A process for desulphurization of petroleum oil, comprising the step of diluting the feed oil with a suitable organic solvent prior to the desulphurization reaction, is disclosed. The organic solvent is selected from alkanes, alkenes, cyclic alkenes and alkynes, and particularly selected from n-hexane, cyclohexane, heptane, pentene, hexene, heptene, octene, toluene and xylene. The solvent concentration in the mixture of feed oil and solvent is in the range of 0.1-70%.
PROCESS FOR DESULPHURIZATION OF PETROLEUM OIL

FIELD OF DISCLOSURE

[0001] The present disclosure relates to desulphurization processes. Particularly, the disclosure relates to a process for desulphurization of petroleum heavy oils and residual petroleum oils, more particularly carbon black feed oil.

BACKGROUND

[0002] Petroleum oils are complex mixtures of primarily hydrocarbons and other carbon containing compounds. The overall composition of the petroleum oil or crude oil is known to vary significantly from its origin or geographical location of the refinery. The elemental composition of these oils consists of about carbon (84-87%), hydrogen (12-14%) along with oxygen, nitrogen, sulfur, moisture and ash. The sulfur content may vary substantially from 0.2-8%. In addition to these main components, there are traces of metal impurities, that may be present initially or get associated with the oil during various refinery processing steps. The crude oils may also contain hydrocarbons, paraffins, asphaltenes, resins and ash. The crude oil compositions can be differentiated into various individual fractions at different boiling ranges. The low boiling fractions (<170 °C) are typically napthas, those between 180-250°C are kerosene and the ones boiling in the range of 250-350°C are termed as gas oils. The fractions boiling above 350°C are generally termed as residues and are obtained after all or most of the distillable products have been removed from the petroleum oil. These residue fractions could be further distinguished as light vacuum gas oils, heavy vacuum gas oils and vacuum residues. Each of these different fractions have different molecular distribution of various hydrocarbon species and related compounds. In particular, one of the significant aspects is the distribution of sulfur containing species in these fractions. The use of the petroleum oil residues includes heating (as a fuel), and as a feedstock for the manufacture of carbon black. The presence of sulfur in the petroleum oil residue has a number of shortcomings. During the complete or partial combustion of the petroleum residue, sulfur gets converted to SO₂ and SO₃. These cause major environmental issues in the form of acid rains and adversely affect health. Further, the sulfur species cause poisoning of catalyst systems used in the refineries. These are also known to be the primary cause of corrosion of equipment and exhaust. The presence of sulfur in the residue fraction has further ramifications in case of use of this as raw material for carbon black manufacturing. Apart from significant air pollution, these species remain associated with the final carbon black product which is detrimental to various applications. Furthermore, high sulfur content affects the throughput of the manufacturing process.

[0003] Carbon black feed oil (CBFO) is a raw material used for manufacturing carbon black, an important material used in the tyre industry. Carbon black feedstock is a mixture of C₁₂ and higher components rich in naphthalene, methylenes, anthracene, fluorene and other poly-aromatic components. CBFO is essentially procured either from oil refineries or from coal tar distillers. There are two types of CBFO viz. High BMCI type and General type. "BMCI" (Bureau of Mines Co-relation Index) effectively measures the degree yield of carbon black. Higher the BMCI, better the yield of carbon black. High BMCI CBFO is used as a raw material by carbon black manufacturers while the other grade is used by various consumers to manufacture rubber process oils, incense sticks etc.

[0004] Sulfur content in CBFO reduces the effective BMCI value. Moreover, this sulfur gets carried to the final carbon black product as an impurity. Hence, it is of interest to reduce the sulfur content of the CBFO. Hence, it would be of interest to discover a method for reducing the sulfur content of the petroleum oil residue to be used as CBFO.

[0005] A desulphurization process is usually carried out to remove sulfur (S) from natural gas and petroleum products such as gasoline or petrol, jet fuel, kerosene, diesel fuel and fuel oils. The refinery feedstock (naphtha, kerosene, diesel oil and heavier oils) contains a wide range of organic sulfur compounds, including thioles, thiophenes, organic sulfides, disulfides and many others. These organic sulfur compounds are the products of degradation of sulfur containing biological components, present during the natural formation of the fossil fuel, petroleum crude oil. The purpose of removing sulfur is to reduce sulfur dioxide (SO₂) emissions that result from using these fuels in automotive vehicles, aircrafts, railroad locomotives, ships, gas or oil burning power plants, residential and industrial furnaces, and other forms of equipment using fuel for combustion.

