shown as a function of time-on-stream during the hexane washing. The washing step was carried out after adsorption of oxidized real diesel ORD 300 in a fixed-bed adsorption system using activated carbon PQR-01 as described in Example 6. Aromatic hydrocarbons consist of mono-aromatic hydrocarbons (MAH), di-aromatic hydrocarbons with two rings (DAH), and polycyclic aromatic hydrocarbons with 3 or more rings (T+AH).

[0025] FIG. 9 shows the pore size distribution of activated carbon PQR-01 before and after regenerations using solvent-washing process as described in Example 11.

[0026] FIG. 10 shows the FT-IR spectra of activated carbon PQR-01 before and after regenerations using solvent-washing process as described in Example 11.

[0027] FIG. 11 shows breakthrough curves of Hexyl-benzene, Naphthalene, Anthracene and 4,6, DMDBT in a fixed-bed adsorption system using activated carbon PQR-01 as described in Example 12.

[0028] FIG. 12 shows adsorption capacities of the activated carbons used in present process as compared to other types of activated carbons disclosed in US Patent No. 6,565,741.

Description

[0029] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practised. These embodiments are described in sufficient detail to enable those skilled in the art to practise the invention. Other embodiments may be utilized and structural, logical, and electrical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0030] Various embodiments provide for a process for removing sulfur-containing compounds from fuels in order to obtain ultra-low sulfur fuels. Various embodiments also provide for an economical process for effective removal of polycyclic aromatic hydrocarbons (PAH) from fuels which are not easily removed through conventional HDS processes. The process may include contacting the fuel with an adsorbent which

adsorbs the sulfur-containing compounds in the fuel. The sulfur-containing compounds may contain sulfur in oxidized forms, such as not but limited to, sulfones or sulfoxides. The adsorbent may comprise, consist essentially of or consist of activated carbon derived from biomass. Activated carbon derived from biomass may include wood, coconut shell, or apricot stone shell.

[0031] In various embodiments, the activated carbon may possess large surface area of more than $1,000 \text{ m}^2/\text{g}$. For example, the activated carbon possess surface area of more than $1,000 \text{ m}^2/\text{g}$, more than $1,200 \text{ m}^2/\text{g}$, more than $1,400 \text{ m}^2/\text{g}$, more than $1,600 \text{ m}^2/\text{g}$, more than $1,800 \text{ m}^2/\text{g}$, or more than $2,000 \text{ m}^2/\text{g}$. In one embodiment, the activated carbon may possess surface area of between $1,000$ to $2,000 \text{ m}^2/\text{g}$.

[0032] In various embodiments, the activated carbon may possess large pore volume of at least $0.7 \text{ cm}^3/\text{g}$. For example, the activated carbon may possess pore volume of at least $0.7 \text{ cm}^3/\text{g}$, at least $0.8 \text{ cm}^3/\text{g}$, at least $1.0 \text{ cm}^3/\text{g}$, at least $1.2 \text{ cm}^3/\text{g}$, at least $1.4 \text{ cm}^3/\text{g}$, at least $1.6 \text{ cm}^3/\text{g}$, at least $1.8 \text{ cm}^3/\text{g}$, or at least $2.0 \text{ cm}^3/\text{g}$. In one embodiment, the activated carbon may possess pore volume of at least $0.8 \text{ cm}^3/\text{g}$.

[0033] In various embodiments, the activated carbon may possess high meso-pore volume ratio (i.e. ratio of meso-pore volume to the total pore volume) of at least 20%. For example, the activated carbon may possess high meso-pore volume ratio of at least 20%, of at least 25%, of at least 30%, of at least 35%, at least 40%, at least 45%, at least 50%, at least 55%, at least 60%, at least 65%, at least 70%, at least 75%, or at least 80%. In one embodiment, the activated carbon may possess meso-pore volume ratio of at least 50%.

[0034] Suitable fuels may include those having initial sulfur content ranging from several hundred to several thousand ppm. Fuels containing sulfur content less than 100 ppm may also be treated by various embodiments of the present process.

[0035] Sulfur content of a fuel that is to be treated may vary, depending for example on the geographical location from which the original crude oil is obtained, as well as the type of fuel treated (e.g. whether the fuel is from a cracked or straight run). Non-limiting examples of fuels which may be treated by various embodiments of the present process include gasoline, kerosene, diesel, jet fuel, furnace oils, lube oils and residual oils. Additionally, the fuels that can be processed are not limited to straight-run fractions, i.e. fractions obtained directly from atmospheric or vacuum distillation in refineries, but include cracked fuels and residues which are obtained from catalytic cracking of heavy crude oil fractions.

