UPGRADING OF PEROXIDE TREATED PETROLEUM STREAMS

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Abstract

This invention relates to a method for upgrading petroleum streams which have been treated with peroxide, extracted to remove oxidized sulfur and nitrogen compounds, dewaxed and hydrofinished. More particularly, peroxides are generated in-situ by combining the petroleum stream with a high neutralization number (HNN) crude and adding an oxygen-containing stream. Alternatively, the oxidation of sulfur and nitrogen compounds may be accomplished by adding peroxides in the presence of oil soluble metal catalysts. The peroxides oxidize nitrogen and sulfur compounds in the petroleum stream to more polar compounds which are solvent extracted.
FIGURE 1
FIGURE 2
FIGURE 4
UPGRADING OF PEROXIDE TREATED PETROLEUM STREAMS

FIELD OF THE INVENTION

[0001] This invention relates to a method for upgrading petroleum streams which have been treated with peroxide, extracted to remove oxidized sulfur and nitrogen compounds, dewaxed and hydrofinishing. More particularly, peroxides are generated in-situ by combining the petroleum stream with a high neutralization number (HN) crude and adding an oxygen-containing stream. HN crude contain molecules sufficient for peroxide generation. Alternatively, the oxidation of sulfur and nitrogen compounds may be accomplished by adding peroxides in the presence of oil soluble metal catalysts. The peroxides oxidize nitrogen and sulfur compounds in the petroleum stream to more polar compounds which are solvent extracted. The raffinate from solvent extraction is then upgraded.

BACKGROUND OF THE INVENTION

[0002] Opportunity crudes are crudes that present some difficulties to the refineries and are therefore sold at discount. These crudes may, for example, possess more corrosion problems because they have high levels of napthenic acids. Another property of HN crude is their elevated levels of large multi-ring naphthene and naphtheno-aromatic molecules. Examples of HN crude are Gryphon or Heidrun crude with TAN (total acid number) values of 3.9 and 2.5, respectively. Examples of non-HN crudes would include Arab Light with a TAN of 0.12 and Olmeca with a TAN of 0.10. However, the supply of such HN crudes is likely to increase as compared to other low acid crudes. Many strategies have been proposed to deal with acid crudes including corrosion resistant metals, corrosion inhibitors and process modifications.

[0003] Almost all crudes contain contaminants that must be removed. The conventional method for removing sulfur (HDS) and nitrogen (HDN) contaminants from lubricant feedstocks in large integrated refineries involves hydrotreating over hydrodewaxing catalysts. Although hydrodewaxers involve an up-front capital expense, hydrodewaxers are effective and produce a marketable intermediate. Many strategies have been proposed to deal with acid crudes including corrosion resistant metals, corrosion inhibitors and process modifications.

[0004] Some refineries use solvent refining techniques to produce lubricant basestocks. Solvent refining techniques use solvents to separate a more paraffinic raffinate from a more aromatic extract. As many sulfur and nitrogen contaminants occur in aromatic compounds, they tend to accumulate in the aromatic extract. Solvent refining techniques alone are limited in the economic production of basestocks having a VI greater than about 105. The ever increasing performance standards for modern automobile engines are resulting in demands for basestocks with higher VI. Thus many original equipment manufacturers specify that lubricating oils meet Group II requirements (90+ saturates, <0.03% sulfur, 80-119 VI) and the trend is to even higher basestock qualities of Group III (90+ saturates, <0.03% sulfur and 120+ VI). In order to meet Group II standards, solvent extraction has been combined with hydrodewaxing wherein hydrodewaxing is used to boost the VI of the raffinate.

[0005] Another approach to remove sulfur and nitrogen contaminants is the use of chemical oxidants to convert the sulfur and nitrogen compounds to more polar oxidised species such as sulfoxides, sulfones, nitro compounds, nitroso compounds or amine oxides. The most commonly used oxidant is peroxide based, including for example, inorganic and organic peroxy acids and hydrogen peroxide. The chemical oxidant may be combined with a catalyst to further reduce sulfur and nitrogen contaminants.

[0006] Peroxides have also been added to fuels for producing oxygenated components which components impart beneficial properties to the fuels. Peroxides are, however, relatively expensive and may raise operational concerns.

[0007] Conventional upgrading of raffinates from a solvent extraction unit involves hydrodewaxing, demetallation and hydrofinishing. An example of such a process is U.S. Patent No. 5,911,874. A problem presented by the conventional upgrading process is that the raffinate from the solvent extraction contains levels of sulfur and/or nitrogen contaminants that will adversely impact subsequent catalytic dewaxing steps. Thus, the conventional upgrading typically uses a hydrodewaxing step in order to lower nitrogen and sulfur contaminant levels.