[0006] A number of techniques including catalytic transformation processes such as hydrodesulfurization and physico-chemical processes such as solvent extraction, alkylation, oxidation, precipitation, adsorption, and the like, have been worked in order to reduce the sulfur content from various fractions of the petroleum oils. The hydro-desulphurization is commonly used for this purpose. This process is based on catalytic hydrogenation of the sulfur species to convert it into H₂S. However, the hydro-desulphurization is known to work efficiently on lower boiling fractions such as gasoline, naphtha, kerosene, and the like. The catalyst systems generally include transition metals such as Ni, Co, Mo supported on Al₂O₃. Several efforts have been made in the past to provide a hydrodesulfurization technique. Some typical prior art examples are disclosed in U.S. Pat. No. 2,516,877, U.S. Pat. No. 2,604,436, U.S. Pat. No. 2697682, U.S. Pat. No. 2,866,751, U.S. Pat. No. 2,866,752, U.S. Pat. No. 2,911,359, U.S. Pat. No. 2,992,182, U.S. Pat. No. 3,620,968, U.S. Pat. No. 3,688,116, U.S. Pat. No. 4,193,864, U.S. Pat. No. 4,328,127, U.S. Pat. No. 4,960,506 and U.S. Pat. No. 5,677,259. Most of these processes are highly suitable for treating lower boiling fractions or crude oils. However, their efficiency drops when treating high boiling fractions or vacuum residues. This is due to the fact that lower boiling oil fractions primarily contain sulfur in the form of mercaptans or lower homologous ring compounds, which are relatively easier to desulfurize. However, the high boiling fractions or residues contain sulfur species that are part of the more stable ring compounds such as substituted benzothiophenes and higher derivatives or large molecule ring compounds which are extremely difficult to desulfurize. Some prior art examples for treating residues by hydro-desulfurization include U.S. Pat. No. 2,640,011, U.S. Pat. No. 2,992,182, U.S. Pat. No. 4,328,127 and U.S. Pat. No. 4,576,710. In most of the cases, the treatment parameters are extreme i.e. use of high temperatures in excess of 400°C and pressures in excess of 1000 psig. Moreover, the desulfurization efficiencies are low. Further, due to these difficult processing conditions hydro-desulfurization results in coke formation, leading to deactivation of the catalyst systems. In addition, the hydro-desulfurization process results in the for-
In addition to hydro-desulfurization, there are several other techniques that are being explored for the desulfurization of the petroleum oils. These include oxidative, adsorptive, solvent extraction and bio-enzymatic processes. Some typical prior art examples of oxidative desulfurization processes are disclosed in U.S. Pat. No. 3,816,301, U.S. Pat. No. 3,163,593, U.S. Pat. No. 3,413,307, U.S. Pat. No. 3,505,210, U.S. Pat. No. 3,816,301, U.S. Pat. No. 3,847,800, U.S. Pat. No. 6,274,785, U.S. Pat. No. 6,277,271, U.S. Pat. No. 7,144,499, U.S. Pat. No. 7,179,368, U.S. Pat. No. 7,276,152, U.S. Pat. No. 7,314,545, US20050189261, US200600226049, US200800308463 and US20090148374. The common oxidizing agents used are H₂O₂ or H₂O₃ in combination with acetic acid and in the presence of an oxidizing catalyst system. In addition, tert-butyl hydroperoxide can also be used as an oxidant as it tends to be soluble in oil. The adsorptive processes generally use absorbents such as clay, Al₂O₃, bauxite, transition metal oxides systems supported on silica or alumina, zeolites, activated carbon, etc. Some typical examples of these processes are disclosed in U.S. Pat. No. 2,436,550, U.S. Pat. No. 2,537,756, U.S. Pat. No. 2,988,499, U.S. Pat. No. 3,620,969, U.S. Pat. No. 4,419,224, U.S. Pat. No. 4,695,366, U.S. Pat. No. 5,219,542, U.S. Pat. No. 5,310,717, U.S. Pat. No. 6,558,533, U.S. Pat. No. 6,500,219, U.S. Pat. No. 7,291,259, US20030029777, US20030188995, US20060283780 and US20090000990. The solvent extraction processes use various solvent systems such as dimethyl formamide, dimethyl sulfoxide, phenols, dichloroethers, nitrobenzene, and the like. Some typical prior art processes are disclosed in U.S. Pat. No. 2,486,519, U.S. Pat. No. 2,623,004, U.S. Pat. No. 2,634,230 and U.S. Pat. No. 3,779,895. However, most of the above mentioned processes are aimed at desulfurization of crude oils or low boiling fractions. Similarly, most of the above mentioned processes (except bio-enzymatic) are aimed at targeting and removing the entire sulfur containing molecule rather than removal of the sulfur atom specifically. This may not have a significant effect while considering desulfurization of crude oil or lower boiling fractions as the net sulfur content is less and also the sulfur would be distributed over small number of low molecular weight compounds. However, in case of residues where the sulfur content can be as high as 4-5%, the sulfur appears to be essentially distributed over a majority of the molecules contained in the oil. Thus, removing the entire sulfur containing molecule would result in substantial material loss of the oil part.

