

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
5 July 2007 (05.07.2007)

PCT

(10) International Publication Number
WO 2007/075331 A2

(51) International Patent Classification: **Not classified**

(21) International Application Number:
PCT/US2006/047391

(22) International Filing Date:
12 December 2006 (12.12.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11/303,511 16 December 2005 (16.12.2005) US

(71) Applicant (for all designated States except US): **EXXON-MOBIL RESEARCH AND ENGINEERING COMPANY** [US/US]; 1545 Route 22 East, P. O. Box 900, Annandale, NJ 08801-0900 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **PALMER, Thomas, Rainier** [US/US]; 942 Woodhue Drive, Baton Rouge, LA 70810 (US). **MURPHY, William, John** [CA/US]; 224 Highland Trace Drive, Baton Rouge, LA 70810 (US).

(74) Agents: **CARTER, Lawrence, E.** et al.; Exxonmobil Research And Engineering Company, 1545 Route 22 East, P. O. Box 900, Annandale, NJ 08801-0900 (US).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

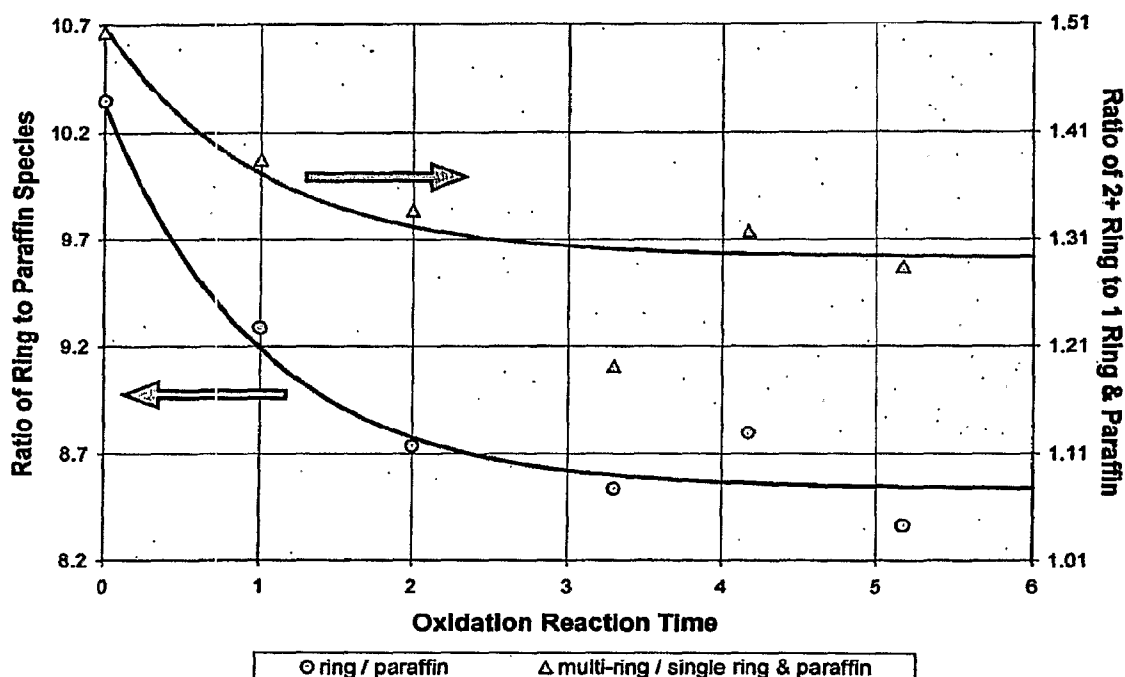
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: SELECTIVE RING OPENING BY OXIDATION PROCESS



(57) Abstract: This invention relates to the selective ring opening of naphthenic and aromatic rings, and more particularly, to any petroleum or hydrocarbon streams derived from crudes containing naphthene and aromatic species. The rings may be selectively ring opened using an oxidation catalyst in the presence of an oxygen.

SELECTIVE RING OPENING BY OXIDATION PROCESS

FIELD OF THE INVENTION

[0001] This invention relates to the selective ring opening of naphthenic and aromatic rings, and more particularly, to any petroleum or hydrocarbon streams derived from crudes containing naphthene and aromatic species. The rings may be selectively ring opened using an oxidation catalyst in the presence of an oxygen-containing gas.

