Upgrading of residual oil.

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US-A-3 480 540
US-A-3 796 653

The file contains technical information submitted after the application was filed and not included in this specification.

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Residual petroleum oil fractions produced by atmospheric or vacuum distillation of crude petroleum are characterized by a relatively high metals content. This occurs because substantially all of the metals present in the original crude remain in the residual fraction. Principal metal contaminants are nickel and vanadium, with iron and small amounts of copper sometimes present.

The high metals content of the residual fractions generally preclude their effective use as chargestocks for subsequent catalytic processing such as catalytic cracking and hydrocracking, because the metal contaminants deposit on the special catalysts used in these processes and cause the formation of inordinate amounts of coke, dry gas and hydrogen.

It is current practice to upgrade certain residual fraction by a pyrolytic operation known as coking. In this operation the residuum is destructively distilled to produce distillates of low metals content and leave behind a solid coke fraction that contains most of the metals. Coking is typically carried out in a reactor or drum operated at 427°C—593°C (800°F—1100°F) temperature and a pressure of 101—1010 kPa (1—10 atmospheres). The economic value of the coke byproduct is determined by its quality, particularly its sulfur and metals content. Excessively high levels of these contaminants make the coke useful only as low-valued fuel. In contrast, cokes of low metals content, for example up to about 100 ppm (parts per million by weight) of nickel and vanadium, and containing less than about 2 weight percent sulfur may be used in high-valued metallurgical, electrical, and mechanical applications.

Presently, catalytic cracking is generally accomplished by utilizing hydrocarbon chargestocks lighter than residual fractions which usually have an API gravity less than 20. Typical cracking chargestocks are coker and/or crude unit gas oils, vacuum tower overhead, and the like, the feedstock having an API gravity from 15 to 45. Since these cracking chargestocks are distillates, they do not contain significant proportions of the large molecules in which the metals are concentrated. Such cracking is commonly carried out in a reactor operated at a temperature of 427°C—816°C (800°F—1500°F), a pressure of 101—505 kPa (1—5 atmospheres), and a space velocity of 1—1000 WHSV.

The amount of metals present in a given hydrocarbon stream is often expressed as a chargestock’s “metals factor”. This factor is equal to the sum of the metals concentrations, in parts per million, of iron and vanadium plus ten times the concentration of nickel and copper in parts per million, and is expressed in equation form as follows:

\[ F_m = Fe + V + 10(Ni + Cu) \]

Conventionally, a chargestock having a metals factor of 2.5 or less is considered particularly suitable for catalytic cracking. Nonetheless, streams with a metals factor of 2.5—25, or even 2.5—50, may be used to blend with or as all of the feedstock to a catalytic cracker, since chargestocks with metals factors greater than 2.5 in some circumstances may be used to advantage, for instance with the newer fluid cracking techniques.

In any case, the residual fractions of typical crudes will require treatment to reduce the metals factor. As an example, a typical Kuwait crude, considered of average metals content, has a metals factor of 75 to 100. As almost all of the metals are combined with the residual fraction of a crude stock, it is clear that at least 80 percent of the metals and preferably at least 90 percent needs to be removed to produce fractions (having a metals factor of about 2.5—50) suitable for cracking chargestocks.

The economic and environmental factors relating to upgrading of petroleum residual oils and other heavy hydrocarbon feedstocks have encouraged efforts to provide improved processing technology, as exemplified by the disclosures of various U.S. Patents which include 3,696,027; 3,730,879; 3,775,303; 3,876,530; 3,882,049; 3,897,329; 3,905,983; 3,901,792; 3,964,955; 3,985,643; 4,016,067; U.S. Patent No. 2,958,573. U.S. Patent 2,958,573 describes a process in which a reduced crude is visbroken by heating in the presence of a finely powdered coke to produce gas oil, gasoline and a heavy cracked residuum, the residuum is coked to produce coke, gasoline and gas oil, the gas oil is solvent extracted to remove aromatics and the extracted gas oil and gas oil produced in visbreaking combined to form a cracking feedstock.

The present invention provides a process for converting a heavy hydrocarbon oil comprising the steps of:

1. Heating under visbreaking conditions a mixture of the heavy hydrocarbon oil and a particulate coal having an average particle size of less than 2000 μm;
2. Cooling the heat-treated mixture to a temperature between 204 and 370°C in a settling zone to provide an oil fraction and a fraction of asphaltene-flocculated fine solids; and
3. Separating and recovering the oil fraction and the solids fraction from the cooled mixture.