[0036] In one embodiment, HDS may first be carried out to lower sulfur content in the fuel to the range of about 300 to 800 ppm. Thereafter, the process of the present invention may be used to further lower sulfur content to less than 100 ppm or even less than 50 ppm, or even less than 30 ppm, or even less than 20 ppm, or to about 10-15 ppm, if desired. For economic reasons, the initial removal of high levels of sulfur from fuel is more suitably carried out by a conventional HDS process which exists in most fuel refineries. The present process may be used for processing low viscosity fuels such as diesel and other fuels having viscosities that are comparable or lower than diesel. Nevertheless, if required, this process can still be applied to heavier fractions such as lube oils and residual oils.

[0037] In the context of the invention, the term 'lowered sulfur content' refers to fuel that has sulfur content of less than 100 ppm by weight. The present invention is able to reduce sulfur content in fuels to less than 100 ppm, such as less than 50 ppm, such as less than 30 ppm, such as less than 20 ppm, or even to about 10-15 ppm.

[0038] Sulfur-containing compounds that are typically found in petroleum fractions and which can be removed by the process of the invention include aliphatic or aromatic

sulfur-containing compounds such as sulfides (e.g. diphenylsulfide, dibutylsulfide, methylphenylsulfide), disulfides, and mercaptans, as well as heterocyclic sulfur-containing compounds such as thiophene, benzothiophene (BT), dibenzothiophene (DBT), 4-methyl- dibenzothiophene (mDBT), 4,6-dimethyl-dibenzothiophene (dmDBT) and tribenzothiophene, and other derivatives thereof, for example.

[0039] The oxidation of the above sulfur-containing compounds occur at varying degrees of ease. Simple sulfur-containing compounds such as aliphatic or aromatic mercaptans and sulfides are generally more easily oxidized than heterocyclic sulfur-containing compounds. Heterocyclic compounds typically comprise thiophenic substances such as thiophenes, BT, DBT, alkylated DBTs such as 4-methyl-dibenzothiophene, 4,6-dimethyl-dibenzothiophene as well as other higher boiling point derivatives. One possible reason for the resistance to oxidation in the latter class of sulfur-containing compounds is the shielding of the sulfur by bulky hydrocarbon structures in the molecule. This class of sulfur-containing compounds are not easily oxidised or decoupled from the hydrocarbons by means of conventional HDS processes, and have thus become known as 'hard' or 'refractory' sulfur compounds.

[0040] Thiophenic compounds may be oxidized, for example by air under appropriate conditions, into polar sulfones and/or sulfoxides, which may be removed from the fuel by various embodiments of the present process.

[0041] In line with the general accepted meaning, adsorption as used in the present invention refers to the property of an interface between two immiscible phases (solid, liquid, or vapor) to attract and concentrate components of either phase or both phases as an adsorbed interfacial film ("the adsorbate"). Adsorption is a basic thermodynamic property of interfaces, resulting from a discontinuity in intermolecular or interatomic forces. It is different from absorption in which a substance diffuses into a liquid or solid

to form a solution. The term sorption encompasses both processes, while desorption is the reverse process. Several kinds of adsorption are known and are encompassed in the present invention. Physical adsorption is reversible adsorption by weak interactions only. In case of physical adsorption no covalent bonds occur between adsorbent and the adsorbate. Chemical adsorption is adsorption involving stronger interaction between adsorbate and adsorbent usually accompanied by rearrangement of atoms within or between adsorbates. In case of chemical adsorption the reaction occurs between the surface of the adsorbent and the adsorbate.

[0042] In various embodiments the process may include oxidizing the fuel to form sulfur-containing compounds comprising sulfur in oxidized forms prior to contacting the fuel with the adsorbent. In one embodiment, the fuel may be oxidized by contacting the fuel in liquid phase with air or oxygen as oxidant to selectively oxidize the sulfur-containing compounds using a transition metal oxide catalyst as disclosed in PCT Publication No. WO 2005/116169 A1, the contents of which are hereby incorporated by reference in its entirety for all purposes. The oxidation step aims at forming oxidized sulfur species since they have a much higher polarity than the parent molecules, substantially facilitating the separation step.

[0043] The fuel is introduced into an adsorbing unit containing the adsorbent. The adsorption step may be carried out in a fixed-bed adsorbing unit.

[0044] Various embodiments of the process may further include washing the adsorbent with an organic solvent after contacting the fuel with the adsorbent. Spent adsorbent may be contacted with the solvent to wash out paraffins, naphthenes, mono-aromatics, and di-aromatics, which are subsequently recovered and blended with the low sulfur diesel to improve the yield. The organic solvent may include hexane, heptane, octane, nonane, toluene, naphtha, or a paraffinic solvent.

[0045] The washed adsorbent may further be contacted with an organic acid after washing the adsorbent with the organic solvent. In various embodiments, acetic acid, formic acid, or propionic acid may be used to regenerate the adsorbent by removing the remaining adsorbed sulfur-containing compounds, including sulfones and polycyclic aromatics with 3 or more rings, which can be further separated by non-miscible solvent(s) which selectively remove oxidized sulfur aromatic compounds and multi-ring aromatics. All organic solvents and acids may be recovered and recycled via distillation.