BACKGROUND OF THE INVENTION

[0002] Most petroleum and hydrocarbon streams derived from crude contain naphthene and aromatic compounds. Distressed crudes contain substantial amounts of naphthenes and aromatics which result in lower prices paid for these crudes. Naphthenes and aromatics are considered undesirable in some product streams as they may degrade product quality. The desirability of these types of molecules depends on the use intended. For example, aromatics may be desirable in gasoline due to their high octane number. On the other hand, aromatics raise potential environmental and health concerns so that the amount allowed in products may be limited. Aromatics are not desirable in lube basestocks due to their poor VI properties. Since the world supply of high quality crudes is diminishing, the need to process poorer quality crude is increasing.

[0003] Distillate fuels typically contain paraffins, naphthenes, and aromatics. For fuel quality parameters such as cetane, gravity and emissions, paraffins are the most desirable components, followed by naphthenes, followed by aromatics. The least desirable are multi-ring aromatic compounds. While various refinery processes produce distillate fuels, these processes are typically limited in their capability to produce high quality distillate fuel and/or high yields of distillate fuel. For example, conventional hydrogenation processes saturate aromatic rings to naphthenes, thereby increasing the cetane number and increasing the API gravity (lower density). The disadvantage of hydrogenation alone is that naphthenes have generally lower cetane

- 2 -

values and are more dense than paraffins having substantially the same number of carbon atoms. The greater density of naphthenes results in reduced volume of the distillate fuel blend relative to a composition containing similar concentrations of paraffins instead of naphthenes. Similarly, multi-ring naphthenes are generally more dense and have lower cetane values than single-ring naphthenes having substantially the same number of carbon atoms. In addition, naphthenes can be converted to aromatics via oxidation reactions. Since combustion of naphthenes in fuels occurs under oxidizing conditions, there is the potential for naphthenes to revert to aromatics under combustion conditions, thus further reducing fuel quality.

[0004] For lubricant basestocks, multi-ring naphthenes can present drawbacks with regard to VI and oxidative stability. Multi-ring naphthenes tend to have poor VI compared to paraffinic molecules. In addition, such naphthenes typically have poor oxidation stability which is undesirable in a high temperature environment due to thermal breakdown and sludge formation. Aromatics generally have poor VI and oxidation stability properties as well. Multi-ring aromatics have very poor VI properties and are usually hydrogenated for environmental and health reasons.

[0005] Processes and catalysts which promote ring opening of cyclic compounds such as naphthenes have been developed. Cyclic C_6 hydrocarbons may be opened with metal loaded zeolites such as zeolite Beta. Ring opening of cyclic hydrocarbons can be accomplished with a catalyst comprising a hydrogenation/dehydrogenation metal and an acidic component containing a Group IVB metal oxide modified with a Group VIB metal. Another catalyst for ring opening is rhodium or ruthenium on a halogen promoted refractory oxide. Selective ring opening of naphthenes has been disclosed using Ir, Ru or Rh on a catalyst support.

[0006] While there are descriptions of ring opening reactions in the prior art as noted above, owing to the increasing demand for more environmentally friendly lubricants and clean-burning, high performance fuels, it is highly desirable to have a process which is more selective for ring opening as well as providing a cost

- 3 -

effective ring opening process. Selectivity for ring opening is related to the propensity for cleavage of a ring bond which results in product molecules having an equivalent number of carbon atoms and one less ring than the original molecule, rather than cleavage of a bond which results in a product molecule having fewer carbons than the original molecule. A perfectly selective ring opening process would give only ring bond cleavage to produce molecules having an equivalent number of carbon atoms and one less ring than the original molecule. For example, from a hydrocarbon stream containing only single ring naphthenes of n number of carbon atoms, the product from perfect ring opening selectivity would be only paraffins of n number of carbon atoms.

[0007] Thus, the greater number of product molecules from a ring opening process having an equivalent number of carbon atoms and one less ring than the original molecule, the greater the selectivity for ring opening. Greater selectivity for ring opening is important for the reasons that a) the number of ring structures in a product stream will be decreased, b) significant dealkylation of any pendant substituents on the ring, which will reduce the volume of product in a specified boiling range, will be minimized and c) the density of the product stream will be decreased providing volume swell.