One or more objects of the present invention are accomplished by the provision of a process for heavy hydrocarbon oil demetallation which comprises (1) heating an admixture of heavy hydrocarbon oil and particulate coal under visbreaking conditions; (2) removing a light end fraction and then subjecting the visbroken admixture to solvent deasphalting to provide an oil fraction and a precipitated asphaltic solids fraction; and (3) distilling the said oil fraction to remove the deasphalting solvent and yield a demetallized liquid hydrocarbon product.

In a more particular embodiment, this invention provides a process for heavy hydrocarbon oil demetallation and coal liquefaction which com-
prises (1) heating an admixture of heavy hydrocarbon oil and particulate coal under visbreaking conditions; (2) removing a light end fraction and then subjecting the visbroken admixture to solvent deasphalting to provide an oil fraction and a precipitated asphaltic solids fraction; (3) distilling the said oil fraction to remove the deasphalting solvent and yield a demetallized liquid hydrocarbon product; and (4) treating the said asphaltic solids fraction under flotation conditions in an aqueous medium to separate a float phase of organic solids product from a sink phase of inorganic ash.

The term "heavy hydrocarbon oil" is meant to include petroleum oil residua and tar sand bitumen feedstocks, in which mixtures at least 75 weight percent of the constituents have a boiling point about 371°C (700°F).

Typically, a heavy hydrocarbon oil suitable for treatment in accordance with the present invention has a metals content of at least 80 ppm, and a Conradson Carbon Residue content of at least 10 weight percent.

The coal component of the invention process can be any of a variety of carbonaceous materials which include bituminous and sub-bituminous types of coal, lignite, peat, and the like. The nominal analysis of typical coals are as follows:

<table>
<thead>
<tr>
<th>Sub-Bituminous</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur</td>
<td>0.21%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.88</td>
</tr>
<tr>
<td>Oxygen</td>
<td>15.60</td>
</tr>
<tr>
<td>Carbon</td>
<td>65.53</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.70</td>
</tr>
<tr>
<td>Ash</td>
<td>3.99</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Lignite</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur</td>
<td>0.53%</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.74</td>
</tr>
<tr>
<td>Oxygen</td>
<td>32.04</td>
</tr>
<tr>
<td>Carbon</td>
<td>54.38</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>5.42</td>
</tr>
<tr>
<td>Ash</td>
<td>5.78</td>
</tr>
</tbody>
</table>

Ball mills or other types of conventional apparatus may be employed for crushing and pulverizing coarse coal in the preparation of the particular coal feed for the visbreaking step (1) of the process. The crushing and grinding of the coal can be accomplished either in a dry state or in the presence of a liquid such as the heavy hydrocarbon oil being employed in the practice of the invention process. The average particle size of the coal feed is preferably below .63 cm (0.25 inches), such as finely divided bituminous coal which has a particle size of less than 3 mesh (U.S. Sieve Series).

The oil and coal are slurried in a mixing zone and pumped through a visbreaking reaction zone. The weight ratio of heavy hydrocarbon oil to coal is in the range between 1.5—10:1.

The step (1) visbreaking heat treatment is conducted at a temperature between 427°C—510°C (800°F—950°F), and at a weight hourly space velocity between 1—100.

It is preferred that the visbreaking heat treatment is conducted under a hydrogen partial pressure between 345—13790 kPa (50—2000 psi). Addition of steam to the level of 0.1—5 weight percent of the combined charge stock is also advantageous.

Demetallation occurs at the incipient temperature of coking for the heavy hydrocarbon oil, i.e., a temperature above 427°C (800°F). The demetallation proceeds rapidly, particularly because the oil is in contact with solid particles. At 427°C (800°F) and above thermal conversion of the heavy hydrocarbon oil yields light distillates. Any coke which is coproduced effectively becomes incorporated in the surrounding matrix of coal and ash particles.

Simultaneously, coal depolymerization occurs with the production of gas and liquid constituents. The heavy hydrocarbon oil is a polycyclic aromatic hydrocarbon component which can function as a solvent to convert at least a portion of the coal to liquid constituents.

The visbreaker effluent is passed through a high pressure separator to vent the light end constituents. If hydrogen gas is present, the gas mixture is at least partially recycled to the visbreaking zone. Alternatively, the gas mixture can be fractionated to recover the hydrogen gas for recycle.

The degassed visbreaker effluent from step (1) is subjected to deasphalting fractionation with a light solvent. It is preferred that the deasphalting zone is a liquid-liquid countercurrent contacting system.

