HEAVY OIL UPGRADING PROCESS

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ABSTRACT

A process for upgrading heavy oils and bitumen to a crude oil with properties acceptable as a refinery feedstock includes the steps of solvent de-asphalting by separating the polynuclear aromatics including asphaltenes from the heavy oil or bitumen and contacting the de-asphalted oil with biological and chemical reagents to reduce the concentrations of contaminants so as to render the resulting oil an acceptable feedstock for petroleum refineries.
HEAVY OIL UPGRADING PROCESS

BACKGROUND

[0001] Many fossil fuels such as hydrocarbons from oil sand deposits, tar sands and bitumen, herein referred to as heavy oil, contain polyaromatics composed of asphaltenes and resins, heavy metals with nickel and vanadium being the predominant ones and hetero-atoms like oxygen, sulphur and nitrogen in their chemical composition. During refinery operations, the presence of asphaltenes results in the formation and/or separation of coke—that plugs the fixed bed of catalysts. The plugging of a catalyst bed by coke deleteriously leads to the formation of a layer of coke over the catalyst—a phenomenon that prevents the catalyst from functioning at its efficiency. The nitrogen, sulphur, nickel and vanadium in heavy oils and bitumen also have detrimental effect on refining operations in that they constitute the poisoning or de-activation agents of the catalyst. Thus the presence of asphaltenes, heavy metals and heteroatoms in heavy oil make the oil an undesirable feed for many refinery operations—specifically in fixed bed units or fluidized catalytic units and ultimately has a negative effect on the value or price of heavy oil.

SUMMARY

[0002] We disclose here a process for the upgrading of heavy oil that provides a solution to catalytic poisoning by substantially reducing the concentrations of contaminants to levels that enable the residual product to be used as a desirable feedstock for refineries.

[0003] In one embodiment of a heavy oil upgrading process, the concentrations of contaminants of heavy oils can be reduced substantially by dissolving the heavy oil in a de-asphalting hydrocarbon solvent to separate the insoluble asphaltenes from the soluble oil fraction, and thereafter subjecting the oil fraction to oxidation, including biological and chemical treatments.

[0004] In one embodiment, a heavy oil upgrading process uses a hydrocarbon solvent composed of a mixture of paraffinic, iso-paraffinic and aromatic solvents ranging from C₄ to C₁₅ hydrocarbons in the de-asphalting of heavy oils to produce asphaltenes that are black shiny crystalline solids that are easily separated from the heavy oil. Examples of the constituents of the solvent include butane, iso-butane, n-pentane, iso-pentane, n-heptanes, iso-octane and metaxylene with iso-octane being the preferred solvent.

[0005] For example, in the de-asphalting step the heavy oil may be initially contacted with the solvent and heated to a moderate temperature. The mixture is maintained at temperatures in the range of 75°C-110°C for a period of 2 to 3 hours. Following the dissolution of the oil over a predetermined time, the asphaltenes are separated from the oil through gravity or vacuum filtration. Due to the nature of the solvent used in the de-asphalting phase, the asphaltenes recovered are black, shiny and crystalline solids that are easily separated from the oil fraction.

[0006] In one embodiment of a heavy oil upgrading process, bio-chemical catalytic oxidation of nickel, vanadium, sulphur and unsaturated compounds present in high concentrations in heavy oil is conducted in the presence of biological and/or chemical reagents at moderate temperatures and pressures.

[0007] In another embodiment of a heavy oil upgrading process, pressures in the range of 1 atm to 14 atm are applied along with oxidizing reagents and catalysts to reduce the concentrations of metallic contaminants, unsaturated compounds, and hetero-atoms such as sulphur and nitrogen contained in heavy oil.

[0008] In another embodiment of a heavy oil upgrading process, an adsorbent material is used along with the biological and chemical reagents to absorb the oxidized products from the heavy oil. In one embodiment, a heavy oil upgrading process enhances the API gravity of the heavy oil from less than 10 to 30 and above by reducing the concentrations of contaminants contained in the oil by a minimum of 50% by weight.

