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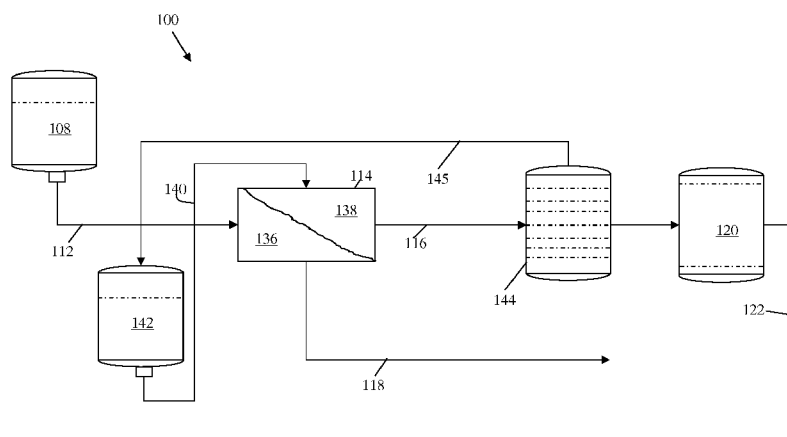


FIG. 2

(57) Abstract: The process of the present invention is directed to the desulfurization of a sulfur-containing hydrocarbon stream with a membrane contactor, where sulfur compounds are concentrated in a sulfur-rich stream on a permeate side of the membrane using an extractive liquid, and a sulfur-lean stream is recovered as a retentate. The sulfur-rich stream, which has a small volume relative to the original hydrocarbon stream, is conveyed to a recovery zone to recover extractive liquid, and the remaining hydrocarbon stream having an increased concentration of sulfur compounds is passed to a downstream desulfurization apparatus or system, such as a hydrotreating system, to recover the hydrocarbons associated with the organosulfur compounds.

**MEMBRANE DESULFURIZATION OF LIQUID HYDROCARBONS USING AN
EXTRACTIVE LIQUID MEMBRANE CONTACTOR SYSTEM AND METHOD****Related Applications**

[01] This applications claims priority to U.S. Provisional Patent Application Serial Number 61/222,411, which is incorporated by reference in its entirety herein.

Field of the Invention

[02] The invention relates to processes for desulfurization of a hydrocarbon feed using membrane separation, and more particularly to a process and system for desulfurization of a hydrocarbon feed using an extractive liquid membrane separation contactor.

Background of the Invention

[03] Compositions of natural petroleum or crude oils vary significantly, generally based upon the source. However, virtually all crude oils contain some level of sulfur compounds, including inorganically combined sulfur and organically combined sulfur, i.e., organosulfur compounds. Whole crude oil that contains a substantial concentration of sulfur compounds, such as hydrogen sulfide, and organosulfur compounds such as mercaptans, thiophenes, benzothiophenes, and dibenzothiophenes is referred to as “sour,” whereas whole crude oil that does not contain a substantial concentration of sulfur compounds is referred to as “sweet.”

[04] Crude oil is generally converted in refineries by distillation, followed by cracking and/or hydroconversion processes, to produce various fuels, lubricating oil products, chemicals, and chemical feedstocks. Fuels for transportation are generally produced by processing and blending distilled fractions from crude oil to meet the particular product specifications. Conventionally, distilled fractions are subject to various hydrocarbon

desulfurization processes to make sulfur-containing hydrocarbons more marketable, attractive to customers and environmentally acceptable.

[05] The evolution of sulfur compounds during processing and end-use of the petroleum products derived from sour crude oil poses safety and environmental problems. Laws have been enacted to reduce sulfur content of fuels, including diesel and gasoline. For instance, in 2007 the United States Environmental Protection Agency required sulfur content of highway diesel fuel to be reduced 97%, from 500 parts per million (low sulfur diesel) to 15 parts per million (ultra low sulfur diesel). The European Union has enacted even more stringent standards, requiring diesel and gasoline fuels sold in 2009 to contain less than 10 parts per million of sulfur.

[06] Furthermore, the price differential between sour crude oil and sweet crude oil (crude oil having relatively low level of sulfur compounds) favors sweet crude oil. Sweet crude oil commands a higher price than sour crude oil because it has fewer environmental problems and requires less refining to meet sulfur standards imposed on end product fuels. Hydrocarbon desulfurization processes are required to reduce the sulfur content. However, most desulfurization processing occurs after varying levels of refining of the crude oil.

[07] The most common hydrocarbon desulfurization process is hydrotreating, in particular, hydrodesulfurization. In typical hydrodesulfurization processes, oil and hydrogen are introduced to a fixed bed reactor that is packed with a hydrodesulfurization catalyst, commonly under elevated operating conditions, including temperatures of about 300 to 400°C and pressures of about 30 to 200 atmospheres. The temperatures and pressures in hydrotreating processes must be further elevated to achieve the low and ultra low sulfur content requirements. However, under these more severe conditions, hydrocarbons are typically converted to less desirable intermediates or products.

[08] Typical advances in the industry for minimizing these undesirable effects include development of more robust hydrotreating catalysts and advanced hydrodesulfurization reactor designs. Alternative processes are also being developed to meet the requirements of decreased sulfur levels in fuels and other petrochemical products.