Suitable deasphalting solvents include liquefied normally gaseous hydrocarbons such as ethane, ethylene, propane, propylene, n-butane, isobutane, n-pentane, isobutylene, pentane, and isopentane; cyclohexane; hexane; heptane; decane; octane; nonane; decalin; and mixtures thereof. The yield of liquid products extracted in the deasphalting operation can be increased if a light C₆—C₁₆ aromatic solvent is employed, e.g., benzene, toluene, xylene, m-tolylene, naphthalene, and the like. In general, the deasphalting solvent of choice is a liquid hydrocarbon containing between 3—12 carbon atoms.

The weight ratio of deasphalting solvent to visbroken admixture in step (2) normally will be in the range between 0.5—5:1.

The deasphalting treatment in step (2) preferably is conducted at a temperature between 38°C—260°C (100°F—500°F) and at a sufficient
pressure to maintain the deasphalting solvent in liquid form, and for a period between 0.1—1.5 hours.

The liquid solvent extract phase and the precipitated asphaltic solids are withdrawn separately from the deasphalting zone. The solvent-oil effluent is charged to an atmospheric distillation tower to strip off the deasphalting solvent. The distillation bottom fraction is a demetallized liquid hydrocarbon product. The metals content of the liquid hydrocarbon product is less than about 50 ppm.

The quantity yield of the demetallized liquid hydrocarbon product on the average constitutes between 45—90 weight percent of the total weight of heavy hydrocarbon oil and coal (on a moisture/ash free basis—m.a.f.) fed into the processing system.

The precipitated asphaltic solids fraction which is recovered tends to be saturated with adsorbed solvent and oil. Preferably the asphaltic solids fraction is subjected to washing with light solvent or steam stripping to remove the adsorbed liquid and provide residual solids in a substantially dry form.

Preferably, the stripped asphaltic solids recovered in the manner described above are in the form of a fine powder. In some cases mechanical crushing may be required, depending on the nature of the coal and the processing conditions.

The powdered asphaltic solids are treated under flotation conditions in an aqueous medium to yield a float phase of organic solids product which has been separated from a sink phase of inorganic ash.

The flotation of the organic solids product is facilitated by air-frothing, particularly in combination with flotation aids such as ionic and nonionic surfactants, and the like.

The organic solids product on the average constitutes between 10—50 weight percent of the total weight of heavy hydrocarbon oil and coal (m.a.f.) fed into the processing system. The organic solids product usually contains between 5—30% of char and unreacted coal.

Illustrative of the invention process, the drawing is a schematic representation of visbreaking, deasphalting and flotation units in series for coprocessing of heavy hydrocarbon oil and coal, with recovery and recycle of deasphalting solvent to the deasphalting unit.

Referring to the drawing, coal is charged through line 10 and heavy hydrocarbon oil is charged through line 11 into Mixing Unit 15 where they are admixed to form a slurry.

The coal is a High Volatile A bituminous stock which has been ground to a particle size of about 50 mesh. The coal has the following elemental analysis:

- Sulfur 1.33%
- Nitrogen 1.63
- Oxygen 7.79
- Carbon 80.88
- Hydrogen 5.33
- Ash 2.77

The heavy hydrocarbon oil is an Arabian light vacuum residual fraction which has the following analysis:

- API, gravity 8.3
- H, wt, % 10.67
- S, wt % 3.93
- N, wt % 0.28
- CCR, wt % 16.13
- V, ppm 68
- Ni, ppm 17
- MW 810

The oil-coal slurry admixture is withdrawn from Mixing Unit 15 and pumped through a preheating unit and passed into Visbreaker Unit 20 via line 16. The weight ratio of oil to coal is about 2:1, and the weight hourly space velocity of the oil-coal is about 20.

Hydrogen is entered into Visbreaker Unit 20 through line 21 to provide a hydrogen partial pressure of 4137 kPa (600 psig) in the visbreaking zone at a temperature of 361°—456°C (625°—850°F).

The visbreaker effluent is passed through line 22 to High Pressure Separator 25, where a gaseous fraction is vented through line 26. A portion of the hydrogen-rich gas is recycled to Visbreaker Unit 20 via line 27.

The degassed visbreaker effluent is transferred through line 28 to the top section of Deasphalting Unit 30, where it flows downward in counter-current contact with heptane which is fed into Deasphalting Unit 30 through line 31.

The weight ratio of heptane to visbroken admixture in the deasphalting zone is maintained at about 3:1, with the temperature being at 149°C (300°F) and the pressure at 4137 kPa (600 psig). The liquid-liquid contact time in the deasphalting zone is about 10 minutes.