[0008] It would be desirable to have an alternative to the hydrodewaxing step in a conventional upgrading process.

SUMMARY OF THE INVENTION

[0009] One embodiment of the invention relates to an upgrading process for upgrading a petroleum feed containing sulfur and nitrogen compounds which comprises:

[0010] (a) mixing the petroleum feed with a high neutralization number crude having a total acid number (TAN) greater than 1.0 to produce a mixture of feed and high neutralization crude,

[0011] (b) adding an oxygen-containing gas to the mixture from step (a) for a time sufficient to generate peroxides in a concentration sufficient to oxidize at least a portion of the sulfur and nitrogen compounds in the mixture,

[0012] (c) solvent extracting oxidized sulfur and nitrogen compounds from step (b) to separate a raffinate containing less than 100 p.p.m., on a mass basis, of sulfur compounds and less than 5 p.p.m. of nitrogen compounds,

[0013] (d) contacting the raffinate with a catalytic dewaxing catalyst under catalytic dewaxing conditions to form a dewaxed raffinate and

[0014] (e) hydrofinishing the dewaxed raffinate under hydrofinishing conditions.

[0015] Another embodiment of the invention relates to an upgrading process for upgrading a petroleum feed containing sulfur and nitrogen compounds which comprises:

[0016] (a) combining the petroleum feed with a high neutralization number crude having a total acid number (TAN) greater than 1.0,

[0017] (b) adding a catalytically effective amount of an oil soluble metal catalyst to produce a mixture of feed, high neutralization crude and oil soluble metal catalyst,

[0018] (c) adding an oxygen-containing gas to the mixture from step (b) for a time sufficient to generate...
peroxides in a concentration sufficient to oxidize at least a portion of the sulfur and nitrogen compounds in the mixture,

(d) solvent extracting oxidized sulfur and nitrogen compounds to separate a raffinate containing less than 100 wppm, based on raffinate of sulfur compounds and less than 5 wppm of nitrogen compounds,

(e) contacting the raffinate with a catalytic dewaxing catalyst under catalytic dewaxing conditions to form a dewaxed raffinate and

(f) hydrofinishing the dewaxed raffinate under hydrofinishing conditions.

Another embodiment of the invention relates to an upgrading process for upgrading a petroleum feed containing sulfur and nitrogen compounds which comprises:

(a) combining the feed with an oil soluble metal catalyst to produce a mixture of feed and oil soluble metal catalyst,

(b) adding at least one peroxide to the mixture in a concentration sufficient to oxidize at least a portion of the sulfur and nitrogen compounds in the mixture,

(c) solvent extracting oxidized sulfur and nitrogen compounds to separate a raffinate containing less than 100 wppm, based on raffinate of sulfur compounds and less than 5 wppm of nitrogen compounds,

(d) contacting the raffinate with a catalytic dewaxing catalyst under catalytic dewaxing conditions to form a dewaxed raffinate and

(e) hydrofinishing the dewaxed raffinate under hydrofinishing conditions.

**BRIEF DESCRIPTION OF THE DRAWINGS**

**FIG. 1** is a schematic drawing of the integrated process for upgrading a petroleum feed.

**FIG. 2** shows the FTIR subtraction spectra of four sequential samples undergoing oxidation across a wavelength range from 600 to 2000 cm⁻¹.

**FIG. 3** shows FTIR subtraction spectra of four sequential samples undergoing oxidation reactions generally associated with the region where oxidation products are measured.

**FIG. 4** is a graph showing the performance of ZSM-48 followed by MCM-41 at moderate operating pressures.

**DETAILED DESCRIPTION OF THE INVENTION**

**0032** Crude oils and distillate fractions that are considered corrosive generally contain organic acids. The organic acids most commonly associated with acidic properties are naphthenic acids. The acidity of a crude or distillate is normally measured as the Total Acid Number or TAN. The TAN is measured by standard ASTM methods such as D-664 and is expressed as the number of milligrams of KOH needed to neutralize one gram of oil. Crudes and distillates with TAN values below 0.5 are considered non-corrosive, those with TAN values between 0.5 and 1.0 are considered moderately corrosive and those with TAN values above 1.0 are considered corrosive. These corrosive crudes are known as High Neutralization Number crudes or “HNHN” crudes.