Another such desulfurization process is based on the use of alkali metal, especially sodium metal as the desulfurizing agent. In this process, the sulfur is primarily removed as a metal sulfide instead of the removal of the entire sulfur containing molecule. Some typical prior art examples of this process are U.S. Pat. No. 1,938,672, U.S. Pat. No. 1,952,616, U.S. Pat. No. 2,902,441, U.S. Pat. No. 3,004,912, U.S. Pat. No. 3,093,575, U.S. Pat. No. 3,617,530, U.S. Pat. No. 3,755,149, U.S. Pat. No. 3,787,315, U.S. Pat. No. 4,003,824, U.S. Pat. No. 4,120,779, U.S. Pat. No. 4,123,350, U.S. Pat. No. 4,147,612, U.S. Pat. No. 4,248,695, U.S. Pat. No. 4,437,980, U.S. Pat. No. 6,210.564, U.S. Pat. No. 7,192,516, U.S. Pat. No. 7,507,327, U.S. Pat. No. 7,588,680. These documents thus describe the desulfurization of crude oils and residues by sodium metal. The sodium metal can be used as pure metal or in an alloy, supported on inert species, or as dissolved in solvent such as ammonia. Also, these processes use hydrogen at high pressures in combination to the sodium metal for desulfurization. In some processes, sodium-based compounds such as NaH, NaNH₂, and the like, are used for the desulfurization. A major product formed as a reaction of the sodium metal with the sulfur in the feed oil is sodium sulfide (Na₂S). Some of the above-mentioned prior art documents also describe the regeneration of sodium from Na₂S. These processes report the effectiveness of desulfurization of recalcitrant sulfur especially from that of high boiling resid oils. However, these sodium-based desulfurization processes are associated with limitations such as low yield of desulfurized feed oil, formation of large amount of insoluble sludge, requirement of hydrogen and safety concerns. The inherent high viscosity of heavy oils and petroleum residues makes it difficult for the processing and separation operations before and after the desulfurization process. A large amount of valuable residual feed oil remains associated with the precipitated sodium sulfide residue or the unreacted sodium in the form of a highly viscous sludge. Also, the sludge is extremely difficult to filter and separate due to its inherent viscosity and sticky nature. Thus, there is a substantial loss of feed during the process, especially during filtration or separation. Furthermore, due to lower density of sodium metal as compared to that of the residual oil, the sodium metal may tend to float at the surface of the oil and may lead to a hazardous situation during failed reactions or during incomplete mixing.

Thus, the known desulfurization processes are associated with a number of limitations such as low yield of desulfurized feed oil, formation of large amount of insoluble sludge, requirement of hydrogen and safety issues. The inherent high viscosity of heavy oils and petroleum residues makes it difficult for the processing and separation operations before and after the desulfurization process. A large amount of valuable residual feed oil remains associated with the precipitated sulfur residue or unreacted sodium in the form of a highly viscous sludge. Also, the sludge is extremely difficult to filter and separate due to its inherent viscosity and sticky nature. There is a substantial loss of feed during the process, especially during filtration or separation. Further, it was observed that the sodium-based desulfurization processes result in retention of sodium/metal in the oil. The presence of sodium metal, even at concentration as low as <100 ppm, results in change in the morphology of the carbon black during the manufacturing processes. Therefore, there is a need to develop a process to minimize the loss of feed during desulfurization of petroleum oils. The present invention is an improved process for petroleum oil desulfurization, especially carbon black feed oil (CBFO) desulfurization, which reduces the sulfur content in the oil.
Another object of the present disclosure is to provide a process for further treatment of the desulfurized oil for removal of the residual sodium content.

SUMMARY

In accordance with the present disclosure, there is provided a process for desulfurization of petroleum oils, said process comprising the following steps:

- Diluting petroleum oil with a hydrocarbon organic solvent selected from the group consisting of alkanes, alkenes, cyclic alkenes and alkynes, to obtain an oil-solvent mixture, wherein the organic solvent concentration in the oil-solvent mixture is in the range of 0.1-70%.
- Transferring the oil-solvent mixture to a reactor vessel.
- Adding solid sodium metal to the oil-solvent mixture in the reactor vessel, wherein the sodium concentration is between 0.1-20% of the petroleum oil concentration.
- Reacting the oil-solvent mixture with sodium at a temperature in the range of 240-350° C. and a pressure in the range of 0-500 psig for 15 minutes-4 hours under mixing to obtain a resultant mixture.
- Cooling and settling the resultant mixture; and
- Decanting the cooled mixture and filtering the decanted solution of desulfurized petroleum oil.

Typically, in accordance with the present disclosure, the organic solvent is selected from a group consisting of n-hexane, cyclohexane, heptane, pentene, hexene, heptene, octene, toluene and xylene.

Preferably, in accordance with the present disclosure, the process includes the step of purging the reactor vessel with hydrogen gas at a pressure in the range of 50-500 psig.

Preferably, in accordance with the present disclosure, the process includes the step of separating the organic solvent from desulfurized petroleum oil by distillation.

Preferably, in accordance with the present disclosure, the process includes the step of mixing sodium with the oil-solvent mixture in the reactor vessel by using high shear mixing by means of a mixer selected from an inline mixer, a mechanical mixer, a pump around loop and an ultrasonic mixer.