A liquid oil fraction of heptane-soluble hydrocarbon constituents exits to the top of Deasphalting Unit 30 and is passed through line 32 to Atmospheric Distillation Unit 35. Heptane is recovered from the distillation column and recycled via line 36 to Deasphalting Unit 30.

Demetallized liquid hydrocarbon product is withdrawn from the processing system via line 37. The liquid hydrocarbon product has a metals content of about 20 ppm, and a CCR weight percent of about 10. The yield of demetallized liquid hydrocarbon product constitutes about 65
weight percent of the total weight of heavy hydrocarbon oil and coal (m.a.f.) fed into the processing system.

Precipitated asphaltic solids are withdrawn from Deasphalting Unit 30 through line 33 and entered into Stripper Unit 40. The asphaltic solids contain small quantities of unreacted coal and inorganic ash.

Steam is fed into Stripper Unit 40 through line 41 to remove residual naphtha and oil from the asphaltic solids. The stripped liquid hydrocarbons are recycled through line 42 to Deasphalting Unit 30.

The stripped asphaltic solids are removed from Stripper Unit 40, mechanically crushed to a fine powder and transferred via line 43 to Flotation Unit 45.

Water is supplied to Flotation Unit 45 through line 46, and air is supplied through line 47. A small quantity of No. 2 oil is added to the aqueous medium in Flotation Unit 45 to facilitate the flotation of organic solids product.

An inorganic ash sink phase is withdrawn from Flotation Unit 45 through line 48 and discarded. An organic solids float phase is removed from the processing system via line 49. The organic solids product constitutes about 30 percent of the total weight percent of heavy hydrocarbon oil and coal (m.a.f.) fed into the processing system. The organic solids product contains less than 10 weight percent of char and unreacted coal.

In another of its embodiments, the present invention provides an improved process for heavy hydrocarbon oil conversion which comprises (1) heating an admixture of heavy hydrocarbon oil and particulate coal under visbreaking conditions, wherein the average particle size of the coal is less than about 2000 microns; (2) cooling the heat-treated admixture in a settling zone to a temperature in the range between 204°—570°C (400°—1050°F) to provide an oil fraction and a fraction of asphaltene flocculated fine solids; and (3) separating and recovering the oil fraction and the solids fraction.

In a typical operation, the heavy hydrocarbon oil feedstock is crude oil or a distillation residuum of crude oil (e.g., atmospheric or vacuum), the particular coal is bituminous coal, the average particle size of the coal is in the range between 20—2000 microns, and the weight ratio of heavy hydrocarbon oil to coal in the step (1) admixture is in the range between 1.5—20:1.

Preferably, the step (1) heat treatment is conducted at a temperature between 427°—510°C (800°—950°F) and a pressure between 0—13790 kPa (0—2000 psi), and at a weight hourly space velocity between 0.1—100.

It is particularly advantageous to conduct the step (1) heat treatment in the presence of a hydrogen partial pressure between 345—13790 kPa (50—2000 psi) to increase demetallation of the feedstock and to suppress formation of coke. The presence of hydrogen also functions to increase liquefaction of the particulate coal phase, with a resultant increase in the yield of liquid hydrocarbon product.

The hydrogen is employed as a component in the visbreaking zone, the heat-treated effluent is passed through a high pressure separator to vent the hydrogen and other light end constituents. The hydrogen gas is recovered and recycled in the process.

As a further variation, the step (1) heat treatment can be conducted in the presence of an inert gas to aid in the control of the flow dynamics of the system. Illustrative of inert gases are steam, helium, nitrogen, methane, ethane, propane, butane, and the like. An inert gas such as steam has the additional advantage of reducing the quantity of coke deposition.

With respect to step (2) of the process, in a typical operation the step (2) settling zone is maintained at a temperature between 232°—363°C (450°—650°F) and a pressure between 0—13790 kPa (0—2000 psi) for a period between 0.1—5 hours.

It is also advantageous to include a deasphalting solvent in the step (2) settling zone to promote the settling of asphaltene flocculated fine solids. Illustrative of suitable deasphalting solvents are those previously described liquid hydrocarbons containing between 3—12 carbon atoms.

An important aspect of the step (2) settling phase is the precipitation of asphaltene from the heat-treated effluent, and the concomitant asphaltene flocculation of the fine solids in the settling zone. The flocculation of fine solids serves to facilitate the step (3) separation and recovery of the oil fraction and solids fraction.