[0009] In one embodiment of a heavy oil upgrading process, the de-asphalted oil is contacted with biological reagents that contain enzymes that catalyze the oxidation of the contaminants in the oil. In one embodiment of a heavy oil upgrading process, biological materials or agricultural wastes are used as reagents to upgrade heavy oil into products that are acceptable as refinery feedstock. The biological oxidation in one embodiment is accomplished by the introduction of an oxidant and an adsorbent along with the biological reagents into the de-asphalted oil and then subjecting the mixture to temperatures of between 85°C and 150°C and at pressures ranging from 1 atm to 14 atm for a period of time, preferably between 2 to 3 hours, and thereafter separating the oil from the oxidized contaminants. The oil from this stage is then subjected to chemical oxidation by the introduction of chemical reagents including adsorbents into the oil and heating the mixture to between 165°C and 180°C for 1 hour to 3 hours at between 1 atm and 14 atm. Upon completion of the chemical treatment, the oil is separated from the oxidized contaminants through filtration.

[0010] In one embodiment of a heavy oil upgrading process, adsorbents are added to the oil to extract from the biochemically treated oil the polar or oxidized compounds. The separation of the adsorbent and any or all accompanying oxidized compounds from the oxidized oil may be, for example, accomplished through gravity or vacuum filtration, or preferably through a centrifuge or pressure leaf filter. The oil recovered from the oxidized contaminants is composed of the upgraded oil and the de-asphalting solvent which is ultimately separated from the upgraded oil. The separation of solvent from the upgraded oil may be achieved by various processes such as distillation. The residual oil, following the separation of the solvent, is an upgraded oil which is substantially reduced in contaminants' concentration and possesses characteristics that make it acceptable as a refinery feed stock.

[0011] In one embodiment, a heavy oil upgrading process provides a bio-chemical catalytic process for the oxidation of nickel, vanadium, sulphur, nitrogen and unsaturated compounds by the application of waste biological reagents in the oxidation of the contaminants and also the application of waste iron oxide along with other chemical reagents including a hydrogen donor solvent such as acetic acid.

[0012] In one embodiment, a heavy oil upgrading process provides still a bio-chemical catalytic oxidation of nickel, vanadium, sulphur, nitrogen and unsaturated compounds contained in heavy oils and bitumen at pressures ranging...
from 1 atm to 14 atm and at temperatures between 85°C and 180°C for 1 hour to 3 hours.

**BRIEF DESCRIPTION OF THE DRAWINGS**

**[0013]** Embodiments of a heavy oil upgrading process will now be described by way of example with reference to FIG. 1, which is a flow diagram of a heavy oil upgrading process.

**DETAILED DESCRIPTION**

**[0014]** This detailed description of a heavy oil upgrading process is exemplary and not intended to limit the scope of the claimed heavy oil upgrading process. Immaterial variations from the precise examples set forth here are intended to be included within the scope of the claims. In the claims, the word “comprising” is used in its inclusive sense and does not exclude other elements being present. The indefinite article “a” before a claim feature does not exclude more than one of the feature being present.

**[0015]** Heavy oil from source **10** is transferred to tank **14** where it is mixed with solvent from tank **12**. The mixture is heated (source of heat not shown) for a desired period of time; and upon completion of the reaction between the solvent and the heavy oil, the insoluble asphaltenes are separated through the separation device **16**. The asphaltenes are collected and stored in tank **36** while the de-asphalted oil is transferred to Tank **24**. Tank **18** contains biological reagents that are added to the contents of tank **24** where biological oxidation takes place. The biologically oxidized oil is separated from the oxidized contaminants through separator **30** and transferred to reactor **28** leaving the residue which is stored in tank **38**. Chemical reagents from Tank **22** are added to the contents of reactor **28** for a chemical oxidation phase. Following the chemical oxidation, the oxidized oil is separated from the oxidation residue through separator **34**. The chemical oxidation residue is transferred to storage tank **42** while the oxidized oil is transferred to distillation unit **44** where the initial de-asphalted oil is separated from the upgraded oil through atmospheric or vacuum distillation. The solvent recovered is transferred back into Tank **12** while the upgraded oil from unit **44** is collected and stored in Tank **48**.