In accordance with the present disclosure, there is provided a process for removing residual sodium metal, said process including the steps of: treating the desulfurized petroleum oil with 0.1-10% carboxylic acid and an organic acid at a temperature in the range of 50-150° C. for 30 minutes to 90 minutes under vigorous stirring; and filtering the resultant mixture to obtain desulfurized petroleum oil having sodium content between 10-50 ppm.

Typically, in accordance with the present disclosure, the carboxylic acid is selected from acetic acid, formic acid and propionic acid.

Preferably, in accordance with the present disclosure, the organic solvent is selected from alkanes, alkenes, cyclic alkenes, alkynes and alcohol. More preferably, the organic solvent is xylene.

In accordance with the present disclosure, there is provided a process for removing residual sodium metal by purging the desulfurized petroleum oil with air at a temperature in the range of 30-150° C.

The present disclosure relates to a process for desulfurization of carbon black feed oil (CBFO). The feed oil (CBFO) has high viscosity at ambient conditions. The process comprises diluting the feed oil with a suitable organic solvent, prior to the desulfurization reaction. The organic solvent can be selected from the group of hydrocarbon solvents consisting of alkanes, alkenes, cyclic alkenes and alkynes. Similarly, other oils such as petrol, kerosene, crude oil, and the like, can also be used for diluting the feed oil. The organic solvent is particularly selected from the group consisting of n-hexane, cyclohexane, heptane, pentene, hexene, heptene, octene, toluene and xylene, preferably the solvent is xylene. The solvent concentration used is in the range of 0.1-70%, preferably in the range of 0.1-50%, more preferably in the range of 1-30%, in the mixture of CBFO and solvent.

The feed to the process of the present disclosure is carbon black feed oil having a sulfur content in the range of 0.1%-20%. The process of the present disclosure can also be used for petroleum oils of various boiling fractions. Further, the process of the present disclosure can be used to desulfurize coal tar, shale oil or other organic sulfur bearing compounds. The organic solvent is removed after the desulfurization process. The present process results in a desulfurized stream (after xylene removal) with a substantially reduced viscosity. The formation of insoluble sludge (unsuitable material) due to polymerization reactions of the desulfurized species is reduced due to improvement in the feed oil viscosity. Further, the improvement in the feed oil viscosity enhances the processing of the feed oils required in applications such as manufacturing of carbon black product.

The process results in improvement of feed oil quality by means of reducing the asphaltene content in the feed oil. Asphaltenes are considered as the n-hexane insoluble, toluene soluble components of a carbonaceous material such as crude oil, bitumen or coal. Asphaltenes are high molecular weight hetero-atom species that are generally considered detrimental to the quality of the processed carbon black product.

The process of the present disclosure is carried out in the absence of hydrogen at a pressure in the range of 0-500 psig, this results in a higher C:H ratio of the processed oil as compared to processes carried in the presence of high pressure hydrogen. This is beneficial for converting most of the processed oil into carbon black, as the hydrogen leaves the process in the form of water vapor without contributing to the formation of product. The process removes moisture present in the CBFO. The CBFO generally contains about <1% moisture. Nuc metal is known to have strong affinity to water and thereby react with moisture. The present process uses sodium metal in a concentration between 0.1-20% of the CBFO oil concentration. Thus, moisture present in the CBFO is completely removed.

In one aspect of the present disclosure, the process is carried out in the presence of hydrogen. The hydrogen added could be in the range of 0-500 psig, preferably in the range of 0-300 psig, and more preferably in the range of 0-100 psig. In addition, the hydrogen may not be present in the form of closed system i.e. under no hydrogen pressure or a pressure-less system. Thus, it could be added in a continuous or a semi continuous flow of hydrogen gas.

The process of desulfurization of the present disclosure gives crystalline sodium sulfide as the by-product. The by-product so formed is easier to separate and filter and...
thus results in a better recovery of the desulfurized oil as well as better separation and processing efficiency of the desulfurized oil.

[0035] An important aspect of the present disclosure is that it provides a process for reducing the size of dispersed sodium—as solid particles or molten form as droplets. Finer dispersion of sodium metal increases the efficiency of the desulfurization process. In the conventional process, the by-product, sodium sulfide tends to cover the surface of sodium metal thereby reducing the efficiency of the process. Therefore, mixing, preferably high shear mixing, for a duration in the range of 15 minutes-4 hours at a temperature in the range of 240–350°C is provided; high shear mixing causes the breaking of sodium sulfide and thereby provides new sodium surfaces for enhancing the reaction. Any form of mixing may be used, such as an inline mixer, a pump around loop, a mechanical mixer, or an ultrasonic mixer, that provides the required amount of dispersion to the sodium metal.

[0036] In the absence of hydrogen, there is formation of insoluble sludge (unsuitable material) due to the polymerization reactions amongst the desulfurized species.