The said recovered oil fraction (i.e., the overflow stream) usually is sufficiently demetallized to qualify as chargestock to a hydrotreating unit for the production of low sulfur distillate product. Alternatively, the recovered oil fraction can be subjected to distillation to provide gas oil distillate and residual tar bottoms. The gas oil distillate is suitable as feed to a fluidized catalytic cracking unit, or as feed to a hydrotreating unit. The tar bottoms fraction can be employed directly as heavy residual fuel or it can be reserved as chargestock for the production of asphalt or coke.

The solids fraction (i.e., the underflow stream) recovered in step (3) of the process is constituted essentially of flocculated solids material, but normally will include asphaltenes and some adsorbed oil. The said solids fraction can be recycled to the step (1) heat-treating zone. The high temperature of the heat-treating zone functions to deflocculate the asphaltene flocculated solids. The said solids provide the particle surfaces required for metal and coke deposition. The presence of the particle surfaces has the advantage of both catalyzing and adsorbing metal deposition, and has the further advantage of adsorbing coke deposits which otherwise would collect in the tubes of a heating unit.

Alternatively, in another embodiment either a portion or all of the solids fraction recovered in step (3) of the process can be diverted from the
main train of the system and reserved for use as coal-oil solid fuel composition. The metals contents of the said coal-oil solid fuel composition may be sufficiently high to warrant metal recovery from the ash of the solid fuel after combustion.

In a further embodiment, either a portion or all of the solids fraction recovered in step (3) of the process can be diverted from the main train of the system and reserved as chargestock for other conversion procedures. For example, the said solids fraction can be extracted with a solvent (e.g., furfural) to yield an extract phase and a fine solids phase. The said solids can be employed as a solid fuel, or recycled to step (1) of the main process. The extract phase can be fractioned to recover the solvent, and to provide a residual asphaltic material.

The advantage of the above described invention process improvement are manifold. The control of fine solids particle size in the series of zones is a significant factor for purposes of optimization of the process results.

In the visbreaking zone, the coal particles are small enough to fluidize readily, while functioning as nuclei for coke deposition and as sites for demetallation residues.

The presence of the fluidized particulate coal permits a higher level of visbreaking severity in step (1), without coke plugging of the heater unit chambers and without destabilizing of the liquid hydrocarbon products. There is achieved a greater degree of viscosity reduction, boiling range lowering, and demetallation and desulfurization of the heavy oil feedstock.

In the settling zone of the process, the cooling of the heat-treated effluent causes precipitation of asphaltenes from the effluent medium, and the asphaltenes then contact the dispersed fine solids in the effluent medium and cause them to flocculate to a degree which depends on the temperature and the residence time of the solids in the settling zone. In step (3), the flocculated particles because of their increased size and weight can be separated more readily from the visbroken oil phase.

The main objectives of the process improve-

ment then are to maximize the yield of fuel range distillates, and to minimize the production of coke.

The yield of fuel range distillates is further enhanced by conversion products which derive from liquefaction of the coal solids, particularly in the presence of hydrogen gas.

The degree and kind of coal liquefaction can be controlled as desired by such parameters as temperature, residence time, and particle size and weight ratio of the coal component in the visbreaking zone of the process.

The following example is further illustrative of the present invention. The reactants and other specific ingredients are presented as being typical, and various modifications can be derived in view of the foregoing disclosure within the scope of the invention.

Example

This Example illustrates the visbreaking heat treatment of admixtures of a heavy hydrocarbon oil and particulate coal.

The heavy hydrocarbon oil is a vacuum residue, the qualities of which are set forth in Table I, and the coal is particulate Illinois No. 6 coal (particle size less than about 2000 microns). The visbreaker unit is a 9.5 cm O.D. x 30.5 cm (3/8 inch O.D. x one foot) stainless steel reactor equipped with feeding, heating, pressure control, gas sampling and product recovery means.

Tables I and II summarize the results of visbreaking heat treatment at 454°C (850°F), 2798 kPa (400 psig) and 12 LHSV, and Table III summarizes the results obtained when the heat treatment is conducted at 456°C (870°F), 2798 kPa (400 psig) and 12 LHSV.