[09] One alternate desulfurization process that has been proposed for treating various refined fractions of hydrocarbons is membrane separation. In general, membrane separation technology involves selective transport of a material through the membrane, a permeate, leaving behind a retentate on the feed side of the membrane. Permeated components of the mixture are removed by various driving forces. Membrane processes that rely upon pressure driving forces are known as pervaporation processes, and membrane processes that rely upon concentration gradients across the membrane are known as perstraction processes. Membrane separation often relies on the affinity of a specific compound or class of compounds for the membrane. Components in a mixture having affinity for the membrane will permeate the membrane. Membrane separation has been used for desulfurization of refined hydrocarbon fractions.

[10] Saxton et al. United States Patent Number 6,702,945 and Minhas et al. United States Patent Number 6,649,061, both assigned to ExxonMobil, disclose reducing the sulfur content in a hydrocarbon fraction, particularly light cracked naphtha. The membrane system is operated under pervaporation conditions in the examples. In addition, the process discloses a transport agent (such as methanol) as an additive to the hydrocarbon mixture to enhance the permeate flux through the membrane.

[11] White et al. United States Patent Number 6,896,796, and related United States Patent Numbers 7,018,527, 7,041,212 and 7,048,846, all assigned to W.R. Grace & Co., disclose a method for lowering the sulfur content of an FCC light cut naphtha feed under pervaporation conditions. The processes propose to minimize olefin and naphthene hydrogenation during

hydrotreating, particularly problematic in hydrotreating FCC naphtha since the high olefin content is again prone to hydrogenation.

[12] Balko United States Patent Number 7,267,761, also assigned to W.R. Grace & Co., describes another process for treating naphtha streams from an FCC unit, where the feedstream is treated in a fractionation zone to produce a low boiling point fraction and a second fraction, both containing sulfur. The low boiling point fraction is treated in a membrane separation zone, where the sulfur-enriched permeate is combined with the second fraction for treatment in a hydrodesulfurization zone.

[13] Plummer et al. United States Patent Number 6,736,961, assigned to Marathon Oil Company, discloses a process employing a solid membrane process containing a transport facilitating liquid, identified as amines, hydroxyamines, and alcohols. The feed is described as a refinery hydrocarbon product such as naphtha or diesel.

[14] Importantly, the hydrocarbon feed streams in all of the above-mentioned references are products of upstream distillation and cracking processes and/or other refining operations. However, the use of unrefined petroleum products (e.g., crude oil) as a feedstream to a membrane separation process remains heretofore unknown to the inventors.

[15] Another desulfurization process is described in Schoonover United States Patent Number 7,001,504, where hydrocarbon materials are contacted with an ionic liquid to extract organosulfur compounds into the ionic liquid. The ionic liquid is regenerated by various methods including heating, gas stripping, oxidation, or extraction with another solvent or supercritical carbon dioxide. However, this process does not utilize membrane separation units to provide relatively compact and efficient separation.

[16] Various problems exist with the above-described existing membrane desulfurization processes. In some processes, dense layer of polymeric membrane are relied upon to enhance

the selectivity of the membrane to sulfur compounds. However, this required extensive energy consumption to pass the materials through the membrane, and also limits the feed stream.

[17] In addition, some existing membrane desulfurization processes require material to be transformed into a gaseous phase in order to increase the permeate transport rate. The material is transformed by heating and/or vacuum, also increasing the energy requirements. Other membrane desulfurization processes require the use of a transport agent to enhance the transport rate of sulfur compounds in dense layer of polymeric membrane. Transport agents generally cause plasticizing of the selective membrane and has a deleterious impact on its selectivity to sulfur compounds.

[18] Another approach to reducing the sulfur content in hydrocarbons uses dispersed phase contactors. However, dispersed phase contactors require high solvent holdup, which is often associated with other problems such as emulsion formation, foaming, unloading and flooding. Further, conventional extraction techniques such as liquid-liquid extraction, in which the two liquids are intermixed, suffers from many drawbacks, including slow phase separation and production of stable emulsions, resulting in the need to produce high surface area for mass transfer.

[19] Therefore, it is an object of the present invention to provide a membrane separation process and apparatus to desulfurize liquid hydrocarbon streams without the above-described problems associated with conventional membrane desulfurization processes.

[20] It is a further object of the present invention to provide a liquid extraction process and system to desulfurize liquid hydrocarbon streams without the above-described problems associated with dispersed phase contactors.

[21] It would therefore be desirable to provide a system and method that reduces the sulfur content of hydrocarbon streams using an extractive liquid membrane contactor.

Summary of the Invention

[22] The present invention utilizes an extractive liquid membrane contactor to desulfurize a hydrocarbon stream. A sulfur-containing liquid hydrocarbon is passed in contact with the retentate side of a porous membrane, while an extractive liquid is passed along the permeate side of the porous membrane. The membrane provides a controlled interface to allow the extractive liquid to draw sulfur-containing compounds from the hydrocarbon liquid.