[0008] It would be desirable to have a cost effective ring opening process with high selectivity for ring opening while minimizing dealkylation of pendant substituents to maintain a high volume of product in the desired boiling range with preservation of useful properties such as VI, octane and cetane.

SUMMARY OF THE INVENTION

[0009] This invention relates to a method for selectively ring opening naphthenes or aromatics in a petroleum feed containing naphthenic or aromatic ring species which comprises: combining the petroleum feed with a catalytically effective amount of an oil soluble metal catalyst to form a mixture of feed and

- 4 -

catalyst, and adding to the mixture of feed and catalyst an oxygen-containing gas under ring opening conditions.

[0010] Another embodiment relates to a method for selectively ring opening naphthenes or aromatics in a petroleum feed containing naphthenic or aromatic ring species which comprises: (a) contacting the feed with an oxygen-containing gas, (b) adding to the feed contacted with oxygen-containing gas a catalytically effective amount of an oil soluble catalyst and (c) continuing adding oxygen-containing gas under ring opening conditions.

[0011] Yet another embodiment relates to the incorporation of selective ring opening into an upgrading process for upgrading a petroleum feed which comprises: contacting the feed in an upgrading process incorporating selective ring opening and including at least one of hydrocracking, hydrotreating, hydrodewaxing, solvent dewaxing, solvent extracting and hydrofinishing wherein selective ring opening is by (a) combining the petroleum feed with a catalytically effective amount of an oil soluble metal catalyst to form a mixture of feed and catalyst, and adding to the mixture of feed and catalyst an oxygen-containing gas under ring opening conditions or (b) contacting the feed with an oxygen-containing gas, adding to the feed contacted with oxygen-containing gas a catalytically effective amount of an oil soluble catalyst and continuing adding oxygen-containing gas under ring opening conditions.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] Figure 1 shows the output from a GC-FIMS measurement of the saturate fraction of dewaxed oil processed from three different crudes, Balder, Heidrun, and Olmeca.

[0013] Figure 2 shows the concentration of species during air oxidation with cobalt acetate of the 82N white oil at 125°C.

DETAILED DESCRIPTION OF THE INVENTION

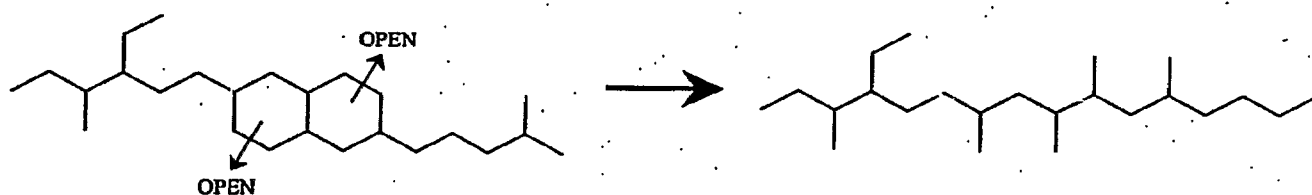
[0014] The petroleum feeds to the present process include crude oils, distillate fractions, and other petroleum streams that may contain ring species in the form of naphthene and aromatic compounds. Such feeds may be feeds for the production of lubricant oil basestocks or may be feeds for the production of distillate fuels such as diesels. Naphthenes are cycloparaffins having one or more cyclic rings. The rings may have 5 or more carbon atoms and may be substituted with substituents such as alkyl groups containing 1-20 carbon atoms. Examples of one ring naphthenes include cyclopentane, cyclohexane, cyclooctane, methyl cyclohexane, ethyl cyclohexane, and the like. Naphthenes may also be polycyclic, i.e., containing multiple rings. Heavier petroleum fractions commonly include polycyclic 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 polycyclic naphthenes may also be bridged. Naphtheno-aromatics are fused polycyclic 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, norborane, 3-methyl-1,2-cyclopentenophenanthrene, 1,2,3,4-tetrahydrophenanthrene, indane, perhydroanthracene, perhydrofluorene and perhydroterphenyl,

[0015] The oil soluble catalysts added to the present process 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 acetylacetonates, 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, naphthenic oils, paraffinic oils, synthetic oils, etc. The metal concentrations are from 1 to 1000 wppm based on the petroleum feed. The preferred reaction temperatures for operation are from 50-250°C, most preferably in the range of 100-160°C.