**0033** Suitable petroleum feeds for mixing with HNN crudes or oil soluble metal catalysts include crude having a TAN less than 1.0, reduced crudes, raffinates, hydrotreated oils, hydrocrackates, atmospheric gas oils, vacuum gas oils, coker gas oils, atmospheric and vacuum residua, desphalted oils, slack waxes and Fischer-Tropsch wax. Such feeds may be derived from distillation towers (atmospheric and vacuum), hydrotreaters and solvent extraction units, and may have wax contents of up to 50% or more. Both the HNN crudes and the feeds mixed with HNN crudes normally contain sulfur and nitrogen compounds as contaminants. Sulfur compounds may be present in amounts up to 50000 wppm or more, based on total feed and nitrogen compounds up to 3000 wppm or more.

**0034** HNN crudes, and distillates derived therefrom are not typically used for the production of lubricant basestocks because of their inherent instability to oxidation. These crudes contain multi-ring naphthenes and naphtheno-aromatic compounds that are easily oxidized because they have exposed tertiary hydrogens that are readily susceptible to oxidation. It is this oxidation instability which has been used to advantage in the instant process.

**0035** In one embodiment of the present process, the multi-ring naphthenes and naphtheno-aromatic compounds in HNN crudes and distillates are oxidized by exposing these compounds to an oxidizing medium to form in-situ generated hydroperoxides. An example of such a reaction is as follows:

\[
\text{Multi-ring naphthenes} + \text{O}_2 \rightarrow \text{Initi} \text{t} \text{a} \text{t} \text{u} \text{a} \text{t} \text{i} \text{g} \text{e} \text{d} \text{ H} \text{i} \text{d} \text{r} \text{o} \text{p} \text{e} \text{x} \text{o} \text{r} \text{i} \text{d} \text{e} \text{s} (\text{ROOH})
\]

**0036** Naphthenes are cycloparaffins having one or more cyclic rings, preferably more than one. The rings may have 5 or more carbon atoms and may be substituted with substituents such as alkyl groups. Examples of one ring naphthenes include cyclopentane, cyclohexane, cyclocotane, methyl cyclohexane, ethyl cyclohexane, and the like. Naphthenes may also be poly cyclic, i.e., containing multiple rings. Heavier petroleum fractions commonly include poly cyclic naphthenes containing 2, 3, 4, 5 or more cyclic rings which may be fused. The cyclic rings may contain 5 or more carbon atoms and may bear substituents such as alkyl. The poly cyclic naphthenes may also be bridged. Naphtheno-aromatics are fused poly cyclic hydrocarbons containing both aromatic and naphthene ring systems. The fused ring systems may contain 2 or more rings and the rings may contain 5 or more carbon atoms. Preferred naphthenes and naphtheno-aromatics contain 2 or more rings which may be substituted with alkyl groups. Examples include decalin,
adamantane, cholestane, tetralin, norborne, 3-methyl-1,2-cyclopentenophenanthrone, 1,2,3,4-tetrahydrophenanthrone, indane, perhydroanthracene, perhydrofluorene and perhydronaphthalene.

[0037] The amount of HNN crudes that are mixed with other crudes, distillates or mixtures thereof range from 10 to 100 wt. %, based on total mixture of HNN crude and other crude or distillate, preferably 30 to 100 wt. %. The mixing of HNN crudes with other petroleum crudes and distillates occurs at temperatures greater than about 50°C.

[0038] The oxidizing medium is preferably an oxygen-containing gas, more preferably oxygen, most preferably air. Ozone may also be used as an oxidizing medium. The oxidizing medium may be mixed with other non-oxidizing gases or may be mixed with inert solvent. In order to form in-situ hydroperoxides, an oxygen-containing gas is added to the mixture by any conventional means for mixing gases and liquids. Oxygen-containing gas is added for a time sufficient to form hydroperoxides.

[0039] The oxygen-containing gas may be added by conventional means such as frits, spargers, bubbles and the like, or may be added under pressure to a vessel containing the HNN mixture and allowed to diffuse into HNN mixture. The conditions for adding oxygen-containing gas include temperatures from ambient to 700°C, pressures from atmospheric to 34576 kPa (5000 psig), and treat gas rates up to 534 m³/m³ (3000 scf/ft³). The oxygen-containing gas is preferably added to the mixture for a time sufficient to generate peroxides in a concentration of at least about 1 wt. %, based on mixture.

[0040] In another embodiment not involving the addition of HNN crudes, peroxides may be combined with crude and/or distillate containing oil soluble metal catalyst. In this embodiment, the peroxide may be added directly to the mixture of crude/distillate and oil soluble metal catalyst. Suitable peroxides include hydrogen peroxide, inorganic peroxide compounds, salts of peracids such as perborates, and organic peroxides such as benzoyl peroxide.