[23] In particular, the proposed membrane contactor relies on extractive liquids to solubilize and transfer the sulfur compounds through pores of the membrane, so that the transfer rate of the sulfur compounds is not hindered. The membrane contactor brings the extractive liquid and the liquid feedstream into controlled contact without intermixing. The requirements for creating a vacuum or to convert the permeate in a gaseous phase in order to enhance the transport of the sulfur compounds are obviated, and the operating costs associated with the use of vacuum and energy of vaporization are eliminated.

[24] In one aspect, a process of the present invention is directed to desulfurization of a sulfur-containing hydrocarbon stream with a membrane separation apparatus in which sulfur compounds are concentrated in a sulfur-rich stream on a permeate side of the membrane and a sulfur-lean stream is recovered as a retentate. The sulfur-rich stream, which has a small volume relative to the original hydrocarbon stream, is subsequently conveyed to a desulfurization apparatus or system, such as a hydrotreating system, to recover the hydrocarbons associated with the organosulfur compounds. The stream desulfurized by conventional processes, such as hydrotreating, and the hydrocarbon stream desulfurized by the membrane separation apparatus can be combined to provide a low sulfur hydrocarbon effluent with minimal or no significant loss of the original volume of hydrocarbons.

Brief Description Of The Drawings

[25] Further advantages and features of the present invention will become apparent from the detailed description of a preferred embodiment of the invention that follows and reference to the accompanying drawings, in which:

[26] FIG. 1 is a schematic diagram of a combined membrane separation desulfurization process and an alternate desulfurization process according to embodiments of the invention; and

[27] FIG. 2 is a schematic diagram of a combined membrane separation desulfurization process and an alternate desulfurization process according to embodiments of the invention using extractive liquid as a sweep stream and including an extractive liquid regeneration/recovery zone.

Detailed Description of the Invention

[28] As used herein, the term “unrefined hydrocarbon” is to be understood to mean crude oil and a distillate product of crude oil (including impurities such as sulfur) that has not been subjected to hydroprocessing, hydrodesulfurization, hydrodenitrogenation, catalytic processing, or cracking, and includes unrefined diesel, unrefined naphtha, unrefined gas oil, or unrefined vacuum gas oil. Additionally, as used herein, the term “crude oil” is to be understood to include a mixture of petroleum liquids and gases (including impurities such as sulfur) as distinguished from refined fractions of hydrocarbons.

[29] With reference to FIG. 1, a schematic overview of a desulfurization system 10 is described. A hydrocarbon feedstream 12, such as a hydrocarbon feedstream containing organosulfur compounds is introduced into a membrane separation unit 14 where the feedstream 12 is separated into streams 16, 18. Sulfur-containing hydrocarbon compounds permeate a membrane of the membrane separation unit 14 by transfer to an extractive liquid

stream on the permeate side of the membrane. The sulfur-containing hydrocarbons thus are concentrated into a sulfur-rich hydrocarbon stream 16. The portion of the feedstream remaining on the feed side of the membrane, the retentate, is conveyed as a sulfur-lean hydrocarbon stream 18. The sulfur-lean hydrocarbon stream 18 has a substantially reduced concentration of sulfur-containing compounds as compared to the feedstream 12. The sulfur-rich stream 16, typically a small volume as compared to the volume of the original feedstream 12, is transferred to a second stage desulfurization system 20, such as a hydrotreating unit, after a post treatment step to remove at least a portion of the extractive liquid, to recover useful hydrocarbons associated with the organosulfur compounds. Effluent from the second stage desulfurization system 20, a second stage sulfur-lean stream 22, and the membrane desulfurized hydrocarbon stream 18, can be combined to provide a low sulfur hydrocarbon stream 24 with minimal or no loss in hydrocarbon product volume. In an alternative embodiment of the process, the second stage sulfur-lean stream 22 that may be rich in aromatics is transferred to one or more subsequent processing steps.

[30] The combined membrane separation system 10 described herein advantageously is conducted as a liquid separation process. The hydrocarbon feedstream 12, the sulfur-rich hydrocarbon stream 16 and the sulfur-lean hydrocarbon stream 18 are all maintained in the liquid phase. The feedstream 12, which can be a crude oil feedstream, a diesel feedstream, a naphtha feedstream, a gas oil feedstream, or a vacuum gas oil feedstream, is generally in the liquid phase initially, and the permeate and retentate remain in the liquid phase, without conversion into vapors and subsequent condensation, thereby conserving energy. A majority of hydrocarbon gases that are in the feedstream, in particular a crude oil feedstream, are generally dissolved in the liquid and do not pass through the membrane, and thus remain in the sulfur-lean hydrocarbon stream 18. Accordingly, the prior art pervaporation operations described above relating to processes for separation of particular fractions using sulfur-selective

membranes and which consume large amounts of energy due to vaporization and vacuum maintenance, are not required.

[31] The sequence of a membrane separation zone followed by second stage desulfurization zone is also conducive to integration with existing commercial hydrotreating units. This sequence realizes substantial economic savings, since the cost of operating a hydrotreating unit is proportional to the feed volume and is generally not sensitive to the sulfur content of the feed. The cost of a membrane separation unit is generally much less than the cost of a hydrotreating unit; therefore, technically mature hydrodesulphurization units can be employed with the attendant economic savings. The use of common and well understood processing units in combination will facilitate the capability for rapid scale-up or development of hydrocarbon feedstream desulfurization.