[0046] FIG. 1 illustrates a schematic flow-diagram of the present process for removing sulfur-containing compounds from a fuel in one embodiment. A high-sulfur content diesel feed stream 1 is supplied to a catalytic oxidation reactor 201, containing a fixed or ebullient-bed or a slurry-phase of a transition metal oxide catalyst. Liquid phase oxidation takes place using gaseous air or diluted air (stream 2), preferably in counter-current flow mode.

[0047] After oxidation and reaction, the oxidized diesel containing sulfones is then delivered to adsorbing unit 301 via line 4 and switch valve SV1. The sulfur adsorbing unit 301 consists of a fixed-bed adsorber loaded with a high surface area (1,000 to 2,000 m²/g), large pore volume (≥ 0.8 cm³/g), and high meso-pore volume ratio (ratio of meso-pore volume to the total pore volume $\geq 50\%$) activated carbon, which is derived from biomass such as wood, coconut shell, or apricot stone shell. The diesel fuel is desulfurized by the sulfone removal and leaves the adsorbing unit 301 as low-sulfur diesel product (stream 7), ready for storage.

[0048] Two adsorbing units 301 and 302 can be operated in parallel, where one of the adsorbing unit 301 or 302 is operational for adsorption by conveying the oxidized diesel stream 4 via valve SV1 switched to the line 5, while the other adsorbing unit containing the spent adsorbent is being regenerated by solvent-washing.

[0049] The regeneration process has two operation steps. The first operation is using hexane to wash out paraffins, naphthenes, mono-aromatics (MAH), and di-aromatics (DAH), which are held up in the adsorbing unit 301 or 302. The second operation is using acetic acid to extract the sulfone species, and polycyclic aromatics (PAH) with 3 or more rings, which are adsorbed on the adsorbent. The activated carbons exhibited higher adsorption selectivity for sulfones and PAH than paraffins, naphthenes, MAH, and DAH.

[0050] In FIG. 1, the solvent tanks 401 and 402 contain hexane and acetic acid, respectively. The switch valve SV2 is switched to connect line 9 and line 10, and then convey the solvent hexane to the adsorbing unit loaded with the spent adsorbent, while the switch valve SV3 is switched to connect line 11 and line 12. The stream 12 containing paraffins, naphthenes, MAH, DAH and hexane is fed to distillation tower 501, where the mixtures are separated into a bottom stream 14 and a solvent overhead stream 13, which is then recycled back to the solvent tank 401. The bottom stream 14 can be blended with the desulfurized diesel stream 7 to minimize yield loss.

[0051] After hexane washing, the valves SV2 and SV3 are switched to connect line 16 with line 10 and line 11 with line 17 for the second regeneration step, i.e. the removal of the sulfur-containing compounds and PAH. Acetic acid stored in the solvent tank 402 is supplied to the adsorbing unit via line 16 and line 10 to remove the sulfones adsorbed on activated carbon. The stream 17 leaving the adsorbing unit not only contains sulfones but also PAH with 3 or more aromatic rings, as well as a small quantity of oxygenated compounds which are produced during the diesel oxidation. These oxygenated compounds, which have higher polarity than paraffins, are strongly adsorbed on the activated carbon and can be desorbed using acetic acid but not using hexane. The stream 17 is then supplied to distillation tower 502, where the mixtures are

separated into a high-sulfur bottom stream **19** and an overhead stream **18** that is recycled back to acetic acid tank **402**. The objective of the two-step process is to provide a method for producing diesel in which both sulfur and PAH contents are reduced.

[0052] The entire process is conducted in a closed loop with no emissions. The high-sulfur bottom may carry small amounts of solvents away, requiring make up streams. Stream **8** is the hexane make up while stream **15** is the acetic acid make up.

[0053] In order that the invention may be readily understood and put into practical effect, particular embodiments will now be described by way of the following non-limiting examples.

Examples

Example 1: Diesel Fuels Used

[0054] The diesel fuels used are SRC 300 and SRC 400 obtained from Singapore Refinery Co. Ltd (SRC), and Exx1 from ExxonMobil. The Oxidized diesels (ORD 300 and ORD 400) were obtained by oxidizing diesels SRC 300 and SRC 400, respectively. The aromatic content and distribution of diesels are shown in **Table 1** below.