[0037] Furthermore, the pure CBFO has a high viscosity of above 1500 cP at ambient conditions. The process of the present disclosure results in a desulfurized stream (after xylene/solvent removal) having a substantial viscosity reduction to the range of 100-150 cP at ambient conditions. Thus, the overall effect is that the desulfurization process is carried out in the absence of hydrogen and results in lower loss of feed oil caused by insoluble sludge formation as well as improvement in the feed oil viscosity which is further expected to enhance the characteristics of the processed carbon black product. Further, if the process is carried out in the presence of hydrogen, there may be a reduction in the aromatic content of the feed due to hydrogenation (reduced C:H ratio), resulting in lower yield of the carbon black product. Thus, if the process is carried out in the absence of hydrogen the C:H ratio of the treated feed would increase thereby increasing the carbon black product yield. It may be noted that the process of the present disclosure can also be extended by means of carrying the desulfurization with Na and organic solvent, along with hydrogen. These results with simultaneous presence of organic solvent and hydrogen before desulfurization also show benefits in terms of product quality and yield, wherein the desulfurized feed oil yield is greater by 15-20% as against the known processes. The scope of our process could thus be further extended as an improved desulfurization process involving simultaneous use of organic solvent and hydrogen, however, in an optimized combination (or absence) of each of the reactants.

[0038] Another aspect of the process of the present disclosure is the by-product formation and processing after the desulfurization reaction. The desulfurization of feed oil using Na metal, results in the formation of Na₂S as the by-product. However, a large amount of valuable residual CBFO is lost as it remains associated to this Na₂S residue or unreacted sodium in the form of a highly viscous sludge. The presence of organic solvent in the feed oil prior to the desulfurization reaction, results in the formation of a crystalline and pure by-product. This product is easier to separate and filter as there is substantially less CBFO loss. This results in a better recovery of the desulfurized oil as well as a better separation and processing efficiency post the desulfurization reaction.

[0039] The present disclosure uses high shear mixing apparatus aimed at reducing the size of dispersed sodium—as solid particles or molten form as droplets. This gives finer dispersion of sodium metal in the feed oil which increases the desulfurization efficiency of the process. Secondly, during the desulfurization process, the by-product formed tends to cover the surface of sodium metal thereby reducing the efficiency. The high shear mixing helps in breaking these surfaces and bringing new sodium surfaces for enhancing the reaction. Any form of mixing may be used, such as an inline mixer, a pump around loop, a mechanical mixer, or an ultrasonic mixer, that provides the required amount of dispersion to the sodium metal.

[0040] The carbon black feed oil is highly viscous with a viscosity of above 1500 cP at ambient conditions. Addition of organic solvent prior to desulfurization reduces its viscosity to a substantial extent (less than 50 cP at ambient conditions, depending upon the amount of solvent added), making it simpler to transfer and handle as well as facilitate better mixing and contact with other reactants. Apart from viscosity, the density of CBFO is also high, typically between 1.01-1.08 g/cm³. The density of sodium solid at 30°C is about 0.96 g/cm³ and that of molten sodium is about 0.927 g/cm³. Thus, there is a tendency for the sodium to remain floating at the top of CBFO surface. Thus, in order to carry the reaction, it is to be ensured that the sodium remains well immersed in the liquid, primarily by means of a continuous stirring mechanism. This may lead to severe safety concerns in case stirring fails or whenever the reaction fails. The result will be that all of the sodium (due to low density) will rise to the top of the feed and may come in contact with atmospheric moisture. Addition of appropriate amount of organic solvent (say xylene having a density of about 0.86 g/cm³) lowers the density of CBFO to less than that of sodium and ensures that all of the sodium remains well immersed in the liquid feed at all times.

[0041] A process for removal of residual sodium metal from the desulfurized oil is also disclosed. During the desulfurization process the sodium metal gets finely dispersed in the oil. After the desulfurization process completes, some sodium metal invariably remains in the system either as a suspension or bound to the molecular chain in the oil. The separation or removal of this sodium from the oil system is considerably difficult by means of pure mechanical processes. The presence of this residual sodium even in trace quantities has serious implications on the overall quality of product for the carbon black industry. The process of the present disclosure uses acetic acid in the organic solvent mixture. The role of acetic acid is that of scavenging the sodium metal and the organic solvent promotes a better mixing between the feedstock oil and acetic acid. Alternatively, apart from acetic acid, various carboxylic acids such as formic acid, propanonic acid, and mixtures thereof, can be used. In addition, ethanol and such alcohols can also be used for scavenging the sodium. Still further, the residual sodium removal was also achieved by purging the oil with air at elevated temperatures between 30-150°C. Such treatment is not limited to air alone and would cover other gaseous agents such as oxygen, ozone, etc.