[32] The overall performance of the integrated process and system generally depends on the performance of the membrane separation unit, which in turn is enhanced by the selectivity and permeability of the membrane used. Accordingly, the membrane material is selected based on the permeation rate and selectivity for the range of sulfur compounds that are present in the hydrocarbon stream. The selection of the type of membrane can also increase efficiency and reliability of the separation unit, and hence increase efficiency and reliability of the overall process.

[33] The membrane is generally formed of a porous material, which provides sites for controlled interface between liquid hydrocarbon feed and extractive liquid. The transport of sulfur compounds mainly occurs between the liquids in the membrane pores. In certain embodiments, the porous membrane provides a non-dispersive contact interface between the extractive liquid and the hydrocarbon feedstream. The non-dispersive contact via the porous membrane contactor improves performance as compared to conventional dispersed-phase contactors, such as liquid-liquid extraction. In addition, solvent holdup is low, which is

advantageous especially in embodiments in which expensive extractive liquid solvents are used. The membrane contactor of the present invention also avoids problems often encountered in conventional contactors, such as formation of emulsions, foaming, unloading and flooding.

[34] Preferably, the porous membrane is formed of a material which has good wettability properties and is insoluble in the hydrocarbon and the extractive liquid. Further, the material for the membrane is selected so as to minimize swelling in the presence of the hydrocarbon and the extractive liquids.

[35] Membrane materials include those conventionally used for ultrafiltration and microfiltration membranes, for instance, formed of polymeric materials such as polyethersulfone (PES), polycarbonate, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), including hydrophilic PVDF, polyester, fluorinated polyimide, polyethyl-oxazoline, Nafion®, nylon and polyether terephthalate (PET). Other non-polymer materials can also be used.

[36] The membrane contactor provides a contact interface between the hydrocarbon feed and the extractive liquid. The selectivity of the membrane system to sulfur compounds is generally impacted by the choice of extractive liquid. In addition, because of the porous nature of the membrane, much higher flux and permeability are obtainable when compared to nonporous (solid) membranes, such as those used in pervaporation membrane processes.

[37] In certain embodiments, the extractive liquid comprises a compound or mixture selected from the group consisting of fumaronitrile; maleonitrile; glyoxal; 2-nitrofur; acetonitrile; acrylonitrile; nitramine; isoxazole; furfural; 5-methylfurfural; benzoylacetonitrile; vinyl formate; methyl formate; oxazole; sulfuric acid; diketene; benzonitrile; acrolein; dimethyl-oxalate; furan; benzaldehyde; acetic anhydride; methacrylonitrile; dimethyl sulfide; lactic acid; acetic acid; dimethyl formamide; dimethyl sulfoxide; aqueous potassium

hydroxide; furfuryl alcohol; vinylacetylene; nicotinonitrile; pyridazine; methylmaleic anhydride; acetaldehyde; cis-crotonitrile; 3-nitrobenzotrifluoride; methyl phenyl ketone; vinyl acetate; p-tolualdehyde; m-tolualdehyde; o-tolualdehyde; propylene-carbonate; methanol; methanol and aqueous sodium hydroxide; dimethylsulfoxide and methanol; 1-ethyl,3-methylimidazolium ethyl sulfate; 1-ethyl,3- methylimidazolium methyl sulfate; 1-ethyl,3-methylimidazolium hexafluorophosphate; 1-butyl,3- methylimidazolium tetrafluoroborate; 1-ethyl,3-methylimidazolium bis(trifluoromethanesulfonyl)imide; 1-*n*-propyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide; 1-*n*-butyl-3-methylimidazolium; 1-*n*-butyl-3-methylimidazolium trifluorotris(pentafluoroethyl)phosphate; 1-*n*-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide; and 1-*n*-decyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide.

[38] The following Table 1 summarizes the performance of certain extractive solvents for sulfur removal from diesel having a 1.4% w/w sulfur content, based on equilibrium partitioning of sulfur compounds between the hydrocarbon phase and extractive liquid phase:

Table 1	
<u>Solvent</u>	<u>Weight % Sulfur removal</u>
Furfural	28.6
Acetonitrile	26.2
Methanol	16.1
5-Methyl furfural	47.3
Propylene carbonate	16.0
Dimethyl sulfoxide	10.5
Acetone/water (50/50)	3.7
Furfuryl alcohol	18.8
Acetic acid	22.6
Lactic acid	2.0
Dimethylformamide	40.8

[39] The following Table 2 summarizes the performance of certain extractive solvents for sulfur removal from Arab Light crude oil having a 1.9% w/w sulfur content, based on equilibrium partitioning of sulfur compounds between the hydrocarbon phase and extractive liquid phase:

Table 2

<u>Solvent</u>	<u>Weight % Sulfur removal</u>
Furfural	13.6
Acetonitrile	3.9
Methanol	1.5

[40] In certain embodiments in which the target sulfur compounds comprise aliphatic sulfur molecules, the extractive liquid is selected from the group consisting of acetonitrile; dimethyl sulfoxide; acrylonitrile; benzonitrile; dimethyl formamide; aqueous sodium hydroxide; aqueous potassium hydroxide; furfuryl alcohol; vinylacetylene; sulfuric acid; dimethylsulfoxide and methanol; furfural; and 5-methylfurfural.