Diesel	SRC 400	SRC 300	ORD 300	Exx1	Method
Sulfur (ppm)	400	300	295	10110	ASTM D5453- 06
Mono aromatic hydrocarbons (MAH), wt%	30.9	28.8	27.9	17	IP 391/01
Di-aromatic hydrocarbons (DAH), wt%	5.3	3.9	3.8	10.2	
Tri + aromatic hydrocarbons (T+AH), wt%	1.4	0.8	0.8	1.7	
Total aromatics, wt%	37.6	33.5	32.5	28.9	

Table 1. Sulfur Content and Aromatic Hydrocarbons Content and Distribution of Diesels

Example 2: Materials Used

[0055] The following commercially available activated carbons (AC) were used as adsorbents (Table 2) and their physical properties are listed in Table 3.

No	Activated Carbon Name	Company	Raw Material
1	SP	Kureha Cor. Japan	Pitch
2	GH-16	Beijing Guanghua Activated Carbon Co. Ltd. China	Apricot
3	GH-15		Apricot
4	GH-16A		Apricot
5	GH-11		Apricot
6	GH-6		Coconut
7	GH-82/H		Coconut
8	GG-K	Kuraray Chemical Co.,Ltd. Japan	Coconut

9	XC-18	Shanghai Xingchang activated carbon Co.Ltd. China	Wood
10	XC-19		Wood
11	XC-20		Wood
12	PQR-01	Xin-Sen Carbon Co., Ltd. China	Wood
13	GAC-1240 P	Norit Activated Carbon, USA	Coal

Table 2. Commercially Available Activated Carbon

AC Name	Particle Size (mm)	Surface area (m ² /g)	Pore Volume (cm ³ /g)	V _{meso} (%)
SP	0.4	1403	0.673	5.2%
GH-16	0.65-2	729	0.472	19.8%
GH-15	0.55-0.6	713	0.557	33.9%
GH-16A	0.4 - 0.8	1322	0.815	46.2%
GH-11	0.55-0.6	1020	0.734	28.4%
GH-6	0.65-2	800	0.439	3.5%
GH-82/H	< 0.154	986	0.801	37.5%
GG-K	0.4 - 0.8	1771	0.965	3.6%
XC-18	powder	1104	1.049	46.4%
XC-19	powder	1136	0.933	37.9%
XC-20	powder	1753	1.489	75.6%
PQR-01	2.3 - 3.4	1917	1.481	66.2%
GAC-1240 P	granular	882	0.574	20.7%

Table 3. Physical Properties of Activated Carbons (AC)

Example 3: Experimental Methods and Sulfur Analysis

Nitrogen Adsorption

[0056] Specific surface areas and pore volumes were determined by N₂ adsorption. An automated adsorption apparatus (Quantachrome, Autosorb-6) was used for these measurements. N₂ adsorption was carried out at liquid N₂ temperature (77 K). Prior to

analysis, the samples were degassed at 150 °C in a vacuum system at about 10^{-4} Torr.

The specific surface areas were calculated using the BET equation.

Fourier Transform Infrared Spectroscopy (FTIR)

[0057] FTIR spectra ($4,000\text{--}400\text{cm}^{-1}$) of various AC samples were recorded on a Nicolet Impact 410 FTIR spectrometer (Nicolet Instrument Corporation). The transmission spectra of the samples were recorded using KBr wafers containing 0.5 wt % of carbon. These wafers were dried overnight at 120 °C before the spectra were recorded. The spectra were obtained by adding scans of 64 with a resolution of 4 cm^{-1} .

Adsorption of Diesel in Fixed bed reactor

[0058] To estimate the adsorption capacity of AC samples, dynamic adsorption experiments were carried out by flowing diesel through a fixed bed reactor at constant temperature, usually 75 °C.

[0059] A packed-column was prepared containing about 6 to 15 g of activated carbon. A stainless steel tube column of 1 cm (diameter) $\times$ 33 cm (length) was used. External controlled heat was supplied to the column to control the bed temperature. A number of activated carbons were tested. The fixed-bed volume was kept constant (ca. 26 cm^3) and, typically, a LHSV of 0.5 hr^{-1} was used.

[0060] Once the adsorption process started, effluent samples were continuously collected at regular time intervals. The sulfur content of the effluent samples was then analyzed using Total Sulfur Analyzer (TS-100, Mitsubishi Chemical Co). The analysis was carried out in accordance with a certified method; Oxidation decomposition and ultraviolet fluorescence (ASTM-D5453).

[0061] Before and after treatment of diesels, the content and distribution of aromatic hydrocarbons in diesel were also analyzed to determine the concentration of mono-aromatic hydrocarbons (MAH), Di-aromatic hydrocarbons (DAH), and Tri or poly aromatic hydrocarbons (T+AH) using the IP391-01 method.

Example 4

[0062] A numbers of activated carbons used as adsorbent were tested in a fixed-bed adsorbing unit as previously described. Breakthrough curves, using commercial diesel (SRC 300) as feedstock, are shown **FIG. 2(a)** and **(b)**. **FIG. 2(a)** shows breakthrough curves of total sulfur using real diesel SRC 300 as feedstock and the activated carbons. The sulfur analysis data are obtained from total sulfur analyzer (TS-100).