[0016] 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. 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 feed/feed mixture and allowed to diffuse into the petroleum/catalyst 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/B).

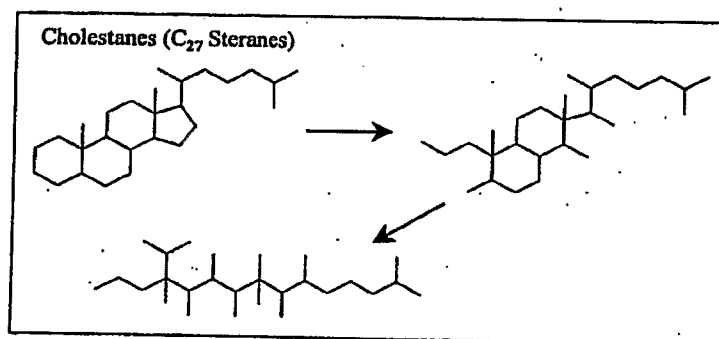
[0017] An example of paraffin production from a multi-ring naphthene is as follows:



[0018] Another example of selective ring opening relates to immature crudes. Immature crudes have an abundance of "biomarker" type molecules, which have retained enough of their original carbon skeleton to be identified by their biological precursors. These molecules can be multi-ring naphthenes that have not yet gone through biodegradation where the "bugs" have cracked off the hydrocarbon branches from the ring structures. The inherent advantages of these crudes for ring opening include lube property improvements such as low temperature

- 7 -

characteristics, (i.e. pour point and cold cranking simulator), increased oxidative stability, and possible viscosity index benefits. Additionally, the improvements for fuels include the potential for these long chains to be cracked into species with high cetane quality due to their opportunity for intramolecular hydrogen abstraction. The magnitude of the improvement will be dependent on the branch location and molecular size that remain after the opening occurs. A schematic of the ring opening of the biomarker cholestane has been shown below. This diagram shows possible locations for ring opening, which will be dependent on the selectivity of the mechanism as well as the extent of which the reaction is allowed to proceed.



[0019] In the case of naphtheno-aromatics, opening of the naphthene ring portion leads to an aromatic substituted with an alkyl substituent. This results from the most likely position for attack by peroxide, i.e., the point at which the aromatic and naphthene rings are joined, producing the alkyl substituted aromatic. The aromatic substituted with an alkyl substituent may then react to form an aromatic moiety and an alkyl moiety.

[0020] In another embodiment, the naphthenes and naphtheno-aromatics may be the product of a ring saturation process. Ring saturation typically occurs as a result of a catalytic hydrogenation process. In a polycyclic fused ring system containing both aromatic and naphthenic rings, it may be possible to saturate at least some of the aromatic rings prior to the ring opening process. One such process is hydrotreating. Another is hydrocracking. A mild form of hydrotreating is hydrofinishing. Hydrotreating, in addition to ring saturation, may also remove

- 8 -

sulfur-, nitrogen- and oxygen-containing species by conversion to hydrogen sulfide, ammonia and water.

[0021] For hydrocracking, the catalyst may be any catalyst used for hydrocracking. Such catalysts typically employ an acidic, large pore size zeolite within the porous support material with an added metal hydrogenation/dehydrogenation function. The acidic functionality in the hydrocracking catalyst is provided either by a large pore, amorphous material such as alumina, silica-alumina or silica or by a large pore size crystalline material, preferably a large pore size aluminosilicate zeolite such as zeolite X, Y, ZSM-3, ZSM-18, ZSM-20 or zeolite beta. The zeolites may be used in various cationic and other forms, preferably forms of higher stability so as to resist degradation and consequent loss of acidic functionality under the influence of the hydrothermal conditions encountered during the hydrocracking. Thus, forms of enhanced stability such as the rare earth exchanged large pore zeolites, e.g., REX and REY are preferred, as well as the so-called ultra stable zeolite Y (USY) and high silica zeolites such as dealuminized Y or dealuminized mordenite. Hydrocracking conditions include temperatures of from 300 to 480°C, preferably 315 to 425°C, a hydrogen partial pressure of from 6996 to 20786 kPa (1000 to 3000 psig), preferably 10443 to 17338 kPa (1500 to 2500 psig), a space velocity of from 0.1 to 10 LHSV, preferably 0.5 to 5 LHSV, and a hydrogen to feed ratio of from 178 to 1780 m³/m³ (1000 to 10000 Scf/B), preferably 356 to 1780 m³/m³ (2000 to 10,000 Scf/B).