[0041] In another embodiment, oil soluble catalysts may be added to the HNN mixture. Oil soluble metal catalysts include metals from Groups 4-12 of the Periodic Table based on the IUPAC format having Groups 1-18. Examples of metals include V, Cr, Mo, W, Fe, Ni, Co, Pt, Pd, Ru and Mn. The oil soluble metal catalysts include salts and compounds such as organic acids such as acyclic, alicyclic and aromatic carboxylates including carboxylates, sulfonates, naphthenates, chelates such as acetylatedolines, halides, sulfonates, organic amines, heteropolyacids and the like that render the metal oil soluble. Preferred oil soluble metal catalysts include metal naphthenates, metal acetates and metal beta diketonates. The oil soluble metal catalyst may also be combined with inert solvents, especially non-polar solvents such as hydrocarbons, e.g., mineral oils, turbine oils, napthenic oils, paraffinic oils, and aromatic oils. The metal concentrations are from 1 to 1000 ppm, based on crude or distillate plus HNN crude. The preferred reaction temperatures are from 50-250°C, most preferably from 100-160°C.

[0042] In another embodiment not involving the addition of HNN crudes, peroxides may be combined with crude and/or distillate containing oil soluble metal catalyst. In this embodiment, the peroxide may be added directly to the mixture of crude/distillate and oil soluble metal catalyst. Suitable peroxides include hydrogen peroxide, inorganic peroxide compounds, salts of peracids such as perborates, and organic peroxides such as benzoyl peroxide.

[0043] In an embodiment involving thermal cleavage, the in-situ generated peroxides oxidize sulfur, and under the reaction conditions, weaken the polar-hydrocarbon bonds. The oxidized sulfur compounds may be thermally treated to cleave the polar-hydrocarbon bonds producing hydrocarbons and sulfur dioxide. The oxidation mechanism and thermal cleavage is shown as the follow reaction mechanisms:

\[
\begin{align*}
\text{ROOH} + \text{R-S-R} & \rightarrow \text{R-S-OH} + \text{R-C=O} \\
\text{R-S-OH} & \rightarrow \text{R-H + SO}_2
\end{align*}
\]

[0044] The sulfur can be present in a ring species or as aliphatic sulfur. This allows for a minimum of hydrocarbon loss during the desulfurization process. The temperature is that needed for thermal cleavage of the oxidized sulfur species to produce hydrocarbon and SO₂. This temperature will vary according to the particular oxidized sulfur species to be thermally cleaved.

[0045] The in-situ generated peroxides oxidize nitrogen or sulfur compounds to more polar species that are more readily extracted by solvent extraction. The following reactions are used to illustrate the peroxide oxidation:

\[
\begin{align*}
\text{ROOH} & \rightarrow \text{R-O-O-R} \\
\text{R-O-O-R} & \rightarrow \text{R-O-C=O + SO}_2
\end{align*}
\]

The oxidation reaction may take place at temperatures of from 50 to 250°C.

[0046] The oxidized sulfur and nitrogen compounds are then solvent extracted. Solvent extraction is used to separate aromatic from paraffins, i.e., the naphthases are rich in paraffins while the extract is rich in aromatics. The nitrogen and sulfur compounds are oxidized to more polar species which
makes them more readily separable by solvent extraction. Many nitrogen and sulfur heterocyclic compounds contain paraffinic side chains making the raffinate/extract separation otherwise more difficult. The nitrogen compounds appear as both basic and non-basic nitrogen species. Non-limiting examples of basic nitrogen species may include quinolines and substituted quinolines, and non-limiting examples of non-basic nitrogen species may include carbazoles and substituted carbazoles. Sulfur compounds include both non-heterocyclic species of sulfur as sulfides, polysulfides and mercaptans and heterocyclic species. Heterocyclic compounds include thiophene, thiophene derivatives, benzothiophene, and benzothiophene derivatives as well as mixed sulfur/nitrogen species such as thiazoles.

[0047] The raffinates may be either fully or partially extracted, i.e. under-extracted. By under-extracted it is meant that the extraction is carried out under conditions such that the raffinate yield is maximized while still removing most of the lowest quality molecules from the feed. Raffinate yield may be maximized by controlling extraction conditions, for example, by lowering the solvent to oil treat ratio and/or decreasing the extraction temperature.

[0048] Raffinates and extracts can be produced under standard solvent extracting conditions. Typically, the solvent extracting process involves contacting a lube oil boiling range stream with an extraction solvent. The extraction solvent can be any solvent known that has an affinity for aromatic hydrocarbons in preference to non-aromatic hydrocarbons. Non-limiting examples of such solvents include sulfolane, furfural, phenol, and N-methyl pyrrolidone ("NMP"). Furfural, phenol, and NMP are preferred.