The data in Tables I and II demonstrate the degree of metals removal from a heavy hydrocarbon oil achieved with a process in accordance with the present invention. The results in Table III indicate that heat treatment at a higher temperature [e.g., 456°C (870°F)] increases the metals removal from a high metals content hydrocarbon oil such as a vacuum residuum.
<table>
<thead>
<tr>
<th>TABLE I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal, % Wt.</td>
</tr>
<tr>
<td>Joliet Residue, % Wt</td>
</tr>
<tr>
<td>Properties</td>
</tr>
<tr>
<td>Gravity, °API, 60/60°F</td>
</tr>
<tr>
<td>Conradson Carbon Residue (CCR), % Wt</td>
</tr>
<tr>
<td>Asphaltene, % Wt</td>
</tr>
<tr>
<td>Viscosity, cS at,</td>
</tr>
<tr>
<td>54°C (130°F)</td>
</tr>
<tr>
<td>100°C (212°F)</td>
</tr>
<tr>
<td>Nickel, ppm*</td>
</tr>
<tr>
<td>Vanadium, ppm*</td>
</tr>
<tr>
<td>Ash, % Wt</td>
</tr>
<tr>
<td>Liquid Product</td>
</tr>
<tr>
<td>Gravity, °API, 60/60°F</td>
</tr>
<tr>
<td>CCR, % Wt</td>
</tr>
<tr>
<td>Asphaltene, % Wt</td>
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<tr>
<td>Viscosity, cS at,</td>
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<tr>
<td>54°C (130°F)</td>
</tr>
<tr>
<td>100°C (212°F)</td>
</tr>
<tr>
<td>Nickel, ppm</td>
</tr>
<tr>
<td>Vanadium, ppm</td>
</tr>
<tr>
<td>Solid Product</td>
</tr>
<tr>
<td>Nickel, ppm</td>
</tr>
<tr>
<td>Vanadium, ppm</td>
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</tbody>
</table>

*Calculated for the mixtures
TABLE II

<table>
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<tr>
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<th>0</th>
<th>5</th>
<th>10</th>
<th>20</th>
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<tbody>
<tr>
<td>Coal, % Wt</td>
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<td>95</td>
<td>90</td>
<td>80</td>
<td>70</td>
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<tr>
<td>Residue, Wt %</td>
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<tr>
<td>Yield, % Wt</td>
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<td>3.4</td>
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<td>Gas</td>
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<tr>
<td>Liquid</td>
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<td>96.1</td>
<td>92.5</td>
<td>86.6</td>
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<td>Solid</td>
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<tr>
<td>Total Coal Conversion, %</td>
<td>—</td>
<td>78</td>
<td>59</td>
<td>53</td>
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</tr>
<tr>
<td>% of Coal Solubilized</td>
<td>—</td>
<td>41</td>
<td>34</td>
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<td>34</td>
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<tr>
<td>% of Coal Converted to Gas</td>
<td>—</td>
<td>37</td>
<td>25</td>
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<tr>
<td>% Demetallation Nickel</td>
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<td>21</td>
<td>36</td>
<td>40</td>
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<tr>
<td>Vanadium</td>
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<td>26</td>
<td>40</td>
<td>46</td>
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TABLE III

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<tr>
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</thead>
<tbody>
<tr>
<td>Coal, % Wt</td>
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<td></td>
</tr>
<tr>
<td>Residue, % Wt</td>
<td>80</td>
<td>70</td>
</tr>
<tr>
<td>Liquid Product</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gravity, *API</td>
<td>5.7</td>
<td>5.7</td>
</tr>
<tr>
<td>Asphaltene, % Wt</td>
<td>—</td>
<td>17</td>
</tr>
<tr>
<td>CCR, % Wt</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>Nickel, ppm (%)*</td>
<td>29(45)</td>
<td>25(53)</td>
</tr>
<tr>
<td>Vanadium, ppm</td>
<td>120(52)</td>
<td>67(73)</td>
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<tr>
<td>Solid Product</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel, ppm</td>
<td>—</td>
<td>110</td>
</tr>
<tr>
<td>Vanadium, ppm</td>
<td>—</td>
<td>360</td>
</tr>
</tbody>
</table>

*Data in parentheses represent extent of demetallation of processed Joliet vacuum residue.

Claims

1. A process for converting a heavy hydrocarbon oil comprising the steps of (1) heating under visbreaking conditions a mixture of the heavy hydrocarbon oil and a particulate coal having an average particle size of less than 200 μm; (2) cooling the heat-treated mixture to a temperature between 204 and 370°C in a settling zone to provide an oil fraction and a fraction of asphaltene-flocculated fine solids; and (3) separating and recovering the oil fraction and the solids fraction from the cooled mixture.

2. A process in accordance with claim 1 wherein the heavy hydrocarbon oil feedstock is a crude oil or a distillation residuum of crude oil.

3. A process in accordance with claim 1 or 2 wherein the particulate coal has a particle size of at least 20 micrometer and less than 2000 micrometer.

4. A process in accordance with any preceding claim wherein the particulate coal is bituminous coal.

5. A process in accordance with any preceding claim wherein the weight ratio of heavy hydrocarbon oil to coal in the step (1) admixture is in the range between 1.5—20:1.