**[0016]** The heavy oil upgrading process described here reduces problems associated with high asphaltenes content and high contaminants’ concentrations of heavy oil. The heavy oil upgrading process provides a process for upgrading heavy oil to crude oils with characteristics that enable them to be used as refinery feedstock. The heavy oil upgrading process provides the dissolution of the heavy oil in a hydrocarbon solvent comprising of paraffinic, iso-paraffinic and/or aromatic solvents. This solvent, by virtue of its composition rejects the asphaltenes which separate from the oil as black, shiny, hard and crystalline solids. Following the separation of asphaltenes from the oil, the heavy oil upgrading process provides the application of biological and chemical reagents for the reduction of contaminants’ concentration from the de-asphalted oil. An embodiment of the heavy oil upgrading process comprises the steps of solvent de-asphalting followed by bio-chemical treatments as illustrated in FIG. 1. Initially, an amount of the hydrocarbon solvent is added to a specified mass of heavy oil or bitumen to give a solvent to oil ratio where the minimum solvent to oil volume ratio is 4:1 and a maximum solvent to oil volume ratio is 40:1 with 10:1 being the preferred solvent to oil volume ratio.

**[0017]** The exemplary hydrocarbon solvent herein described is a mixture of straight and branch chained paraffinic and aromatic solvents ranging from C4 to C10 examples of which include butane, iso-butane, n-pentane, iso-pentane, n-heptane iso-octane and metaxylene with iso-octane being the preferred solvent. The mixture is heated at atmospheric pressure to a desired temperature and for a time sufficient to cause dissolution of the heavy oil in the solvent. The mixture may be heated to a minimum temperature of 60°C and a maximum temperature of 120°C, the preferred temperature being in the range of 105°C -115°C under reflux. The residence time may range from one hour to four hours and most preferably from two to three hours. Under these conditions, the asphaltenes are separated from the oil as insoluble crystalline black shiny solids and recovered through a proper separation device. A suitable separation device comprises gravity or vacuum filtration. The amount of asphaltenes that are typically recovered through this heavy oil upgrading process is approximately 16-20% weight of the heavy oil, although this can vary depending on the source of the heavy oil and also on the operating parameters of the de-asphalting process.

**[0018]** Following the de-asphalting phase of the heavy oil upgrading process, biological reagents are introduced to a reactor containing a mass of the de-asphalted oil, the minimum mass of the said de-asphalted oil being 50 g and a maximum mass being 2 kg with 750 g as the preferred mass in this example. The biological reagents are selected from agricultural wastes, examples of which comprise peat moss, canola hulls, peanut shells, soybean hulls, and cellulose. The biological reagents contain enzymes that are capable of operating at high temperatures and low pH conditions and also catalyze the oxidation of the contaminants, particularly nickel and vanadium to their respective oxides at the expense of an oxidizing agent. The addition of the oxidizing agent follows the biological reagents. The oxidizing agent may comprise oxides of metals of Group IIA such as calcium and magnesium, or oxides of metals of Group VIII such as cobalt, nickel, copper or iron as well as their combinations. Other oxidizing agents which may be used comprise oxygen, air, ozone, hydrogen peroxide, chloramine, per-acetic acid, formic acid, per-benzoic acid, benzoic acid, and acetic acid.

The oxidant, when applied in a liquid form is preferentially added in a range of 0.5% volume to 5.5% volume of the heavy oil/bitumen feed, although volume percentages of between 0.1% and 7.2% are also suitable for the process.

**[0019]** A further embodiment of the heavy oil upgrading process is the introduction of an adsorbent selected from among materials such as: fullers’ earth, alumina, zeolite, clay, silica gel, peat moss or a combination of two or more of them into the reaction chamber. Preferred adsorbents are alumina, peat moss, clay or their combinations. In one embodiment, the adsorbent is applied as a weight percentage of the heavy oil or bitumen from between 0.055% weight and 6.5% weight with the preferred range being 2.5% weight to 5.5% weight.