[0063] **FIG. 2(b)** shows the adsorption capacity as a function of the sulfur concentration of the treated diesel using real diesel SRC 300 as feedstock and the activated carbons. Although sulfur-containing compounds can be removed from real diesels by adsorption on activated carbons, Example 4 clearly shows that adsorption capacity is quite low and strongly depends on the nature of the activated carbon. XC-18, XC-20 and PQR-01 seem to be the best adsorbents.

Example 5

[0064] A numbers of activated carbons used as adsorbent were tested in a fixed-bed adsorber as previously described. Breakthrough curves, using commercial diesel (SRC 400) as feedstock, are shown **FIG. 3**.

[0065] FIG. 3(a) shows breakthrough curves of total sulfur using real diesel SRC 400 as feedstock and the activated carbons. The sulfur analysis data are obtained from total sulfur analyzer (TS-100).

[0066] FIG. 3(b) shows the adsorption capacity as a function of the sulfur concentration of the treated diesel using real diesel SRC 400 as feedstock and the activated carbons.

[0067] FIG. 4 shows the adsorption capacity as a function of the volume of meso-pores for various activated carbons used in Example 4 and 5.

[0068] Example 4 and Example 5 reveal that the activated carbon with different textural surface properties and derived from different raw materials perform very differently on sulfur adsorption of diesels. Activated carbons with large surface areas ($> 1,000$ to $2,000 \text{ m}^2/\text{g}$), large pore volume ($\geq 0.8 \text{ cm}^3/\text{g}$), high meso-pore volume ratio (ratio of meso-pore volume to the total pore volume $\geq 50\%$), show significantly higher adsorption capacity as compared to activated carbons with low meso-pore volumes.

[0069] FIG. 4 presents the adsorption capacity as a function of the meso-pore volume ratio of various carbons. It is clear that the larger of the meso-pore volume ratio, the higher of the adsorption capacity.

[0070] The results suggest that the activated carbons derived from biomass carbon, such as wood, coconut shell or apricot stone shell, showed higher adsorption capacity than those derived from pitch and coal. This is probably due to the larger number of acidic carbonyl functional groups on the surface of activated carbon derived from wood or apricot stone shell.

Example 6

[0071] Example 6 discloses the beneficial effect of performing adsorption after oxidation (sulfone adsorption) instead of adsorption of non-oxidized diesel (dibenzothiophene adsorption). Among all tested activated carbons, PQR-01 shows the highest adsorption capacity for both of SRC 300 and SRC 400 diesel adsorption.

[0072] **Fig. 5(a)** presents the GC-AED analysis results of diesel (SRC 300) before and after oxidation, showing that, after 240 min of reaction, the diesel was 100% oxidized. Then, the oxidized diesel (ORD 300) was used as feedstock in the sulfur removal step using a fixed-bed adsorption system and PQR-01 as adsorbent. Breakthrough curves for the adsorptive desulfurization of ORD 300 over PQR-01 are shown in **FIG. 5(b)** and **(c)**.

[0073] Example 6 reveals that the adsorption capacity of PQR-01 activated carbon for adsorption of oxidized diesel (ORD 300) is four times higher as compared to the one obtained with SRC 300 when the sulfur concentration in de-sulfurized diesel is reduced to 10 ppmw.

Example 7

[0074] The oxidized diesel ORD 400 was also tested in a fixed-bed adsorber using PQR-01 as adsorbent. Breakthrough curves for the adsorptive desulfurization of ORD 300 over PQR-01 are shown in **FIG. 6(a)** and **(b)**.

[0075] Example 7 shows that the adsorption capacity of PQR-01 for oxidized diesel ORD 400 is four times than that for real diesel SRC 400 when the sulfur concentration in de-sulfurized diesel is reduced to 10 ppm. Examples 6 and 7 clearly suggest that the diesel oxidation step significantly enhances the adsorption capacity of activated carbons.

Example 8

[0076] After adsorption of ORD 300 diesel, the spent activated carbon (AC) PRQ-01 was regenerated by a two-step solvent washing: (1) using Hexane (HX) (LHSV=4.6 hr⁻¹) at 60 °C to recover aromatics and hydrocarbons the spent AC; (2) followed by acetic acid (AA) treatment to extract organic sulfones from spent AC. Both treatments were carried out in a Soxhlet system. The HX washing solvent and the extracted liquid phase were analyzed using a sulfur analyzer to determine the total sulfur concentration. The solid adsorbent was also analyzed to determine the recovery degree of the AC. The regenerated AC was recycled three times and the adsorption capacities after each cycle are shown in **FIG. 7**.