6. A process in accordance with any preceding claim wherein the step (1) heat treatment is
conducted at a temperature between 427°C—510°C (800°F—950°F) and a pressure between 0—13790 kPa (0—2000 psig), and at a weight hourly space velocity between 0.1—100.

7. A process in accordance with any preceding claim wherein the step (1) heat treatment is conducted in the presence of a hydrogen partial pressure between 345—13790 kPa (50—2000 psig).

8. A process in accordance with any of claims 1 through 6 wherein the step (1) heat treatment is conducted in the presence of an inert gas.

9. A process in accordance with claim 8 wherein the inert gas is steam of a light hydrocarbon.

10. A process in accordance with any preceding claim wherein the step (2) settling zone is maintained at a temperature between 232°C—363°C (450°F—640°F) and a pressure between 0—13790 kPa (0—2000 psig) for a period of 0.1—5 hours.

11. A process in accordance with any preceding claim wherein the step (2) settling of asphaltene flocculated fine solids is promoted by the addition of a deasphalting solvent.

12. A process in accordance with claim 11 wherein the deasphalting solvent is liquid hydrocarbon containing between 9—12 carbon atoms.

13. A process in accordance with any preceding claim wherein the oil fraction recovered in step (3) is charged to a hydrotreating zone for production of low sulfur distillates.

14. A process in accordance with any of claims 1 through 12 wherein the oil fraction recovered in step (3) is subjected to distillation to provide gas oil distillate and tar bottoms.

15. A process in accordance with any of claims 1 through 12 wherein at least a portion of the solids fraction recovered in step (3) is recycled to the step (1) visbreaking zone.

16. A process in accordance with any of claims 1 through 12 wherein at least a portion of the solids fraction recovered in step (3) is combusted as solid fuel, and the metals content of the resultant ash is recovered.

Patentansprüche

1. Verfahren zur Umwandlung eines schweren Kohlenwasserstofföls mit den Schritten des

(1) Erhitzen unter Visbreaking-Bedingungen einer Mischung des schweren Kohlenwasserstofföls und eine teihlenförmigen Kohle mit einer mittleren Teilchengröße von weniger als 200 μm;

(2) Abkühlen der wärmebehandelten Mischung auf eine Temperatur zwischen 204 und 370°C in einer Absetzzone unter Ausbildung einer Öffraktion und einer Fraktion von ausgeflockten Asphaltene-Feinststoffen; und

(3) Abruhen und Gewinnen der Öffraktion und der Feststofffraktion aus der abgebühlten Mischung.

2. Verfahren nach Anspruch 1, bei dem das Einsatzprodukt aus dem schweren Kohlenwasserstofföl ein Rohöl oder ein Destillationsrückstand von Rohöl ist.

3. Verfahren nach Anspruch 1 oder 2, bei dem die teihlenförmige Kohle eine Teilchengröße von wenigstens 20 μm und weniger als 2000 μm aufweist.

4. Verfahren nach irgendeinem vorausgehenden Anspruch, bei dem die teihlenförmige Kohle bituminöse Steinkohle ist.


6. Verfahren nach irgendeinem vorausgehenden anspruch, bei dem die Wärmebehandlung in Stufe (1) bei einer Temperatur zwischen 427°C bis 510°C (800 bis 950°F) und einem Druck zwischen 0 bis 13790 kPa (0 bis 2000 psig) sowie bei einer stündlichen Gewichts-Raumgeschwindigkeit zwischen 0,1 und 100 durchgeführt wird.

7. Verfahren nach irgendeinem vorausgehenden Anspruch, bei dem die Wärmebehandlung in Stufe (1) in Gegenwart eines Wasserstoff-Partialdrucks zwischen 345 bis 13790 kPa (50 bis 2000 psig) durchgeführt wird.

8. Verfahren nach irgendeinem der Ansprüche 1 bis 6, bei dem die Wärmebehandlung in Stufe (1) in Gegenwart eines Inertgases durchgeführt wird.

9. Verfahren nach Anspruch 8, bei dem das Inertgas Dampf oder ein leichter Kohlenwasserstoff ist.

10. Verfahren nach irgendeinem vorausgehenden Anspruch, bei dem in der Absetzzone in Stufe (2) eine Temperatur zwischen 232 bis 363°C (450 bis 640°F) und ein Druck zwischen 0 bis 13790 kPa (0 bis 2000 psig) für einen Zeitraum zwischen 0 bis 5 Stunden aufrechterhalten werden.