[0049] The feed stream to be extracted can be contacted with the extraction solvent by any suitable solvent extraction method. Non-limiting examples of such include batch, semibatch, or continuous. It is preferred that the extraction process be a continuous process, and it is more preferred that the continuous process be operated in a counter-current fashion. In a counter-current configuration, it is preferred that the feedstream be introduced into the bottom of an elongated contacting zone or tower and caused to flow in an upward direction while the first extraction solvent is introduced at the top of the tower and allowed to flow in a downward direction, counter-current to the upflowing feedstream. In this configuration, the feedstream is forced to pass counter-currently to the extraction solvent resulting in the intimate contact between the extraction solvent and the feedstream. The extraction solvent and the light lube stream migrate to opposite ends of the contacting zone.

[0050] The conditions under which the extraction solvent is contacted with the feedstream can be any conditions known to be effective in the solvent extraction of petroleum feedstreams. In a preferred embodiment, the temperature and pressure are selected to prevent complete miscibility of feedstream in the extraction solvent. Typical extraction process operating ranges for a treat tower with 10-20 trays include a tower bottoms temperature from 50-100°C, tower temperature gradients from 10-30°C, water in solvent concentration of less than 5%, and a down tower solvent treat between 100-300 vol % on feed. More preferably, these conditions would be a tower bottoms temperature from 60-75°C, gradient of 10-20°C, water in solvent from 1-2%, and a treat of 125-200 vol %.

[0051] The contacting of the feedstream with the extraction solvent produces at least a first aromatics-rich extract solution and a first aromatics-lean raffinate solution. It should be noted that as used herein, aromatics-lean is meant to refer to the concentration of aromatics present in the raffinate phase produced by solvent extraction in relation to the concentration of aromatics present in the extract phase produced by solvent extraction. The first aromatics-lean raffinate solution is then treated to remove at least a portion of the extraction solvent and/or raffinate from the aromatics-lean raffinate. The removal of at least a portion of the extraction solvent can be done by any means known in the art effective at separating at least a portion of an extraction solvent from an aromatics lean raffinate solution. Preferably the raffinate is produced by separating at least a portion of the first extraction solvent from the first aromatics-rich extract solution in a stripping or distillation tower. By at least a portion, it is meant that at least about 80 vol %, preferably about 90 vol %, more preferably 95 vol %, based on the first aromatics-lean raffinate solution, of the extraction solvent is removed from the aromatics-lean raffinate solution. Most preferably, substantially all of the extraction solvent is removed from the aromatics-lean raffinate solution. It should be noted that when the solvent extracting method that produces the raffinate is referenced herein, it is meant to encompass this separation step.

[0052] The oxidation step using peroxide may precede or follow the extraction step. The reaction between peroxide and sulfur-containing and nitrogen-containing compounds takes place at temperatures ranging from 50-250°C. Depending on the speed and extent of oxidation desired. The higher the temperature the more rapid the oxidation may take place depending on the availability of oxygen for oxidizing the sulfur and nitrogen containing molecules. For example, a peroxide concentration of about 10-15% peroxide may be employed with a reactor temperature between 120-160°C. However, the peroxide concentration may vary depending on the reactor temperature employed. The raffinate from the extraction step may be processed, typically by distillation, to recover solvent. The recovered solvent may then be recycled back to the extraction step.

[0053] The separated raffinate is then catalytically dewaxed. Dewaxing catalysts may be either crystalline or amorphous. Crystalline materials are molecular sieves that contain at least one 10 or 12 ring channel and may be based on aluminosilicates (zeolites), or may be based on aluminophosphates. Zeolites may contain at least one 10 or 12 channel. Examples of such zeolites include ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-35, ZSM-48, ZSM-57, ferrierite, EU-1, NU-87, ITQ-13, and MCM-71. Examples of aluminophosphates containing at least one 10-ring channel include ECR-42, SAPO-11 and SAPO-41. Examples of molecular sieves containing 12 ring channels include zeolite beta, ZSM-12, MCM-68 ZSM-5, SAPO-31, MAPO-36, ZSM-18, mordenite, faujasite and offretite. It should be noted that any dewaxing catalyst such as ZSM-5 can have altered dewaxing properties by adjusting catalyst properties, such as acidity, metal dispersion and catalyst particle size as noted in U.S. Pat. No. 6,294,077. The molecular sieves are described in U.S. Pat. Nos. 5,246,566, 5,282,958, 4,975,177, 4,397,827, 4,585,747, 5,075,269, 6,305,384 and 4,440,871. MCM-68 is described in U.S. Pat. No. 6,310,265. MCM-71 and ITQ-13 are described in PCT published applications WO 0242207 and WO 0078677. Preferred catalysts include
ZSM-48, ZSM-22 and ZSM-23. Especially preferred is ZSM-48. As used herein, ZSM-48 includes EU-2, EU-11 and ZBM-30 which are structurally equivalent to ZSM-48. The molecular sieves are preferably in the hydrogen form. Reduction can occur in situ during the dewaxing step itself or can occur ex situ in another vessel.