[0077] Example 8 reveals that the regeneration method disclosed in the present invention is feasible and effective to successfully regenerate the spent AC and to recover hydrocarbons and aromatics (mono- and di-aromatics). The adsorption capacity can be fully recovered by this two-step solvent washing procedure.

Example 9

[0078] Adsorption of ORD 300 on PQR-01 was carried out until reaching the cumulative sulfur level in de-sulfurized diesel is reduced up to 10 ppm. Then, the adsorption operation is stopped and followed by regeneration. The spent AC was washed by hexane (LHSV=4.6 hr⁻¹) at 60 °C. The aromatic hydrocarbons, consisting of mono-aromatic hydrocarbons (MAH), di-aromatic hydrocarbons with two rings (DAH), and polycyclic aromatic hydrocarbons with 3 or more rings (T+AH), and sulfur

compounds remaining adsorbed on the activated carbon were determined as a function of the time-on-stream during hexane washing (**FIG. 8**).

[0079] Example 9 reveals that MAH and DAH can be fully recovered by hexane washing in 90 min. The amounts of sulfur and T+AH aromatics adsorbed on activated carbon remain constant during hexane washing. This suggests that the activated carbon PQR-01 adsorbs both sulfones and T+AH aromatics stronger than MAH and DAH. Thus, the adsorbed sulfones and T+AH aromatics can not be extracted by hexane washing, and about 0.6 wt% of T+AH aromatics (0.8 wt% in feed stream) remains adsorbed on the activated carbon. Therefore, paraffins, naphthenes, MAH and DAH can be recovered by hexane. The recovery hydrocarbons can be blended with the desulfurized diesel stream 7 after distillation to minimize yield loss (**FIG. 1**).

Example 10

[0080] After washing spent activated carbon PQR-01 with Hexane as described in Example 9, PQR-01 was further treated with acetic acid (LHSV=1 hr⁻¹) at 100 °C during 2 hr to remove sulfones and T+AH aromatics. Results showed that the extracted liquid contains acetic acid, T+AH aromatic hydrocarbons, organic sulfones and oxygenates. After acetic acid treatment, the remaining amount of sulfur and/or organic compounds onto the solid was determined using Total Sulfur Analyzer (TS-100, Mitsubishi Chemical Co) and FT-IR, showing that neither sulfur compounds nor any other organic compounds were detected. This strongly suggests that the acid washing method is an efficient approach to extract both sulfones and T+AH aromatics from the spent activated carbon. Based on this, it can be estimated that about 75% of T+AH polycyclic

aromatics and 97% of sulfur-containing compounds, initially present in the diesel (sulfur content: 400 ppmw), were removed. The total yield loss does not exceed 1 wt%, mainly consisting of polycyclic aromatics (with 3 or more rings) and oxygenates (aliphatic ketone and alcohols).

Example 11

[0081] After the two-step regeneration using hexane (HX) and acetic acid (AA) treatments, the regenerated solid was analyzed by FT-IR and nitrogen adsorption. The results are shown in **Table 4**, **Fig. 9**, and **Fig. 10**, respectively.

PQR-01 Activated Carbon	Pore Volume cm³/g	Surf area. m²/g	Average Pore size, Å	Volume ratio of Meso-Pore (≥20 Å)
Original PQR-01	1.481	1917	30.91	66.3%
After first cycle adsorption of diesel, Hexane, and Acetic Acid washing	1.409	1900	30.33	67.8%
After second cycle adsorption of diesel, Hexane, and Acetic Acid washing	1.378	1800	30.84	63.2%

**Table 4. Surface Area and Pore Size Measurements for Regenerated PQR-01
Activated Carbon**

[0082] TABLE 4 and FIG. 9 show that acetic acid treatment does not induce any significant change on the pore size distribution. The pore size and surface area are only marginally reduced; in good agreement with the results in Example 8 indicating that the regeneration of spent activated carbons can be successfully achieved by the two-step solvent washing procedure disclosed in this invention.

[0083] The FT-IR surface analysis shows that acetic acid treatment does not reduce the amount of surface carboxylic groups, which are essential for the adsorption of sulfones. In FIG. 10, the band at 1718 cm^{-1} is characteristic of stretching vibrations of carbonyl group $\text{C}=\text{O}$ in carboxylic groups. The strong band at 1578 cm^{-1} can be ascribed to asymmetric and symmetric COO^- vibrations, respectively. The band at 1137 cm^{-1} may have contributions from both C-O stretching and O-H bending modes of phenolic, carboxylic groups. It was observed that the bands at 1718 cm^{-1} and 1578 cm^{-1} are indeed enhanced by acetic acid treatment, which may compensate the slight decrease of surface area and pore volume upon acid treatment.