[0042] The disclosure will now be described with reference to the following examples which do not limit the scope and ambit of the disclosure. The description provided is purely by way of illustration.
EXAMPLE 1

[0043] The experiments were carried on CBFO and xylene mixtures of varying proportion, to evaluate the effect of xylene amount on the CBFO yield. All the following three examples (listed in TABLE 1) were carried in the presence of hydrogen atmosphere. In example 1, 1,150 g of CBFO was mixed with 150 ml of xylene. This resulted in the mixture as CBFS:Xylene=50:50 (weight:volume basis). The solution was mixed thoroughly and then transferred to a high pressure reactor. 9 gm of sodium metal was weighed separately. The sodium metal was then cut into small pieces of 0.5-1.0 cm and added to the CBFS/xylene solution in the reactor. The reactor vessel was first purged with nitrogen to remove air, and then the vessel was purged with hydrogen gas. The reactor was then pressurized up to 300 psi with hydrogen. The reactor was subsequently heated to a temperature of 290°C. The reaction was carried out at this temperature for a period of 4 h. The entire solution was allowed to cool down to room temperature and then the CBFO was decanted. The decanted solution was filtered out and analyzed for sulfur content by XRF (X-ray Fluorescence Spectroscopy). Similarly, the desulfurization process was carried out for other varying CBFO:Xylene ratios viz. 70:30, 80:20 (as shown in examples 2 and 3 in TABLE 1). The results with respect to these different compositions are tabulated in TABLE 1. The CBFO, xylene and sodium content used is also tabulated below, along with the desulfurization efficiency for each of the different CBFS:Xylene ratios.

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Amount of CBFO (g)</th>
<th>Amount of Xylene (ml)</th>
<th>CBFS:Xylene ratio (g/ml)</th>
<th>Amount of Na (g)</th>
<th>Temp. (°C.)</th>
<th>Time (h)</th>
<th>Desul. (%)</th>
<th>Pressure Initial (psig)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>150</td>
<td>150</td>
<td>50:50</td>
<td>9.0</td>
<td>290</td>
<td>4</td>
<td>86</td>
<td>300</td>
</tr>
<tr>
<td>2.</td>
<td>210</td>
<td>90</td>
<td>70:30</td>
<td>13.5</td>
<td>290</td>
<td>4</td>
<td>70</td>
<td>300</td>
</tr>
<tr>
<td>3.</td>
<td>240</td>
<td>60</td>
<td>80:20</td>
<td>15.5</td>
<td>290</td>
<td>4</td>
<td>75</td>
<td>300</td>
</tr>
</tbody>
</table>

[0044] It was observed that more than 70% desulfurization was obtained in all the cases.

Viscosity

[0045] The sample from example 2, after desulfurization and xylene distillation was analyzed for viscosity as a function of temperature. The sample was initially heated to about 175°C and the viscosity measurements were noted at different temperatures as the sample was cooled. Similarly measurements were noted for a second sample of untreated or raw CBFO. The results are tabulated in TABLE 2.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Temp.</th>
<th>CBFO- Untreated</th>
<th>CBFO- Treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>150°C</td>
<td>20</td>
<td>14</td>
</tr>
<tr>
<td>2.</td>
<td>100°C</td>
<td>53</td>
<td>23</td>
</tr>
<tr>
<td>3.</td>
<td>50°C</td>
<td>280</td>
<td>70</td>
</tr>
<tr>
<td>4.</td>
<td>35°C</td>
<td>280</td>
<td>120</td>
</tr>
</tbody>
</table>

[0046] Thus, it was observed that a substantial reduction in the viscosity of the desulfurized sample especially at the lower temperature range of below 50°C was obtained. The basic advantages of viscosity reduction could include easier processing of the oil, thereby reduction in energy cost as well as improvement in quality of carbon black product due to formation of finer droplets during the nebulization process.

EXAMPLE 2

[0047] The samples were further tested for the asphaltene content of the oil. Asphaltenes are found to be detrimental for the carbon black quality as well as manufacturing processes during carbon black formation. Thus, the asphaltene content for treated oil and untreated oil was carried by determining the n-heptane insoluble content in both the oils. It was observed that the asphaltene content of untreated oil was 10.50%. However, the asphaltene content of the treated oil was substantially reduced to 4.65%. This indicated that our process is capable of reducing the asphaltene content by over 50%.

Asphaltene Content

[0048] Following experiments were carried out to optimize the time, temperature and pressure parameters for the desulfurization process. These studies were decided to be carried on the CBFO:Xylene ratio of 70:30. These optimization studies are discussed in example 4-11 listed in TABLE 3.

[0049] TABLE 3 below describes the effect of temperature on the desulfurization efficiency. Thus, in each case the CBFO:Xylene ratio is kept constant to 70:30. The batch con-

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Wt vs Vol.</th>
<th>Na amount (g)</th>
<th>Time</th>
<th>Temperature</th>
<th>Hydrogen Pressure</th>
<th>% Desulfurization</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>70:30</td>
<td>13.5</td>
<td>3 h</td>
<td>290°C</td>
<td>300 psi</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>70:30</td>
<td>13.5</td>
<td>1 h</td>
<td>290°C</td>
<td>300 psi</td>
<td>70</td>
</tr>
</tbody>
</table>
TABLE 3--continued