**[0020]** The biological oxidation, according to one embodiment of the heavy oil upgrading process, is carried out at pressures ranging from 1 atm to 14 atm and at temperatures ranging from 85°C to 150°C, and over a period of time ranging between 2 and 3 hours. Following the biological
oxidation of the de-asphalted oil, the oxidized oil is separated from the contaminants by means of a suitable separation device. Such a device may comprise gravity filtration, vacuum filtration, centrifugation, or pressure-leaf filtration.

[0021] A further embodiment of the heavy oil upgrading process comprises the introduction of chemical reagents to the biologically oxidized oil in a second reactor. The preferred chemical reagents comprise catalysts, examples of which comprise alumina, activated carbon, bituminous coal, lignite char or coemul char. Oxides of Group VIII metals have also been found to be useful as oxidation catalysts with the preferred such catalyst being iron oxide. As an embodiment of this heavy oil upgrading process, iron oxide is derived exclusively from a waste hydrometallurgical metal processing plant. A hydrogen donor solvent, preferably a carboxylic acid solvent may also be employed. Preferred carboxylic acids may comprise formic or acetic acid. As a further embodiment of the heavy oil upgrading process, any one of the oxidants used in the biological oxidation phase can be used in the chemical oxidation. As well, the most preferred oxidants comprise iron oxide, water, and hydrogen peroxide or a mixture of aqueous hydrogen peroxide and an acid. As another embodiment of the heavy oil upgrading process, any one of the adsorbents used in the biological oxidation phase can be used in the chemical oxidation.

[0022] The mixture of oil, chemical reagents and adsorbent may be heated to a sufficient temperature and sufficient pressure over a sufficient amount of time. These parameters comprise a temperature range of 105° C. to 180° C., pressures ranging between 1 atm and 14 atm, and times ranging from 1 hour to 3 hours. Thereafter, the chemically oxidized oil is separated from the contaminants via a separation device. Examples of such separation devices comprise gravity filtration, vacuum filtration, centrifugation and pressure filtration.

[0023] The oil recovered from the separation unit is further subjected to yet another separation system to recover the upgraded oil from the de-asphalting solvent. As an embodiment of the heavy oil upgrading process, the preferred method of separating the solvent from the upgraded oil is by either atmospheric or vacuum distillation. The solvent recovered from the distillation unit is re-used in subsequent de-asphalting phases of the upgrading process. The residual product, following the separation of the solvent is the upgraded oil which is substantially reduced in contaminants’ concentration as disclosed by the results of the chemical and physical analyses of the product. As an embodiment of the heavy oil upgrading process, the chemical oxidation process can precede the biological oxidation.

EXAMPLES OF EXPERIMENTAL WORK

Example 1

[0024] This example illustrates the effect of using virgin and recycled solvent in the de-asphalting phase of the upgrading process.

[0025] In a 1 L beaker was accurately weighed 5 g of Alberta heavy oil. 100 mL of virgin solvent was added to the heavy oil to give a 20:1 solvent to oil ratio and the mixture was stirred with heat from a hot plate until the formation of an emulsion was observed. With continuous stirring, the mixture was heated to a moderate temperature and thereafter, transferred to a 3-neck round bottom 1 L flask provided with a reflux condenser and a thermometer, where the mixture was heated with further stirring for 3 hours at temperatures ranging from 60° C. to 100° C. The mixture was allowed to cool to ambient temperature and thereafter, the asphaltene were separated from the de-asphalted oil through filtration, and the weight of dry asphaltene was recorded. This experiment was repeated five times and the average weight of asphaltene determined. From the average weight of asphaltene, the weight percent of the asphaltene, based on the initial weight of 5 g of the heavy oil, was calculated. In similar experiments, previously used solvent was used in de-asphalted experiments as described above. The average weight of asphaltene recovered from the five experiments with the recycled solvents was determined and the weight percent of the asphaltene calculated. The weight percent of the asphaltene recovered from the experiments with the virgin solvent was approximately 18% while the weight percent of the asphaltene recovered from the experiments with the previously used solvent was approximately 13%.

[0026] The following examples are based on investigations conducted with samples of de-asphalted oil derived from composite de-asphalted oil prepared from the reaction between Alberta heavy oil and the solvent.