[41] In additional embodiments in which the target sulfur compounds comprise aromatic sulfur compounds including thiophenes, benzothiophenes and dibenzothiophenes, and the extractive liquid is selected from the group consisting of acetonitrile; furfural; benzonitrile; dimethyl sulfide; dimethyl formamide; methanol; lactic acid; propylene-carbonate; 5-methylfurfural; methyl formate; 1-ethyl,3- methylimidazolium ethyl sulfate; 1-ethyl,3-methylimidazolium methyl sulfate; 1-ethyl,3- methylimidazolium hexafluorophosphate; 1-butyl,3- methylimidazolium tetrafluoroborate; 1-ethyl,3-methylimidazolium bis(trifluoromethanesulfonyl)imide; 1-*n*-propyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide; 1-*n*-butyl-3-methylimidazolium trifluorotris(pentafluoroethyl)phosphate ; and 1-*n*-butyl-3-methylimidazolium.

[42] In further embodiments in which the target sulfur compounds comprise alkyl derivatives of aromatic sulfur molecules including 4,6-dimethyl-dibenzothiophenes, the extractive liquid is selected from the group consisting of acetonitrile; acrylonitrile; furfural; 5-methylfurfural; benzoylacetonitrile; vinyl formate; diketene; benzonitrile; acrolein; dimethyl-oxalate; benzaldehyde; acetic anhydride; methacrylonitrile; acetic acid; dimethyl formamide; dimethyl sulfoxide; aqueous potassium hydroxide; furfuryl alcohol; 1-ethyl,3-methylimidazolium ethyl sulfate; 1-ethyl,3- methylimidazolium methyl sulfate; 1-ethyl,3-

methylimidazolium hexafluorophosphate; 1-butyl,3- methylimidazolium tetrafluoroborate; and 1-ethyl,3-methylimidazolium bis(trifluoromethanesulfonyl)imide.

[43] In contrast to pervaporation techniques commonly known in the art, the membrane separation system for separating sulfur compounds from hydrocarbon feeds of the present invention operates at temperatures and pressures that maintain the feedstream in liquid phase.

[44] The membrane unit can be in any suitable configuration. For instance, the membrane unit can be in a spirally wound configuration, a hollow fiber configuration, a plate and frame configuration, or a tubular configuration. In certain preferred embodiments, the membrane unit is in a spirally wound or a hollow fiber configuration. In addition, a plurality of membrane units can optionally be operated in parallel or series. In the parallel configuration, one or more membrane units can be decommissioned for maintenance without disrupting the continuity of the desulfurization process.

[45] In a preferred embodiment, the membrane unit is configured and dimensioned to allow maximum contact between the liquid hydrocarbon feedstream and the porous membrane on the retentate side, and to allow maximum contact between the extractive liquid and the porous membrane on the permeate side. The configuration and dimensions are provided to allow substantially all of the liquid hydrocarbon feedstream to come into contact with the porous membrane, and hence with the extractive liquid maintained in the pores of the membrane.

[46] The stream desulfurized by conventional processes, such as hydrotreating, and the hydrocarbons desulfurized by the membrane separation apparatus, can be combined to provide a low sulfur hydrocarbon system effluent with minimal or no loss of the original hydrocarbon volume. This low sulfur hydrocarbon effluent can serve as a feedstream for subsequent fractionating in a downstream process. Alternatively, the low sulfur hydrocarbon effluent may be sold as sweet crude oil, thereby taking advantage of the favorable price differential between sweet and sour crude oils.

[47] Referring to FIG. 2, a configuration of a system 100 of the present invention is schematically depicted. Crude oil or other hydrocarbons are conveyed from a feed tank 108 in a stream 112 to a retentate side 136 of the membrane contactor 114. Extractive liquid is introduced via a sweep stream 140 to the permeate side of the membrane contactor from an extractive liquid vessel 142. At the membrane 114 interface, controlled contact is provided between the feedstream and the extractive liquid so as to minimize intermixing of the liquids. The membrane contactor 114 provides the required surface area to meet the requisite degree of sulfur removal.

[48] The extractive liquids are selected to draw the sulfur-containing compounds out of the hydrocarbon feedstream, such as aliphatic sulfur molecules (including but not limited to sulfides, disulfides and mercaptans) and/or aromatic molecules (including but not limited to thiophenes, benzothiophenes, dibenzothiophenes and alkyl derivatives of aromatic sulfur molecules such as 4,6-dimethyl-dibenzothiophenes). The sulfur-lean stream 118 can be used as is, or combined with the sulfur-rich stream 116 after it has been subjected to further desulfurization.