[0084] In addition, FT-IR spectra clearly showed that organic compounds were totally removed from the activated carbon after treatment with acetic acid. In FIG. 10, the bands near 3000 cm^{-1} , which are attributed to CH, CH_2 , and CH_3 groups in organic compounds, were not observed. This is also in agreement with the results of Example 10, which indicate that acid washing is a feasible approach to remove sulfones, T+AH aromatics, and oxygenates from spent activated carbon. Furthermore, biomass-derived activated carbons are not deactivated by weak organic acid treatments such as acetic acid.

Example 12

[0085] To investigate the adsorption selectivity of activated carbon, a model diesel was used to conduct adsorption experiments in a fixed-bed adsorber packed with PQR-01. The model diesel consists of 400 ppmw of 4,6-DMDBT, hexylbenzene (mono-aromatics), naphthalene (di-aromatics), and anthracene (3-ring aromatics). The composition is reported in **Table 5**. The breakthrough curves of hexylbenzene, naphthalene, anthracene and 4,6-DMDBT are shown in **FIG. 11**.

Hexadecane	78.835 wt%
4,6-DMDBT (400 ppmw-Sulfur)	0.265 wt%
Hexylbenzene (1-ring aromatic)	20.0 wt%
Naphthalene (2-ring aromatic)	0.5 wt%
Anthracene (3-ring aromatic)	0.4 wt%

Table 5. Model Diesel Composition

[0086] **FIG. 11** reveals that PQR-01, a biomass-derived activated carbon, has special adsorption properties, having a strong adsorption affinity not only for DBTs but also for anthracene, a multi-ring aromatics. This is consistent with Examples 9 and 10, showing that MAH (mono-aromatics) and DAH (di-aromatics) can be easily removed from activated carbon by hexane washing, whereas sulfone and T+AH (multi-ring aromatics) can only be removed by acetic acid treatment.

[0087] It is important to stress that the activated carbons employed in the present invention have the required adsorption properties for DBTs, sulfones and T+AH polycyclic aromatics, providing an efficient approach to selectively remove both of sulfur compounds and multi-ring aromatics from diesel. Furthermore, the two-step

solvent washing method is a suitable method to regenerate spent adsorbents since, at the same time, allows for the recovery of mono- and di-aromatics and removal of sulfur compounds and multi-ring aromatics from activated carbon efficiently. In addition, the special types of activated carbons derived from biomass adopted in present invention show higher adsorption capacity than those activated carbons employed in a previous patent (US Patent No. 6,565,741). **FIG. 12** shows the adsorption capacities of the activated carbons disclosed in this invention as compared to the ones previously reported in US Patent No. 6,565,741.

[0088] In summary, various embodiments of the present invention provide a simple, mild, highly effective and inexpensive desulfurization process which utilizes readily available, durable and inexpensive activated carbons. The technical advantages over processes presently known in the art are:

1. The activated carbons derived from biomass (wood, coconut shell or apricot stone shell) originally have higher adsorption capacity for adsorption of dibenzothiophene (DBTs) than other types of carbons, therefore, reducing both capital and processing costs.
2. The adsorption capacity of said activated carbons for adsorption of sulfones is 3 to 4 times higher than the adsorption capacity of dibenzothiophenes (DBTs). Thus, introducing a simple catalytic oxidation step significantly reduces the processing cost and thus increases the economic competitiveness.
3. The activated carbons show high adsorption selectivity for both sulfur compounds and multi-ring aromatics, which could potentially contribute to minimizing atmospheric pollution.
4. The activated carbons are able to be efficiently regenerated and recycled.

5. The two-step regeneration method can efficiently recover mono- and di-aromatics and remove the adsorbed sulfur compounds and multi-ring aromatics by using different solvents, thus, minimizing fuel yield loss.
6. The total yield loss does not exceed 1 wt%.
7. Low consumption of solvents (hexane or naphtha, acetic acid) due to recovery and recycling of solvent using a closed loop system.
8. The disclosed process is a simple and selective adsorption process using activated carbons with high adsorption capacities and mild process operating conditions (25- 125 °C). Thus, the total capital investment and operating cost are relative low.

[0089] By "comprising" it is meant including, but not limited to, whatever follows the word "comprising". Thus, use of the term "comprising" indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

[0090] By "consisting of" is meant including, and limited to, whatever follows the phrase "consisting of". Thus, the phrase "consisting of" indicates that the listed elements are required or mandatory, and that no other elements may be present.

[0091] The inventions illustratively described herein may suitably be practiced in the absence of any element or elements, limitation or limitations, not specifically disclosed herein. Thus, for example, the terms "comprising", "including", "containing", etc. shall be read expansively and without limitation. Additionally, the terms and expressions employed herein have been used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention

claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the inventions embodied therein herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention.

[0092] The invention has been described broadly and generically herein. Each of the narrower species and sub-generic groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

[0093] Other embodiments are within the following claims and non-limiting examples. In addition, where features or aspects of the invention are described in terms of Markush groups, those skilled in the art will recognize that the invention is also thereby described in terms of any individual member or subgroup of members of the Markush group.