Example 2

[0027] This example illustrates the application of a heavy oil upgrading process into a 3-neck II. round bottom flask was measured 350 mL sample of de-asphalted oil. 3 g of biological reagent A and 2 g of biological reagent B were added to the de-asphalted oil followed by the addition of 1 mL of oxidant. Using a magnetic stirrer, the mixture was subjected to stirring while being heated to 175° C. for 3 hours. During the reaction between the oil, the biological reagents, and the oxidant, the enzymes in the agricultural waste or the biological reagents catalytically oxidized the contaminants in the oil. This resulted in the formation of the oxides of nickel and vanadium. Following the biological oxidation, the oil was separated from the oxidized by-products through filtration. The filtrate was transferred to another 3-neck II. round bottom flask to which the chemical reagents were added. The chemical reagents included activated carbon, iron oxide oxidant, a hydrogen donor solvent, water, and the adsorbent. The mixture was subjected to chemical oxidation by heating it to a temperature range of 120° C.-140° C. for 3 hours and at pressures ranging between 1 atm and 14 atm. Following the chemical oxidation, the mixture was cooled and filtered. The oxidized contaminants from the oil, which included the oxides of the metals nickel and vanadium, were thus separated from the oil. The post-treated oil was analyzed for its contaminants concentrations. Table 1 contains the results of the analyses of the upgraded oil.

<table>
<thead>
<tr>
<th>Properties of oil</th>
<th>Concentration of contaminants in the heavy oil as is</th>
<th>Concentration of contaminants in oil treated with Biological Reagents</th>
<th>Concentration of contaminants in oil treated with oxidant only and NO Biological Reagents</th>
</tr>
</thead>
<tbody>
<tr>
<td>SGI @: 60/60° F.</td>
<td>1.000</td>
<td>0.8415</td>
<td>0.9088</td>
</tr>
<tr>
<td>API</td>
<td>11</td>
<td>37</td>
<td>24</td>
</tr>
<tr>
<td>Gravity</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 1-continued

<table>
<thead>
<tr>
<th>Properties of oil</th>
<th>Concentration of contaminants in the heavy oil as in</th>
<th>Concentration of contaminants in oil treated with Biological Reagents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (ppm)</td>
<td>45</td>
<td>14</td>
</tr>
<tr>
<td>V (ppm)</td>
<td>128</td>
<td>30</td>
</tr>
<tr>
<td>S (wt %)</td>
<td>6.20</td>
<td>2.62</td>
</tr>
</tbody>
</table>

Example 3

This example illustrates the effect of using biological reagents as catalysts in the upgrading process. Into a 3-neck II. round bottom flask was measured 500 mL of de-asphalted oil. Specified amounts of the two biological reagents, A and B were added following the addition of an oxidant. Upon heating the mixture for 2 hours at a temperature of 150°C, the mixture was cooled and filtered. The filtrate, which was a mixture of the de-asphaltating solvent and the biologically upgraded oil, was subjected to a separation process from which the solvent was recovered from the upgraded oil. In a comparable experiment, 500 mL of de-asphalted oil was oxidized under the same experimental conditions as before, including the same amount of oxidant, but without any biological reagents. Following the separation of the solvent from the upgraded oil, contaminants concentrations of the two upgraded oils were determined. The results are contained in Table 2.

Table 4 contains a summary by carbon of the fractional composition of a crude oil produced by the bio-chemical catalytic oxidation of Alberta heavy oil.

<table>
<thead>
<tr>
<th>TABLE 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Properties of Oil</td>
</tr>
<tr>
<td>SGI @60/60° F.</td>
</tr>
<tr>
<td>API Gravity</td>
</tr>
<tr>
<td>Ni (ppm)</td>
</tr>
<tr>
<td>V (ppm)</td>
</tr>
<tr>
<td>S (wt %)</td>
</tr>
<tr>
<td>N (wt %)</td>
</tr>
</tbody>
</table>

[0028] In one embodiment, a heavy oil upgrading process provides further a bio-chemical catalytic oxidation process for obtaining, from heavy oils and bitumen containing 6.20% weight of sulphur and 0.30% weight of nitrogen as well as 45 ppm of nickel and 128 ppm of vanadium, an upgraded oil containing a minimum of 50% of the original contaminants.