13. Verfahren nach irgendeinem vorausgehenden Anspruch, bei dem die in Stufe (3) gewonnene Ölfraktion einer Hydoraffinations-Zone zur Herstellung von schweifelarmem Destillat zugeführt wird.

14. Verfahren nach irgendeinem der Ansprüche 1 bis 12, bei dem die in Stufe (3) gewonnene Ölfraktion einer Destillation unterworfen wird, um ein Gasöl-Destillat und Teerrückstände zu gewinnen.

15. Verfahren nach irgendeinem der Ansprüche 1 bis 12, bei dem wenigstens ein Teil der in Stufe (3) gewonnenen Feststofffraktion in die Visbreaking-Zone von Stufe (1) zurückgeführt wird.

Recommandations

1 Un procédé pour convertir un huile hydrocarbonée lourde comprenant les étapes suivantes:
  (1) on chauffe dans des conditions de réduction de viscosité un mélange de l’huile hydrocarbonée lourde et d’un charbon en particules ayant une dimension moyenne de particules de moins de 200 µm;
  (2) on refroidit le mélange traité à chaud à une température comprise entre 204 et 370°C dans une zone de décantation pour donner une fraction d’huile et une fraction de solides fins flouçés par les asphaltenes; et
  (3) on sépare et on récupère la fraction d’huile et la fraction de solides du mélange refroidi.

2. Un procédé selon la recommandation 1, dans lequel la charge d’alimentation d’huile hydrocarbonée lourde est un pétrole brut ou un résidu de distillation de pétrole brut.

3. Un procédé selon la recommandation 1 ou 2, dans lequel le charbon en particules a une dimension de particules d’au moins 20 µm et de moins de 2000 µm.

4. Un procédé selon l’une quelconque des recommandations précédentes, dans lequel le charbon en particules est un charbon bitumineux.

5. Un procédé selon l’une quelconque des recommandations précédentes, dans lequel le rapport pondéral de l’huile hydrocarbonée lourde au charbon dans le mélange de l’étape (1) est compris dans la gamme de 1,5–20 : 1.

6. Un procédé selon l’une quelconque des recommandations précédentes, dans lequel le traitement thermique de l’étape (1) est conduit à une température comprise entre 427 et 510°C (800–950°F) et sous une pression comprise entre 0 et 13790 kPa (0–200 psig), et à une vitesse spatiale horaire en poids comprise entre 0,1 et 100.

7. Un procédé selon l’une quelconque des recommandations précédentes, dans lequel le traitement thermique de l’étape (1) est conduit en présence d’une pression partielle d’hydrogène entre 345 et 13790 kPa (50–200 psig).

8. Un procédé selon l’une quelconque des recommandations 1 à 6, dans lequel le traitement thermique de l’étape (1) est conduit en présence d’un gaz inerte.

9. Un procédé selon la recommandation 8, dans lequel le gaz inerte est la vapeur d’eau ou un hydrocarbure léger.

10. Un procédé selon l’une quelconque des recommandations précédentes, dans lequel la zone de décantation de l’étape (2) est maintenue à une température comprise entre 232 et 363°C (450–640°F) et sous une pression comprise entre 0 et 13790 kPa (0–200 psig) pendant une durée comprise entre 0,1 et 5 heures.

11. Un procédé selon l’une quelconque des recommandations précédentes, dans lequel la décantation des solides fins flouçés par les asphaltenes dans l’étape (2) est provoquée par l’addition d’un solvant de désasphaltage.

12. Un procédé selon la recommandation 11, dans lequel le solvant de désasphaltage est un hydrocarbure liquide contenant entre 3 et 12 atomes de carbone.

13. Un procédé selon l’une quelconque des recommandations précédentes, dans lequel la fraction d’huile récupérée dans l’étape (3) est chargée dans une zone d’hydrotraitement pour la production de distillats à faible teneur en soufre.

14. Un procédé selon l’une quelconque des recommandations 1 à 12, dans lequel la fraction d’huile récupérée dans l’étape (3) est soumise à la distillation pour donner un distillat de gas-oil et des résidus goudronneux.

15. Un procédé selon l’une quelconque des recommandations 1 à 12, dans lequel une portion au moins de la fraction de solides récupérée dans l’étape (3) est recyclée à la zone de réduction de viscosité dans l’étape (1).

16. Un procédé selon l’une quelconque des recommandations 1 à 12, dans lequel une portion au moins de la fraction de solides récupérée dans l’étape (3) est brûlée comme combustible solide, et les métaux contenus dans la cendre résultante sont récupérés.