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Wt vs Vol.</th>
<th>Na amount (g)</th>
<th>Time</th>
<th>Temperature</th>
<th>Hydrogen Pressure</th>
<th>% Desulfurization</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>70:30</td>
<td>13.5</td>
<td>45 min</td>
<td>250°C</td>
<td>300 psi</td>
<td>68</td>
</tr>
<tr>
<td>7</td>
<td>70:30</td>
<td>13.5</td>
<td>30 min</td>
<td>250°C</td>
<td>300 psi</td>
<td>50</td>
</tr>
<tr>
<td>8</td>
<td>70:30</td>
<td>13.5</td>
<td>10 min</td>
<td>250°C</td>
<td>300 psi</td>
<td>50</td>
</tr>
<tr>
<td>9</td>
<td>70:30</td>
<td>13.5</td>
<td>1 h</td>
<td>240°C</td>
<td>300 psi</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>70:30</td>
<td>13.5</td>
<td>1 h</td>
<td>290°C</td>
<td>500 psi</td>
<td>70</td>
</tr>
<tr>
<td>11</td>
<td>70:30</td>
<td>13.5</td>
<td>1 h</td>
<td>290°C</td>
<td>100 psi</td>
<td>62</td>
</tr>
</tbody>
</table>

Further, the desulfurization was carried out at a reduced temperature of 240°C, to understand the effect of temperature on the desulfurization efficiency. Thus in Example 9, appropriate amounts of CBFO:Xylene (70:30) mixture was taken in the high pressure reactor. 13.5 g of Na metal was added and the reactor was pressurized with hydrogen to a pressure of about 300 psig. The reactor was then heated to a temperature of 240°C, with a residence time of 1 h. The reactor was cooled and the CBFO decanted and analyzed for the sulfur content. A desulfurization efficiency of 10% was obtained in this case suggesting that the minimum temperature where effective desulfurization can be carried out was 240°C.

These studies were further extended to understand the effect of partial pressure of hydrogen on the desulfurization efficiency. In examples 10 & 11 different hydrogen pressures of 500 psig and 100 psig were maintained. The temperature was raised to 290°C, with a residence time of about 1 h. The reactor was cooled and the samples decanted and analyzed for sulfur content. It was observed that there was no marginal improvement in the overall desulfurization efficiency at high hydrogen partial pressures.

Thus, it was observed that the minimum temperature required for the desulfurization reaction was about 250°C. Further, a residence time of 1 h was found to be sufficient for optimum desulfurization to occur. It was also observed that the residence time could be further reduced by increasing the sodium content above stoichiometric or also by means of increasing the reaction temperature to above 300°C. The effect of hydrogen partial pressure was not found to affect the desulfurization efficiency significantly.

EXAMPLE 3

Desulfurization experiments were carried out in the presence of hydrogen and xylene. It was observed that the presence of xylene has a significant impact on the processing as well as the by-product formation. Similarly, it was important to understand the effect of hydrogen on the overall desulfurization process. Thus, in order to study the effect of hydrogen and xylene individually and also in combination, the following schemes were investigated: example 12—desulfurization in the presence of xylene and in the absence of H2; example 13—desulfurization in the presence of xylene and in the presence of H2; example 14—desulfurization in the absence of xylene and in the absence of H2.

In case of example 12, 210 g of CBFO and 90 ml of xylene were taken in the high pressure reactor. No hydrogen was added to the reactor. For example 13, 210 g of CBFO and 90 ml of xylene were taken in the high pressure reactor and about 300 psig of hydrogen was added to the reactor. For example 14, 210 g of CBFO was taken and no xylene or hydrogen was added. In all the examples 12-14, stoichiometric amount of sodium metal were added. The reaction temperature was kept to 290°C for a residence time of 1 h. Thus, after the reaction the samples were cooled and decanted for each of the cases. All schemes resulted in free CBFO and sludge (Na2S+CBFO) in varying proportions. The decanted CBFO was weighed; the yields are given in TABLE 4.

<table>
<thead>
<tr>
<th>Ex.</th>
<th>Composition</th>
<th>Desulfurized CBFO yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>No H2 + Xylene</td>
<td>72</td>
</tr>
<tr>
<td>13</td>
<td>H2 + Xylene</td>
<td>78</td>
</tr>
<tr>
<td>14</td>
<td>No H2 + No Xylene</td>
<td>54</td>
</tr>
</tbody>
</table>

It was observed that when xylene was used the CBFO yield was higher as compared to when no xylene was added. Further, to reduce the sodium content from the desulfurized oil, 5% mixture of acetic acid in xylene was prepared. The acetic acid solution was added to the treated or desulfurized oil. The mixture was then heated at 100°C for 1 hr under vigorous stirring. The mixture was then allowed to cool down and filtered. The treatment resulted in significant reduction in sodium content from 2000 ppm to <50 ppm. Alternatively, the treatment of desulfurized oil can also be achieved by purging the oil with air at elevated temperatures. For this, 100 ml of desulfurized CBFO was taken in a glass air treatent tube and in this tube compressed air was continuously purged for a period of 30 minutes. This air reacts with the excess of Na present in the oil to form a precipitated mass which can be filtered out. It was found that this treatment resulted in reduction in Na content by around 50% (from 2000 ppm to 900 ppm). Further to optimize the treatment, same reaction was carried out at elevated temperature at 50°C. It was found that the treatment resulted in significant reduction in Na content by around 96% (from 2200 ppm to 90ppm).