What is claimed is:

1. A method for removing contaminants from heavy oil, where the heavy oil includes asphaltenes and the contaminants include oxidizable contaminants, the method comprising:
   de-asphaltating the heavy oil with a hydrocarbon solvent to produce a de-asphalted oil;
   contacting the de-asphalted oil with a first oxidant in the presence of a first reagent to produce de-asphalted oil containing oxidized contaminants;
   separating the oxidized contaminants from the de-asphalted oil to produce a de-asphalted-de-contaminated oil; and
   separating the hydrocarbon solvent from the de-asphalted-de-contaminated oil to produce upgraded oil.

2. The method of claims 1 in which the hydrocarbon solvent comprises butane, iso-butane, n-pentane, iso-pentane, n-heptanes, metaxylene, or iso-octane.

3. The method of claim 1 in which the de-asphalting step comprises:
   contacting the heavy oil with the hydrocarbon solvent to produce a mixture of heavy oil and hydrocarbon solvent;
   while contacting the heavy oil with the hydrocarbon solvent, heating the mixture of heavy oil and hydrocarbon solvent; and

[0029] Tables 3 and 4 contain some physical and chemical data of upgraded crude oils with characteristics of a refinery feedstock produced from the bio-chemical catalytic oxidation process of the present heavy oil upgrading process.

Table 3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>Alberta Heavy Oil</th>
<th>45/55 Upgraded Oil</th>
<th>59/60 Upgraded Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abs Density @ 15° C.</td>
<td>ASTM D5902</td>
<td>908 kg/m³</td>
<td>811.5 kg/m³</td>
<td>828.8 kg/m³</td>
</tr>
<tr>
<td>API Gravity @ 15° C.</td>
<td>N/A</td>
<td>10</td>
<td>43</td>
<td>39</td>
</tr>
<tr>
<td>Relative Density @ 15° C.</td>
<td>ASTM D5002</td>
<td>1.007</td>
<td>0.8122</td>
<td>0.8295</td>
</tr>
<tr>
<td>Total Sulphur</td>
<td>ASTM D5453</td>
<td>6.20 Mass %</td>
<td>1.8 Mass %</td>
<td>2.67 Mass %</td>
</tr>
<tr>
<td>Total Nitrogen</td>
<td>ASTM D5291</td>
<td>0.30 Mass %</td>
<td>0.11 Mass %</td>
<td>0.16 Mass %</td>
</tr>
<tr>
<td>Nickel</td>
<td>ASTM D5708A</td>
<td>45 mg/kg</td>
<td>8.5 mg/kg</td>
<td>11 mg/kg</td>
</tr>
<tr>
<td>Vanadium</td>
<td>ASTM D5708A</td>
<td>128 mg/kg</td>
<td>27 mg/kg</td>
<td>33 mg/kg</td>
</tr>
<tr>
<td>MCR</td>
<td>ASTM D4550</td>
<td>N/A</td>
<td>2.68</td>
<td>2.72</td>
</tr>
</tbody>
</table>
separating the asphaltenes from the mixture of heavy oil and hydrocarbon solvent to produce the de-asphalted oil.

4. The method of claim 1 in which the first reagent comprises a biological reagent and the oxidized contaminants comprise biologically oxidized contaminants, and further comprising contacting the de-asphalted oil with a second oxidant to produce chemically oxidized contaminants.

5. The method of claim 4 in which the biological reagent is obtained from agricultural waste.

6. The method of claim 4 in which the second oxidant is iron oxide.

7. The method of claim 6 in which the iron oxide is derived from a hydrometallurgical metal processing plant as a waste product.

8. The method of claim 1 in which contacting the de-asphalted oil with an oxidant takes place in the presence of an adsorbent; the adsorbent comprising of; fuller’s earth, alumina, zeolite, silica gel, clay or peat moss.

9. The method of claim 8 in which the adsorbent is added in a concentration comprising between 0.055% weight and 6.5% weight of the de-asphalted oil.