[0022] For hydrotreating, the catalysts are those effective for hydrotreating such as catalysts 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 nickel, tungsten, molybdenum, cobalt and mixtures thereof. These metals or mixtures of metals are typically present as oxides or sulfides on refractory metal oxide supports. The mixture of metals may also be present as bulk metal catalysts wherein the amount of metal is 30 wt. % or greater,

- 9 -

based on catalyst. Suitable metal oxide supports include oxides such as silica, alumina, silica-aluminas or titania, preferably alumina. Preferred aluminas are porous aluminas such as gamma or eta. The amount of metals, either individually or in mixtures, ranges from about 0.5 to 35 wt. %, based on the catalyst. In the case of preferred mixtures of groups 9-10 metals with group 6 metals, the groups 9-10 metals are present in amounts of from 0.5 to 5 wt. %, based on catalyst and the group 6 metals are present in amounts of from 5 to 30 wt. %. The amounts of metals may be measured by methods specified by ASTM for individual metals including atomic absorption spectroscopy or inductively coupled plasma-atomic emission spectrometry.

[0023] Hydrotreating conditions include temperatures of from 150 to 400°C, preferably 200 to 350°C, a hydrogen partial pressure of from 1480 to 20786 kPa (200 to 3000 psig), preferably 2859 to 13891 kPa (400 to 2000 psig), a space velocity of from 0.1 to 10 hr.⁻¹ preferably 0.1 to 5 hr.⁻¹, and a hydrogen to feed ratio of from 89 to 1780 m³/m³ (500 to 10000 scf/B), preferably 178 to 890 m³/m³.

[0024] 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 color bodies. Generally, the hydrofinishing will be carried out at temperatures from about 150 to 350°C, preferably 180 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 hr.⁻¹, preferably 0.5 to 3 hr.⁻¹ and hydrogen treat gas rates of from 44.5 to 1780 m³/m³ (250 to 10,000 scf/B).

[0025] 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

- 10 -

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 is a mesoporous material belonging to the M41S class or family of catalysts. The M41S family of catalysts are mesoporous materials having high silica contents whose preparation is further described in J. Amer. Chem. Soc., 1992, 114, 10834. Examples included MCM-41, MCM-48 and MCM-50. Mesoporous refers to catalysts having pore sizes from 15 to 100 Angstroms. A preferred member of this class is MCM-41 whose preparation is described in United States Patent Number 5,098,684. MCM-41 is an inorganic, porous, non-layered phase having a hexagonal arrangement of uniformly-sized pores. The physical structure of MCM-41 is like a bundle of straws wherein the opening of the straws (the cell diameter of the pores) ranges from 15 to 100 Angstroms. MCM-48 has a cubic symmetry and is described for example, in United States Patent Number 5,198,203 whereas MCM-50 has a lamellar structure. MCM-41 can be made with different size pore openings in the mesoporous range. The mesoporous materials may bear a metal hydrogenation component, which is at least one of Group 8, Group 9 or Group 10 metals. Preferred are noble metals, especially Group 10 noble metals, most preferably Pt, Pd or mixtures thereof.

[0026] The further processing of the peroxide decomposition products is dependent on the proposed use. If the intended end use is as a fuel for internal combustion engines, then the presence of additional branched paraffins, oxygenates and aromatics is useful as these products from peroxide treatment are helpful to the octane value. On the other hand, if the intended use is as a diesel fuel, then the presence of aromatics and oxygenates may not be desirable from the standpoint of

- 11 -

cetane value and/or particulates from combustion. For lubricant oil purposes, aromatics and oxygenates are not desirable as they may result in poor VI and low temperature properties or undesirable oxidation products at high temperatures.

[0027] If the feed contains undesirable amounts of oxygen-, sulfur- or nitrogen-contaminants, then the feed when treated with oxygen in the presence of oil soluble metal catalyst form oxidized species. The oxidized oxygen-, sulfur- and nitrogen- compounds may then be solvent extracted under solvent extraction conditions. Solvent extraction is used to separate aromatics from paraffins, i.e., the raffinates 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 appears 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 such 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.

[0028] 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.