Experiments were performed to check the effect of heavy sheers mixing in which samples were mixed at a low agitation mixing (200-300 rpm) with a stirrer having blunt edged blades (made of Teflon plastic) and samples were mixed under higher agitation speeds (700-800 rpm) mixing in a Parr reactor with metal blades with relatively sharp edges. It was observed that higher desulfurization was obtained when the agitator is capable of breaking the Na2S particles that are formed and bring new Na metal surfaces in contact with the CBFO for further reaction.

TECHNICAL ADVANTAGES

A process for desulfurization of carbon black feed oil, as described in the present disclosure has several technical advantages including but not limited to the realization of the process does not require hydrogen; the process does not require high pressure conditions; the process reduces the loss of feed oil; the process gives a reduction in the asphaltene content of the petroleum oil by >50%; the process improves the viscosity of the desulfurized oil to <200 cP; the process reduces the residual sodium content to <10 ppm; the process enhances the processing and handling conditions of the CBFO; the process provides easy filtration and separation of the desulfurized oil and by-products thereof; and the process is safe as it lowers the density of oil in comparison with sodium metal.
Throughout this specification the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

The use of the expression "at least" or "at least one" suggests the use of one or more elements or ingredients or quantities, as the use may be in the embodiment of the invention to achieve one or more of the desired objects or results.

Any discussion of documents, acts, materials, devices, articles or the like that has been included in this specification is solely for the purpose of providing a context for the invention. It is not to be taken as an admission that any or all of these matters form part of the prior art base or were common general knowledge in the field relevant to the invention as it existed anywhere before the priority date of this application.

The numerical values mentioned for the various physical parameters, dimensions or quantities are only approximations and it is envisaged that the values higher/lower than the numerical values assigned to the parameters, dimensions or quantities fall within the scope of the disclosure, unless there is a statement in the specification specific to the contrary. Wherever a range of values is specified, a value up to 10% below and above the lowest and highest numerical value respectively, of the specified range, is included in the scope of the disclosure.

While considerable emphasis has been placed herein on the specific steps of the preferred process, it will be appreciated that additional steps can be made and that many changes can be made in the preferred steps without departing from the principles of the disclosure. These and other changes in the preferred steps of the disclosure will be apparent to those skilled in the art from the disclosure herein, whereby it is to be distinctly understood that the foregoing descriptive matter is to be interpreted merely as illustrative of the disclosure and not as a limitation.

1. A process for desulfurization of petroleum oils, said process comprising the following steps:
   - Diluting petroleum oil with a hydrocarbon organic solvent selected from the group consisting of alkanes, alkenes, cyclic alkenes and alkyynes, to obtain an oil-solvent mixture, wherein the organic solvent concentration in the oil-solvent mixture is in the range of 0.1-70%;
   - Transferring the oil-solvent mixture to a reactor vessel;
   - Adding solid sodium metal to the oil-solvent mixture in the reactor vessel, wherein the sodium concentration is between 0.1-20% of the petroleum oil concentration;
   - Reacting the oil-solvent mixture with sodium at a temperature in the range of 240-350° C. and a pressure in the range of 0-50 psig for 15 minutes-4 hours under mixing to obtain a resultant mixture;
   - Cooling and settling the resultant mixture; and
   - Decanting the cooled mixture and filtering the decanted solution of desulfurized petroleum oil.

2. The process as claimed in claim 1, wherein the hydrocarbon organic solvent is selected from the group consisting of a-hexane, cyclohexane, heptane, pentene, hexene, heptene, octene, toluene and xylene.

3. The process as claimed in claim 1, which includes the step of purging the reactor vessel with hydrogen gas at a pressure in the range of 0-500 psig.

4. The process as claimed in claim 1, which includes the step of separating the organic solvent from desulfurized petroleum oil by distillation.

5. The process as claimed in claim 1, which includes the step of mixing sodium with the oil-solvent mixture in the reactor vessel by using high shear mixing by means of a mixer selected from an inline mixer, a mechanical mixer, a pump around loop and an ultrasonic mixer.

6. The process as claimed in claim 1, which includes the step of removing residual sodium metal by: treating the desulfurized petroleum oil with 0.1-10% carboxylic acid in an organic solvent at a temperature in the range of 50-150° C. for 30 minutes to 90 minutes under vigorous stirring; and filtering the resultant mixture to obtain desulfurized petroleum oil having sodium content between 10-50 ppm.

7. The process as claimed in claim 6, wherein the carboxylic acid is selected from acetic acid, formic acid and propionic acid.

8. The process as claimed in claim 6, wherein the organic solvent is selected from alkanes, alkenes, cyclic alkenes, alkyynes and alcohol.

9. The process as claimed in claim 6, wherein the organic solvent is xylene.

10. The process as claimed in claim 1, wherein the organic solvent is xylene.