Claims

1. A process for removing sulfur-containing compounds from a fuel, comprising:
 - contacting the fuel with an adsorbent comprising activated carbon derived from biomass.
2. The process of claim 1,
wherein the activated carbon is derived from wood, coconut shell, apricot stone shell, or a mixture thereof.
3. The process of claim 1 or 2,
wherein the activated carbon comprises surface area of more than 1,000 m²/g.
4. The process of any one of claims 1-3,
wherein the activated carbon comprises pore volume of at least 0.7 cm³/g.
5. The process of any one of claims 1-4,
wherein the activated carbon comprises meso-pore volume ratio (i.e. ratio of meso-pore volume to the total pore volume) of at least 20%.
6. The process of any one of claims 1-5,
wherein the sulfur-containing compounds comprise sulfides, disulfides, mercaptans, thiophenes, sulfones, sulfoxides, and derivatives thereof.
7. The process of any one of the preceding claims,

wherein contacting comprises introducing the fuel into an adsorbing unit containing the adsorbent.

8. The process of any one of the preceding claims,
further comprising subjecting the fuel to an oxidation step to oxidize the sulfur-containing compounds prior to contacting the fuel with the adsorbent.
9. The process of claim 8,
wherein the fuel is oxidized with air or oxygen.
10. The process of claim 8 or 9,
wherein the fuel is oxidized in the presence of a transition metal oxide catalyst.
11. The process of any one of the preceding claims,
further comprising washing the adsorbent with an organic solvent after contacting the fuel with the adsorbent.
12. The process of claim 11,
wherein the organic solvent is selected from the group consisting of hexane, heptanes, octane, nonane, toluene, naphtha, and a paraffinic solvent.
13. The process of any one of the preceding claims,
further comprising contacting the adsorbent with an organic acid after contacting the fuel with the adsorbent.

14. The process of claim 13,
wherein the adsorbent is contacted with the organic acid after washing the adsorbent with the organic solvent.
15. The process of claim 14,
wherein the organic acid is acetic acid, formic acid, or propionic acid.
16. A system for removing sulfur-containing compounds from a fuel, comprising:
- a first tank for storing the fuel; and
 - an adsorbing unit containing an adsorbent for adsorbing the sulfur-containing compounds, wherein the adsorbent comprises activated carbon derived from biomass, and wherein the adsorbing unit is configured to receive the fuel from the first tank.
17. The system of claim 16,
further comprising a second tank for storing an organic solvent, wherein the adsorbing unit is further configured to receive the organic solvent from the second tank.
18. The system of claim 16 or 17,
further comprising a third tank for storing an organic acid, wherein the adsorbing unit is further configured to receive the organic acid from the third tank.
19. The system of any one of claims 16-18,

wherein the activated carbon is derived from wood, coconut shell, apricot stone shell, or a mixture thereof.

20. The system of any one of claims 16-19,
wherein the activated carbon comprises surface area of more than 1,000 m²/g.
21. The system of any one of claims 16-20,
wherein the activated carbon comprises pore volume of at least 0.7 cm³/g.
22. The system of any one of claims 16-21,
wherein the activated carbon comprises meso-pore volume ratio (i.e. ratio of meso-pore volume to the total pore volume) of at least 20%.
23. The system of any one of claims 16-22,
wherein the sulfur-containing compounds comprise sulfides, disulfides, mercaptans, thiophenes, sulfones, sulfoxides, and derivatives thereof.
24. The system of any one of claims 16 to 23,
wherein the organic solvent is selected from the group consisting of hexane, heptanes, octane, nonane, toluene, naphtha, and a paraffinic solvent.
25. The system of any one of claims 16 to 24,
wherein the organic acid is acetic acid, formic acid, or propionic acid.

26. An adsorbing unit containing an adsorbent for removing sulfur-containing compounds from a fuel, wherein the adsorbent comprises activated carbon derived from biomass.
27. The adsorbing unit of any one of claims 26,
wherein the activated carbon is derived from wood, coconut shell, apricot stone shell, or a mixture thereof.
28. The adsorbing unit of claim 26 or 27,
wherein the activated carbon comprises surface area of more than 1,000 m²/g.
29. The adsorbing unit of any one of claims 26-28,
wherein the activated carbon comprises pore volume of at least 0.7 cm³/g.
30. The adsorbing unit of any one of claims 26-29,
wherein the activated carbon comprises meso-pore volume ratio (i.e. ratio of meso-pore volume to the total pore volume) of at least 20%.
31. The adsorbing unit of any one of claims 26-30,
wherein the sulfur-containing compounds comprise sulfides, disulfides, mercaptans, thiophenes, sulfones, sulfoxides, and derivatives thereof.