[0029] 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

- 12 -

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 temperatures from 50-100°C, tower temperature gradients from 10-30°, 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°, water in solvent from 1-2%, and a treat of 125-200 vol.%.

[0030] Upgrading processes for petroleum feeds typically involve one or more steps including solvent extraction, hydrocracking or hydrotreating, catalytic or solvent dewaxing and hydrofinishing. The ring opening step may be incorporated into the upgrading process as illustrated in the following. This is meant to be examples of the incorporation of ring opening and should not be construed as limiting. The ring opening in the following process schemes takes place in a ring opening oxidation vessel or "ROOV".

1. ROOV before extraction to increase yield by decreasing loss of multi-ring species to the extract.
2. ROOV after extraction and solvent dewaxing to improve oxidation stability, VI, and possibly swell volume.
3. ROOV after extraction to open rings producing more paraffin-like species followed by hydrodewaxing to isomerize.
4. ROOV to work with or replace existing hydrofinishers used for color reduction and oxidation stability improvements.
5. Use in conjunction with oxidation technique to improve extraction in process scheme #1 or with recycle for #2 & #3.
6. ROOV to work in conjunction with cracking to produce long chain paraffins with high cetane values.

[0031] This invention is further illustrated by the following examples.

EXAMPLE 1

[0032] This example relates to immature crudes. Examples of immature crudes include Chad, Peng Lai, and many high neutralization number crudes (Balder, Gryphon, Heidrun, etc.), all of which are deemed attractive for future use due to their cheap cost. This abundance can be confirmed when analyzing the 4-ring naphthene content of different crudes, where a peak should be present acknowledging the fact that biomarkers such as cholestanes are present. Figure 1 shows the output from a GC-FIMS (field ionization mass spectrometry) measurement of the saturate fraction of DWO (dewaxed oil) processed from three different crudes, Balder, Heidrun, and Olmeca. It shows that the Balder and Heidrun crudes have an abundance of 4-ring naphthenes in the C₂₇ to C₃₀ region indicative of an immature crude and the presence of biomarkers, not present in a typical "good" lube crude such as Olmeca (also shown in Figure 1). Therefore, this invention aims to take advantage of the fact that these immature crudes will have longer branches on their naphthene rings than older crudes that have gone through more extensive biodegradation. This invention will open up the ring structures of these molecular species to produce species for improved lubricant properties.

EXAMPLE 2

[0033] This example is directed to oxidation of a white oil under mild reaction conditions. The oxidation was conducted at 125°C and an air flow rate of 500 cc/min in the presence of 500 ppm Cobalt Acetate catalyst on a medicinal grade white oil with a nominal viscosity of 82 SUS. These samples were analyzed by FTIR, which showed the presence of a small amount of carbonyl species, although the signal was not very strong. In addition to FTIR, the samples were further analyzed by proton NMR, the spectra showed the presence of alcohols and esters. Furthermore, the level of oxygenates (as derived from the relative contribution to the overall hydrogen content) increased with the increased severity of the oxidation in the experimental run.

[0034] The most definitive analysis was conducted using GC-FIMS to understand their molecular composition. It was found that the oxidation caused almost a 20% decrease in the ratio of the relative amount of ring structured molecules to paraffin molecules, as shown in Figure 2. Figure 2 shows the concentration of species during air oxidation with cobalt acetate of the 82N white oil at 125°C. Likewise, the ratio of the concentration of 2-ring and larger species to 1-ring and paraffin molecules decreased by about 15%. These trends support the idea that the oxidation is causing ring opening by the act of breaking down the larger ringed species into smaller ringed and/or paraffin species in the oil. This data gives a better justification of the extent of the reaction and final branching achieved during the oxidation. The branching extent and location becomes crucial when trying to determine the optimal application for this technology. While in lubes service, it would be most beneficial to produce long chained linear molecules for the VI incentives. But when looking at a fuels scenario there exists the cetane versus octane quandary. This could be solved by segregating the products that may best suit a boost in cetane or vice versa, for octane. A potential process for mediating the branch location dilemma could be the use of an acid catalyst such as $\text{SiO}_2/\text{Al}_2\text{O}_3$ or sulfated zirconia to generate, for example, more methyl branches. Additionally, the presence of oxygenates may help or hinder the product properties and may need to be hydrogenated in order to truncate the oxygen species. The low yields in this experiment can be at least in part attributed to the relatively mild conditions and non optimum catalyst levels and solvents e.g. acidic media. Optimizing these operating parameters are expected to lead to much higher yields, and VI's.