[49] The sulfur-rich stream 116, including a high concentration of sulfur compounds and extractive liquids, are passed to a suitable regeneration zone, such as a flash tank 144, within which solvents (extractive liquid) is recovered/regenerated via a recycle line 145, and sulfur rich oil is discharged. The sulfur-rich hydrocarbon stream is passed to a conventional desulfurization process 120 such as a hydrodesulfurization unit. The hydrodesulfurized hydrocarbons 122 and the retentate hydrocarbons 118 can be used as separate product streams or combined as a single product stream.

Example

[50] Membrane contactors using polyvinylidene fluoride (PVDF) flat sheet ultrafiltration membranes were constructed and tested in accordance with the present invention. The membranes were about 125 μm in thickness, had pores of 0.1 μm or 0.2 μm , and a porosity of 70%, 75% or 80%. Furfural was used as the extractive solvent. The flow rate of both the extractive solvent and the hydrocarbon streams was set at 10 milliliters per minute. Table 3 provides the results indicating effective mass transfer coefficients (in centimeters per hour).

Table 3

Hydrocarbon stream	Membrane Contactor	Mass Transfer Coefficient
Arab light crude (1.9 % w/w sulfur)	0.1 μm pore, 70% porosity	0.25
Diesel (1.5 % w/w sulfur)	0.1 μm pore, 70% porosity	0.19
Diesel (1.5 % w/w sulfur)	0.2 μm pore, 75% porosity	0.28
Diesel (1.5 % w/w sulfur)	0.2 μm pore, 80% porosity	0.37

[51] The process of the invention has been described and explained with reference to the schematic process drawings and examples. Additional variations and modifications will be apparent to those of ordinary skill in the art based on the above description and the scope of the invention is to be determined by the claims that follow.

We claim:

1. A method of reducing the sulfur content of a sulfur-containing hydrocarbon feedstream comprising:

passing the feedstream in contact with a membrane on a retentate side of a membrane separation unit;

5 passing an extractive liquid in contact with the membrane on a permeate side of the membrane separation unit under conditions in which the extractive liquid contacts the feedstream;

concentrating sulfur compounds in the extractive liquid in a permeate stream of the membrane separation unit;

10 recovering as a retentate stream a first hydrocarbon product stream of reduced sulfur content;

recovering and subjecting the permeate stream to a fractionation process step for recovery of at least a portion of the extractive liquid; and

recovering a resulting sulfur-rich hydrocarbon stream from the fractionation process step.

2. The method of claim 1, wherein the sulfur-rich hydrocarbon stream is subjected to a hydrodesulfurization process step, and recovering a second hydrocarbon product stream of reduced sulfur content.

3. The method of claim 1, further comprising mixing the first and second hydrocarbon product streams to provide a final product stream of reduced sulfur content.

4. The method of claim 1, wherein the feedstream contains a plurality of different sulfur-containing compounds and at least certain of the sulfur-containing compounds are soluble in the extractive liquid.

5. The method of claim 4, wherein the extractive liquid is selected from the group consisting of fumaronitrile; maleonitrile; glyoxal; 2-nitrofurane; acetonitrile; acrylonitrile; nitramine; isoxazole; furfural; 5-methylfurfural; benzoylacetonitrile; vinyl formate; methyl formate; oxazole; sulfuric acid; diketene; benzonitrile; acrolein; dimethyl-oxalate; furan; benzaldehyde; acetic anhydride; methacrylonitrile; dimethyl sulfide; lactic acid; acetic acid; dimethyl formamide; dimethyl sulfoxide; aqueous potassium hydroxide; furfuryl alcohol; vinylacetylene; nicotinonitrile; pyridazine; methylmaleic anhydride; acetaldehyde; cis-crotonitrile; 3-nitrobenzotrifluoride; methyl phenyl ketone; vinyl acetate; p-tolualdehyde; m-tolualdehyde; o-tolualdehyde; propylene-carbonate; methanol; methanol and aqueous sodium hydroxide; dimethylsulfoxide and methanol; 1-ethyl,3- methylimidazolium ethyl sulfate; 1-ethyl,3- methylimidazolium methyl sulfate; 1-ethyl,3- methylimidazolium hexafluorophosphate; 1-butyl,3- methylimidazolium tetrafluoroborate; 1-ethyl,3-methylimidazolium bis(trifluoromethanesulfonyl)imide; 1-*n*-propyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide; 1-*n*-butyl-3-methylimidazolium; 1-*n*-butyl-3- methylimidazolium trifluorotris(pentafluoroethyl)phosphate; 1-*n*-hexyl-3- methylimidazolium bis(trifluoromethanesulfonyl)imide; and 1-*n*-decyl-3- methylimidazolium bis(trifluoromethanesulfonyl)imide.

6. The method of claim 1, wherein target sulfur compounds comprise aliphatic sulfur molecules, and the extractive liquid is selected from the group consisting of acetonitrile; dimethyl sulfoxide; acrylonitrile; benzonitrile; dimethyl formamide; aqueous sodium hydroxide; aqueous

potassium hydroxide; furfuryl alcohol; vinylacetylene; sulfuric acid; dimethylsulfoxide and
5 methanol; furfural; and 5-methylfurfural.