Amorphous dewaxing catalysts include alumina, fluorided alumina, silica-alumina, fluorided silica-alumina and silica-alumina doped with Group 3 metals. Such catalysts are described for example, in U.S. Pat. Nos. 4,900,707 and 6,383,366.

The dewaxing catalysts are preferably bifunctional, i.e., they are loaded with a metal hydrogenation component, which is at least one Group 6 metal, at least one Group 8-10 metal, or mixtures thereof. Preferred metals are Groups 9-10 metals. Especially preferred are Groups 9-10 noble metals such as Pt, Pd or mixtures thereof (based on the IUPAC Periodic Table format having Groups from 1 to 18). These metals are loaded at the rate of 0.1 to 30 wt. %, based on catalyst. Catalyst preparation and metal loading methods are described for example, in U.S. Pat. No. 6,294,077, and include for example, ion exchange and impregnation using decomposable metal salts. Metal dispersion techniques and catalyst particle size control are described in U.S. Pat. No. 5,282,958. Catalysts with small particle size and well dispersed metal are preferred.

The molecular sieves are typically composed with binder materials that are resistant to high temperatures and may be employed under dewaxing conditions to form a finished dewaxing catalyst or may be binderless (self-bound). The binder materials are usually inorganic oxides such as silica, alumina, silica-aluminas, binary combinations of silicas with other metal oxides such as titania, magnesia, thoria, zirconia and the like and tertiary combinations of these oxides such as silica-alumina -thoria and silica- alumina -magnesia. The amount of molecular sieve in the finished dewaxing catalyst is from 10 to 100, preferably 35 to 100 wt. %, based on catalyst. Such catalysts are formed by methods such as spray drying, extrusion and the like. The dewaxing catalyst may be used in the sulfided or unsulfided form, and is preferably in the sulfided form.

Dewaxing conditions include temperatures of from 250-400°C, preferably 275 to 350°C, pressures of from 791 to 20786 kPa (100 to 3000 psig), preferably 1480 to 17339 kPa (200 to 2500 psig), liquid hourly space velocities of from 0.1 to 10 hr⁻¹, preferably 0.5 to 5 hr⁻¹ and hydrogen treat gas rates of 45 to 1780 m³/m² (250 to 10000 scf/ft²), preferably 89 to 890 m³/m² (500 to 5000 scf/ft²).

Following the dewaxing step, it is preferred to hydrofinishing the product resulting from dewaxing in order to adjust product qualities to desired specifications. Hydrofinishing is a form of mild hydrotreating directed to saturating any lube range olefins and residual aromatics as well as to removing any remaining heteroatoms and carbon bodies. The post dewaxing hydrofinishing is usually carried out in cascade with the dewaxing step.

Generally the hydrofinishing will be carried out at temperatures from about 150°C to 350°C, preferably about 180°C to 250°C. Total pressures are typically from 2859 to 20786 kPa (about 400 to 3000 psig). Liquid hourly space velocity is typically from 0.1 to 5 LHSV (hr⁻¹), preferably 0.5 to 3 hr⁻¹ and hydrogen treat gas rates of from 44.5 to 1780 m³/m² (250 to 10000 scf/ft²).

Hydrofinishing catalysts are those containing Group 6 metals (based on the IUPAC Periodic Table format having Groups from 1 to 18), Groups 8-10 metals, and mixtures thereof. Preferred metals include at least one noble metal having a strong hydrogenation function, especially platinum, palladium and mixtures thereof. The mixture of metals may also be present as bulk metal catalysts wherein the amount of metal is 30 wt. % or greater based on catalyst. Suitable metal oxide supports include low acidic oxides such as silica, alumina, silica-aluminas or titania, preferably alumina. The preferred hydrofinishing catalysts for aromatics saturation will comprise at least one metal having relatively strong hydrogenation function on a porous support. Typical support materials include amorphous or crystalline oxide materials such as alumina, silica, and silica-alumina. The metal content of the catalyst is often as high as about 20 weight percent for non-noble metals. Noble metals are usually present in amounts no greater than about 1 wt. %. A preferred hydrofinishing catalyst contains MCM-41 whose preparation and use for hydrogenation is described in U.S. Pat. Nos. 5,698,684, 5,227,353, 5,573,657 and 5,264,641. Control of the reaction parameters of the hydrofinishing step offers a useful way of varying the stability of the products. The hydrofinishing catalyst together with temperatures of about 150°C-350°C (446-572°F) will minimize aromatics. They will also provide products having good oxidative stability, UV light stability, and thermal stability. Space velocity in the hydrofinisher also offers a potential for aromatics saturation control with the lower space velocities effecting greater aromatics saturation.