- 15 -

CLAIMS:

1. A method for selectively ring opening naphthenes or aromatics in a petroleum feed containing naphthenic or aromatic ring species which comprises: combining the petroleum feed with a catalytically effective amount of an oil soluble metal catalyst to form a mixture of feed and catalyst, and adding to the mixture of feed and catalyst an oxygen-containing gas under ring opening conditions.
2. A method for selectively ring opening naphthenes or aromatics in a petroleum feed containing naphthenic or aromatic ring species which comprises: (a) contacting the feed with an oxygen-containing gas, (b) adding to the feed contacted with oxygen-containing gas a catalytically effective amount of an oil soluble catalyst and (c) continuing adding oxygen-containing gas under ring opening conditions.
3. An upgrading process for upgrading a petroleum feed which comprises: contacting the feed in an upgrading process incorporating selective ring opening, said upgrading including at least one of hydrocracking, hydrotreating, hydrodewaxing, solvent dewaxing, solvent extracting and hydrofinishing, wherein selective ring opening is by (a) combining the petroleum feed with a catalytically effective amount of an oil soluble metal catalyst to form a mixture of feed and catalyst, and adding to the mixture of feed and catalyst an oxygen-containing gas under ring opening conditions or (b) contacting the feed with an oxygen-containing gas, adding to the feed contacted with oxygen-containing gas a catalytically effective amount of an oil soluble catalyst and continuing adding oxygen-containing gas under ring opening conditions.
4. The process of claims 1 or 2 wherein ring opening 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/B).

- 16 -

5. The upgrading process of claim 3 wherein ring opening 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/B).

6. The process of claims 1 to 3 wherein the oil soluble metal catalyst include metals from Groups 4-12.

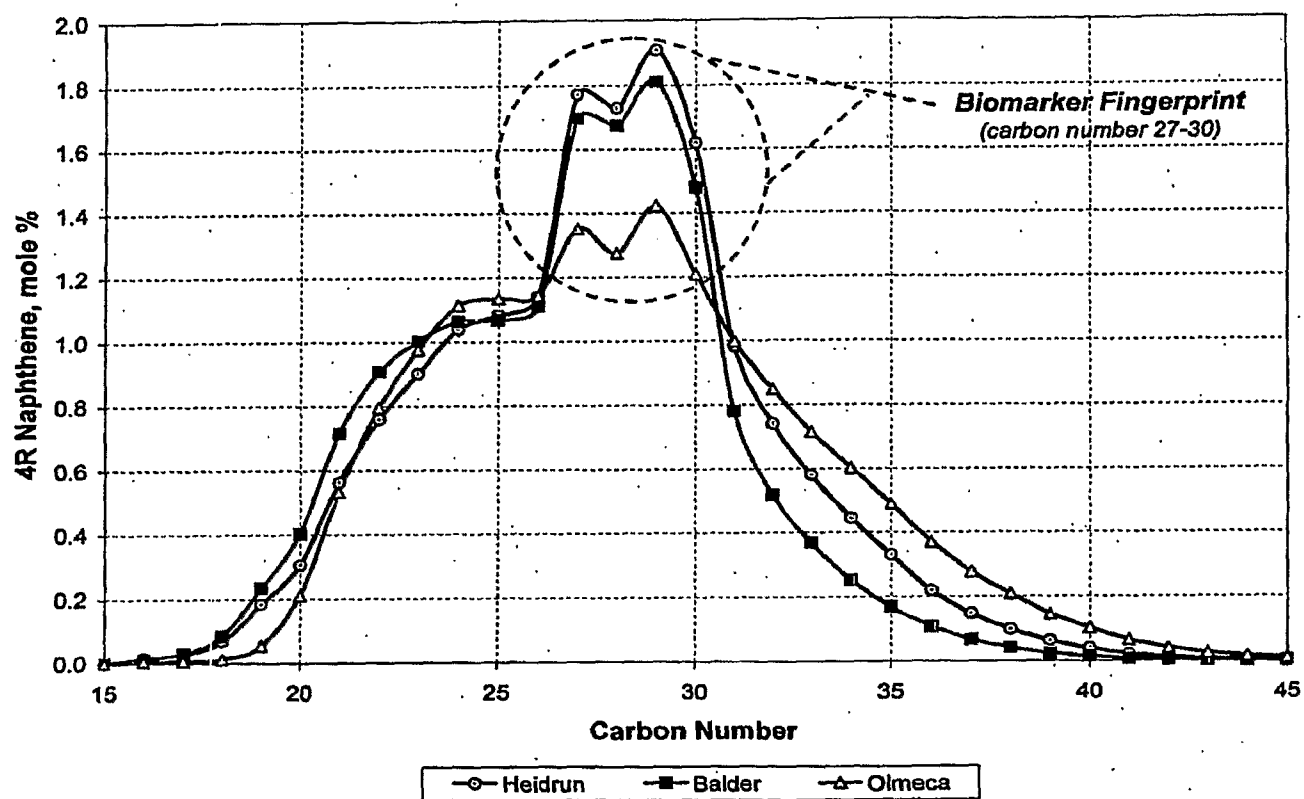
7. The process of claim 6 wherein the metal include at least one of V, Cr, Mo, W, Fe, Ni, Co, Pt, Pd, Ru and Mn.