7. The method of claim 1, wherein target sulfur compounds comprise aromatic sulfur compounds including thiophenes, benzothiophenes and dibenzothiophenes, and the extractive liquid is selected from the group consisting of acetonitrile; furfural; benzonitrile; dimethyl sulfide; dimethyl formamide; methanol; lactic acid; propylene-carbonate; 5-methylfurfural; methyl
5 formate; 1-ethyl,3- methylimidazolium ethyl sulfate; 1-ethyl,3- methylimidazolium methyl sulfate; 1-ethyl,3- methylimidazolium hexafluorophosphate; 1-butyl,3- methylimidazolium tetrafluoroborate; 1-ethyl,3-methylimidazolium bis(trifluoromethanesulfonyl)imide; 1-*n*-propyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide; 1-*n*-butyl-3-methylimidazolium trifluorotris(pentafluoroethyl)phosphate ; and 1-*n*-butyl-3-methylimidazolium.

8. The method of claim 1, wherein target sulfur compounds comprise alkyl derivatives of aromatic sulfur molecules including 4,6- dimethyl-dibenzothiophenes, and the extractive liquid is selected from the group consisting of acetonitrile; acrylonitrile; furfural; 5-methylfurfural; benzoylacetonitrile; vinyl formate; diketene; benzonitrile; acrolein; dimethyl-oxalate;
5 benzaldehyde; acetic anhydride; methacrylonitrile; acetic acid; dimethyl formamide; dimethyl sulfoxide; aqueous potassium hydroxide; furfuryl alcohol; 1-ethyl,3- methylimidazolium ethyl sulfate; 1-ethyl,3- methylimidazolium methyl sulfate; 1-ethyl,3- methylimidazolium hexafluorophosphate; 1-butyl,3- methylimidazolium tetrafluoroborate; and 1-ethyl,3-methylimidazolium bis(trifluoromethanesulfonyl)imide.

9. The method of claim 1, wherein the membrane is a porous membrane.

10. The method of claim 9, wherein the porous membrane constitutes a controlled interface for contact between the hydrocarbon feedstream and the extractive liquid.

11. The method of claim 9, wherein the porous membrane constitutes a non-dispersive contact interface between the extractive liquid and the hydrocarbon feedstream.

12. The method of claim 9, wherein the porous membrane comprises a material which is insoluble in the hydrocarbon and the extractive liquid.

13. The method of claim 9, wherein the porous membrane comprises a material which undergoes minimal swelling in the hydrocarbon and the extractive liquid.

14. A liquid hydrocarbon desulfurization system comprising:

a source of extractive liquid;

a membrane housing including

a porous membrane having a retentate side and a permeate side,

5 a retentate portion configured and dimensioned for maximizing contact between a liquid hydrocarbon feedstream and the retentate side of the membrane, and

a permeate portion configured and dimensioned for maximizing contact between the extractive liquid and the retentate side of the membrane.