The process is shown in FIG. 1 which is a schematic drawing of the integrated process according to the invention.

As can be seen, the upgrading process does not require a hydrotreater. Moreover, the dewaxing step does not require high temperature and pressure.

This invention is further illustrated by the following examples.

**EXAMPLE 1**

Experiments were conducted using a dewaxed HNN distillate as a test fluid and heated to 150°C in the presence of air bubbling through the fluid. The oxidation products were measured by Fourier Transform Infrared Spectroscopy (FTIR) to determine the existence of oxidation products. Additionally a sample was heated in the presence of a nitrogen gas instead of air to determine the effect of any thermal degradation of the fluid under these test conditions. This sample was also measured by FTIR and used as a baseline reading. A subtraction spectrum was generated at different times during the oxidation experiments using the FTIR readings minus the baseline reading. The results are given in FIGS. 2 and 3, where FIG. 2 shows the FTIR subtraction spectra of four sequential samples undergoing oxidation across a wavelength ranging from 600 to 2000 cm⁻¹. FIG. 3 shows FTIR subtraction spectra of four sequential samples undergoing oxidation reactions generally associated with the region where oxidation products are measured. The Figure shows a close-up of products FTIR subtraction spectra for the region of interest to determine oxidation products of four sequential samples undergoing oxidation reactions.

When examining the spectra generated from these samples, it is evident that there was an increase in the amount of oxidation products generated as the oxidation
reaction proceeded, shown by the increase in the area under the peaks in the 1600-1800 cm\(^{-1}\) region. Specifically, there are noticeable peaks present at 1773 representing carbonyls such as ketones, aldehydes, and esters, along with a peak at 1718 cm\(^{-1}\) representing the presence of lactone carbonyls. This data provides proof that oxidation reactions occurred during the experiments. In order for the oxidation pathways necessary for these reactions to occur, an intermediate step must have existed in which peroxides or hydroperoxides were generated. An example reaction is provided below showing the pathway from a hydrocarbon to a ketone carbonyl.

\[
\begin{align*}
&\text{H} \quad \text{R} \quad \text{H} \\
&\text{H} \quad \text{R} \quad \text{ROOH} \quad \text{H} \quad \text{R} \quad \text{O} \\
&\text{H} \quad \text{R} \quad \text{ROH} \quad \text{H} \quad \text{R} \quad \text{O} \\
&\text{H} \quad \text{R} \quad \text{ROH} \quad \text{H} \quad \text{R} \quad \text{O} \\
\end{align*}
\]

**EXAMPLE 2**

[0066] The current example uses real feeds of which are a combination of many species in their native environment. This example is directed to a series of runs comparing various catalyst/peroxide configurations as compared to a base case of a distillate undergoing extraction without the oxidation step (run 1 below). The series of runs include:

[0067] 1. the heating of the distillate followed by extraction,

[0068] 2. the addition of an oil-soluble catalyst, air and heat without peroxides followed by extraction,

[0069] 3. the addition of in-situ peroxides, addition of air and heat without the oil soluble catalyst followed by extraction,

[0070] 4. the formation of in-situ peroxides, addition of oil soluble catalyst, air and heat followed by extraction,

[0071] 5. the formation of in-situ peroxides, addition of hydrogen peroxide, oil soluble catalyst, air, and heat followed by extraction.

[0072] The results of these runs have been shown in Table 1 as an improvement over the sulfur and nitrogen found in the feed distillate. The data shows that the use of peroxides and catalysts removed over 40% of the remaining sulfur and nitrogen that would have been present after extraction without the use of oxidation.

<table>
<thead>
<tr>
<th>Experimental Run</th>
<th>Sulfur</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base Case - No Oxidation</td>
<td>67.0%</td>
<td>85.0%</td>
</tr>
<tr>
<td>No Peroxides</td>
<td>69.2%</td>
<td>91.3%</td>
</tr>
<tr>
<td>In-Situ Peroxides &amp; No Catalyst</td>
<td>77.3%</td>
<td>91.0%</td>
</tr>
<tr>
<td>In-Situ Peroxides &amp; Oil Soluble Catalyst</td>
<td>84.3%</td>
<td>93.0%</td>
</tr>
<tr>
<td>In-Situ &amp; Added Peroxides &amp; Oil Soluble</td>
<td>97.5%</td>
<td>93.6%</td>
</tr>
</tbody>
</table>

**EXAMPLE 3**

[0073] A set of experiments have been conducted using ZSM-48 followed by MCM-41 on hydrocracker bottoms with a pressure of 400 psig. The material contained approximately 25 wppm sulfur and 1.5 wppm nitrogen with a VI of 99. After hydroprocessing, the data showed a potential VI uplift of about 5 points with a conversion of 6-7 wt. % (FIG. 4). FIG. 4 is a graph showing the performance of ZSM-48 followed by MCM-41 at moderate operating pressures.