10. The method of claim 1 in which the step of contacting the de-asphalted oil with a first oxidant comprises heating the mixture comprising of de-asphalted oil, first reagent, and oxidant.

11. The method of claim 1 in which the first oxidant is added in a concentration comprising 0.1% volume and 7.2% volume of the de-asphalted oil and more specifically the first oxidant is added in a concentration between 0.5% volume and 5.5% volume of the de-asphalted oil.

12. The method of claim 1 in which the step of contacting the de-asphalted oil with a first oxidant is carried out at a pressure of between 1 atm and 14 atm.

13. The method of claim 1 in which the first reagent is a biological reagent and in which contacting the de-asphalted oil with the first oxidant is carried out at a temperature between 85°C and 180°C for a period of time between 1 hour and 3 hours.

14. The method of claim 1 in which the step of contacting the de-asphalted oil with an oxidant is carried out in the presence of a hydrogen donor solvent comprising at least one of acetic acid and formic acid.

15. The method of claim 1 in which the step of separating the oxidized contaminants from the de-asphalted oil comprises gravity filtration, vacuum filtration, centrifugation, or pressure-leaf filtration; and also the step of separating the hydrocarbon solvent from the de-asphalted de-contaminated oil comprises using a distillation device.

16. A method for bio-chemical catalytic oxidation of contaminants including nickel, vanadium, sulphur and nitrogen as well as unsaturated compounds and separating the oxidized by-products from heavy oil contaminated with the contaminants, comprising:

- de-asphalting the heavy oil with a solvent comprising paraflinic, iso-paraflinic and aromatic solvents;
- contacting the de-asphalted oil with a biological reagent obtained from agricultural waste along with an oxidant and an adsorbent to produce biologically oxidized oil;
- contacting the biologically oxidized oil with a chemical reagent, iron oxide used as an oxidant, acetic acid as a hydrogen donor solvent and an adsorbent to produce a decontaminated oil; and
- separating the de-asphalting solvent from the decontaminated oil through distillation.

17. A method for the removal of nickel, vanadium, sulphur, nitrogen and unsaturated compounds from heavy oil through bio-chemical catalytic oxidation, comprising:

- de-asphalting the heavy oil to produce a de-asphalted oil;
- providing pulverized biological reagents derived from agricultural wastes of canola hulls, peanut shells and soy bean hulls;
- providing at least one oxidant;
- oxidizing the nickel, vanadium and sulphur contaminants by admixing the de-asphalted oil, pulverized biological reagents and oxidant under pressure which ranges from atmospheric pressure to 14 atmospheres and at a temperature between 100°C to 150°C under reflux such that the de-asphalted oil, the biological reagents and the oxidant are agitated for a time period to obtain a partially biologically oxidized hydrocarbon stream; and filtering the biologically oxidized oil to separate the partially biologically oxidized hydrocarbon stream.

18. A method for obtaining a hydrocarbon stream suitable for use as a refinery feedstock through bio-chemical catalytic oxidation of heavy oil contaminated with nickel, vanadium, nitrogen, sulphur and unsaturated compounds, comprising:

- de-asphalting the heavy oil to produce a de-asphalted oil;
- treating the de-asphalted oil with an oxidant in the presence of a biological reagent;
- contacting the de-asphalted oil at a pressure above atmospheric pressure and reaction temperature above 60°C with; pulverized iron oxide as an oxidant derived exclusively from a hydro-metallurgical processing plant as a waste product, at least one organic acid as a hydrogen donor solvent, activated carbon as catalyst derived from one or more of asphaltenes, coal and coconut shells, water as a catalyst and adsorbent;
- filtering the de-asphalted oil to separate catalyst, oxidized contaminants and adsorbent from hydrocarbons in the de-asphalted oil; and
- separating the upgraded oil from the de-asphalting solvent.

19. The method of claim 18 further comprising enhancing oxidation by contacting the de-asphalted oil with activated carbon and organic acid.

20. The method of claim 18 in which the reaction temperature is between 100°C and 150°C and maintained for a period of at least 3 hours; and the adsorbent is one or more of zeolites, clay, fuller’s earth; and peat moss.

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