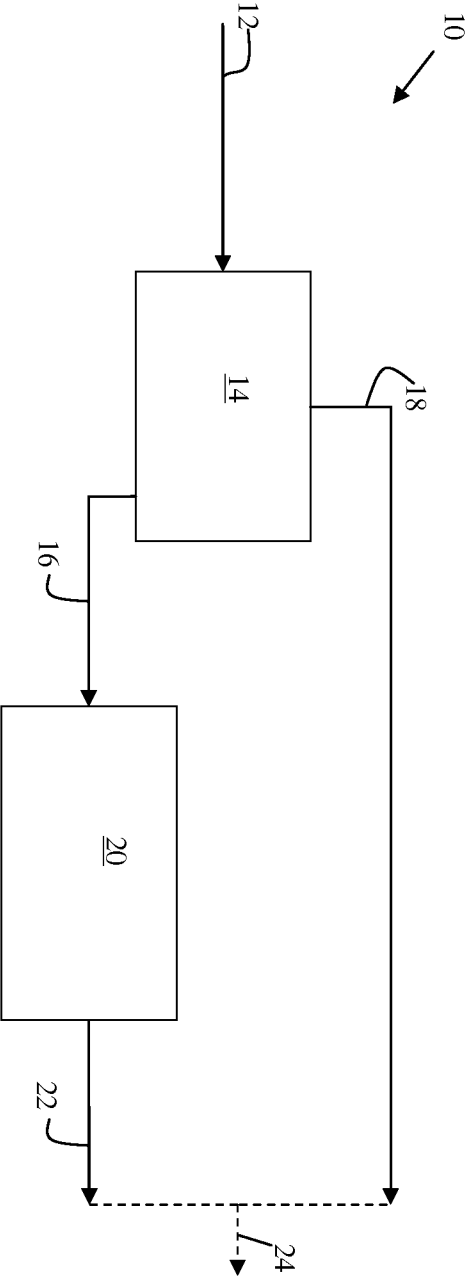


FIG. 1

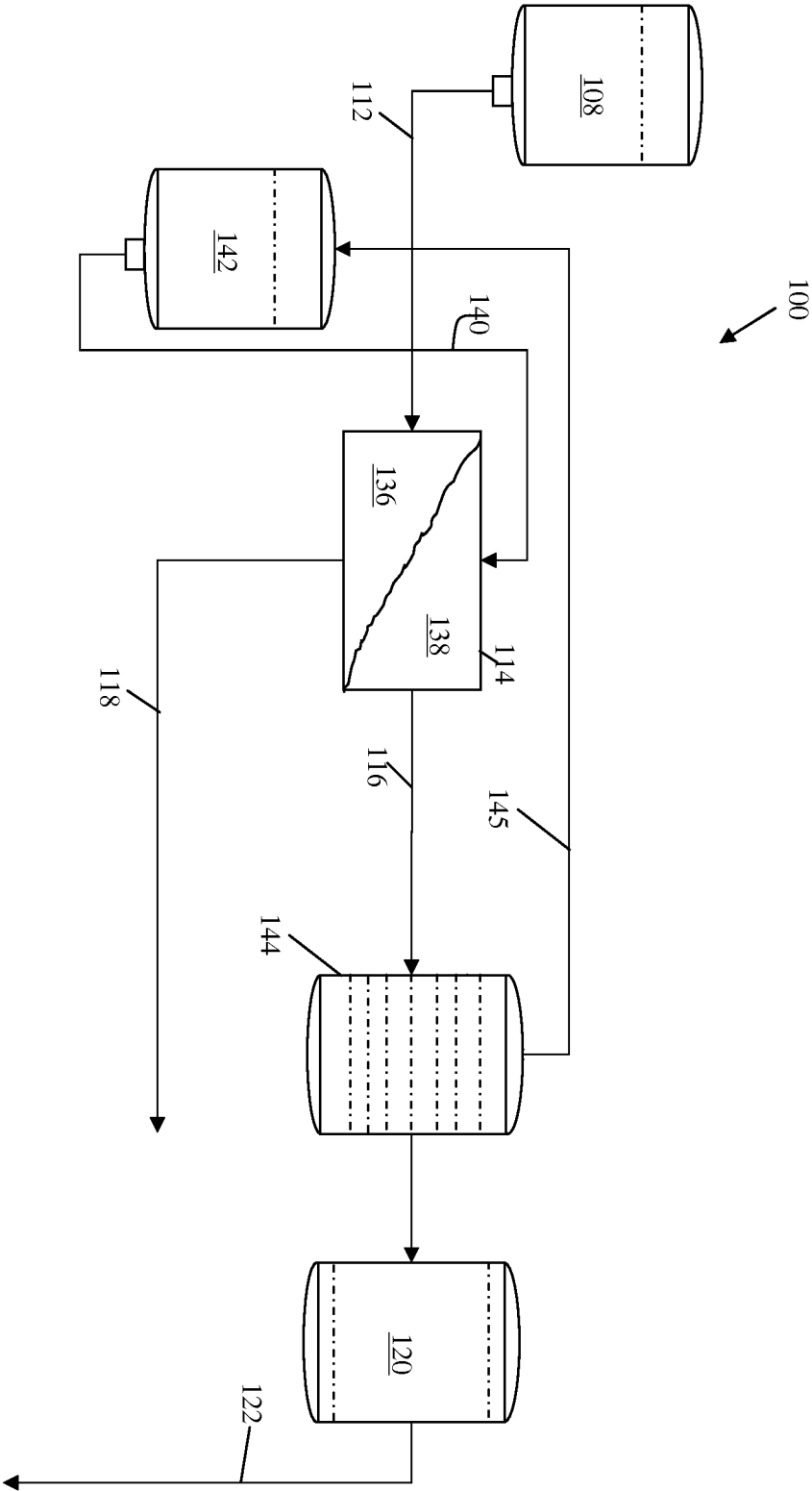


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/40335

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C07C 7/144 (2010.01)

USPC - 208/208R; 585/818

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)

USPC - 208/208R; 585/818

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

USPC - 208/208R; 585/818 (words only)

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

WEST (PGPB, USPT, USOC, EPAB, JPAB); Google

** Please see Extra Sheet for search terms used***

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2005/0067323 A1 (Balko) 31 March 2005 (31.03.2005); especially para [0013]-[0015], [0022], [0024], [0039], [0050] and [0056]-[0057]	1-14
Y	US 5,107,059 A (Chen et al.) 21 April 1992 (21.04.1992); especially col 3, ln 30-39	1-14
Y	US 2009/0107890 A1 (Hamad et al.) 30 April 2009 (30.04.2009); especially para [0013], [0023] and [0033]-[0037]	1-14

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

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

05 August 2010 (05.08.2010)

Date of mailing of the international search report

30 AUG 2010

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 10/40335

*** Search terms used ***

desulfurization, hydrocarbon, membrane, retentate, extractive, extracting, extraction, liquid, hydrodesulfurization, acetonitrile, dimethyl sulfoxide, DMSO, acrylonitrile, benzonitrile, dimethyl formamide, furfuryl alcohol, furfuryl, vinylacetylene, sulfuric acid, 5-methylfurfural, retentate, porous, controlled interface, permeate, fractionation, solvent, thiophenes, benzothiophenes, dibenzothiophenes