[0074] The yield loss is associated with the conversion of normal paraffinic species to iso-paraffinic species, beneficial to the VI. Similar data was generated at a pressure of 900 psig using various other feedstocks. These runs also showed significant VI improvements with minimal yield losses. These experiments provide support for an embodiment using air oxidation followed by solvent extraction followed by ZSM-48 catalytic dewaxing followed by MCM-41 aromatic saturation to improve base stock quality.

[0075] Additionally, this invention would allow for challenged feedstocks to be run through air oxidation to “polarize” and subsequently remove, their inherently oxidizable species, that typically find their way into the base stock regardless of the hydroprocessing step. Therefore, Group II+ base stock can be made using feedstock not typically picked for this type of production and traditionally have a much lower purchase price.

1. An upgrading process for upgrading a petroleum feed containing sulfur and nitrogen compounds which comprises:

   (a) combining the petroleum feed with a high neutralization number crude having a total acid number (TAN) greater than 1.0 to produce a mixture of feed and high neutralization crude,

   (b) adding an oxygen-containing gas to the mixture from step (a) for a time sufficient to generate peroxides in a concentration sufficient to oxidize at least a portion of the sulfur and nitrogen compounds in the mixture,

   (c) solvent extracting oxidized sulfur and nitrogen compounds from step (b) under solvent extraction conditions to separate a raffinate containing less than 100 wppm, based on raffinate of sulfur compounds and less than 5 wppm of nitrogen compounds.

   (d) contacting the raffinate with a catalytic dewaxing catalyst under catalytic dewaxing conditions to form a dewaxed raffinate and

   (e) hydrofinishing the dewaxed raffinate under hydrofinishing conditions.

2. An upgrading process for upgrading a petroleum feed containing sulfur and nitrogen compounds which comprises:

   (a) combining the petroleum feed with a high neutralization number crude having a total acid number (TAN) greater than 1.0,

   (b) adding an oil soluble metal catalyst to produce a mixture of feed, high neutralization crude and oil soluble metal catalyst,

   (c) adding an oxygen-containing gas to the mixture from step (b) for a time sufficient to generate peroxides in a concentration sufficient to oxidize at least a portion of the sulfur and nitrogen compounds in the mixture,

   (d) solvent extracting oxidized sulfur and nitrogen compounds under solvent extraction conditions to separate
3. An upgrading process for upgrading a petroleum feed containing sulfur and nitrogen compounds which comprises:
(a) combining the feed with a catalytically effective amount of an oil soluble metal catalyst to produce a mixture of feed and oil soluble metal catalyst,
(b) adding at least one peroxide to the mixture in a concentration sufficient to oxidize at least a portion of the sulfur and nitrogen compounds in the mixture,
(c) solvent extracting oxidized sulfur and nitrogen compounds under solvent extraction conditions to separate a raffinate containing less than 100 wppm, based on raffinate of sulfur compounds and less than 5 wppm of nitrogen compounds,
(d) contacting the raffinate with a catalytic dewaxing catalyst under catalytic dewaxing conditions to form a dewaxed raffinate and
(e) hydrofinishing the dewaxed raffinate under hydrofinishing conditions.

4. The process of claim 1 wherein the petroleum feed has a TAN less than 1.0.
5. The process of claim 2 wherein the petroleum feed has a TAN less than 1.0.
6. The process of claim 1 wherein the oxygen-containing gas is air.
7. The process of claim 2 wherein the oxygen-containing gas is air.
8. The process of claim 2 wherein the oil soluble metal catalysts include metals from Groups 4-12 of the Periodic Table based on the IUPAC format having Groups 1-18.
9. The process of claim 3 wherein the oil soluble metal catalysts include metals from Groups 4-12 of the Periodic Table based on the IUPAC format having Groups 1-18.
10. The process of claim 1 wherein the oxygen-containing gas is added to the mixture from step (a) for a time sufficient to generate peroxides in a concentration of at least about 1 wt. %, based on mixture.
11. The process of claim 2 wherein the oxygen-containing gas is added to the mixture from step (b) for a time sufficient to generate peroxides in a concentration of at least about 1 wt. %, based on mixture.
12. The process of claim 3 wherein the peroxide includes hydrogen peroxide, inorganic peroxide compounds, salts of peracids, and organic peroxides.