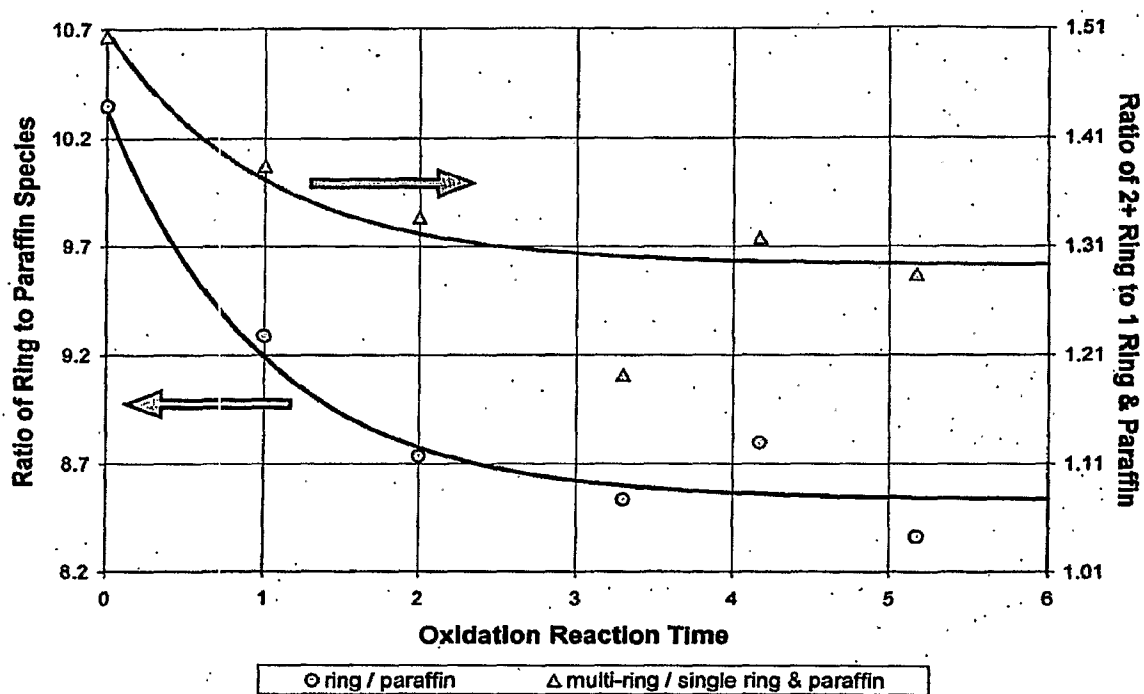
8. The process of claim 6 wherein the metal soluble catalyst is present in an amount from 1 to 1000 wppm, based on feed.

9. The process of claims 1 to 3 wherein the feed may be feeds for the production of lubricant oil basestocks or may be feeds for the production of distillate fuels.

10. The process of claim 3 wherein ring opening is incorporated into the upgrading process.

11. The process of claim 10 wherein ring opening takes place in a ring opening vessel which vessel is incorporated into the upgrading process.

**FIGURE 1.**

**FIGURE 2**