PROCESS FOR THE DEMETALLIZATION OF PETROLEUM RESIDUUMS

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CRUDE OIL

DISTILLATION TOWER

RESIDUUM

FLASH DRUM

DEASPHALTING TOWER

LOW METALS OIL

INTERMEDIATE METALS OIL

HIGH METALS ASPHALT

INTERMEDIATE OIL

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PROCESS FOR THE DEMETALLIZATION OF PETROLEUM RESIDUUMS

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5 Claims:

ABSTRACT OF THE DISCLOSURE

A process for the demetalization of a petroleum residuum fraction wherein the asphalt is contacted with a polar solvent at a (CT+P) of 5—50° F. above the critical temperature of the solvent and a (CP+P) pressure of 300—1000 p.s.i.g. above the critical pressure of the solvent.

5 Petroleum residuum fractions are demetalized in a multistage separation process comprising conventional deasphalting followed by additional separation with a polar solvent at supercritical conditions.

It is well known that organometallic compounds in petroleum fractions tend to poison petroleum refining catalysts employed in continuous operations. It is also well known that it is desirable to avoid high metal contents in fuel oils because metals cause corrosion and other problems when fuels are burned in industrial furnaces.

Certain petroleum residuum fractions have a metals content of over about 200 p.p.m. Conventional propane deasphalting can be used to separate an extract fraction containing about 5—100 p.p.m. metals which is a suitable material for treatment and conversion in the presence of catalysts. However, propane deasphalting is limited in that it will extract only about 40—60% of a petroleum residuum and the bottoms fraction amounting to about half of the residuum is unsuitable for use except as heavy fuel oil.

The object of the process of this invention is to provide an additional quantity of oil having an intermediate quantity of metals that can be used in a number of ways which will be described below.

Briefly summarizing, the process comprises the steps of subjecting a residuum to conventional deasphalting, passing the asphalt to a supercritical separation unit, contacting the asphalt with a polar solvent at supercritical conditions and recovering demetalized fractions.

Further details of the invention will be disclosed with reference to the drawing which discloses a preferred embodiment of the invention.

Referring to the drawing, a petroleum crude oil is fed by line 1 to distillation tower 2. The most appropriate crude oils for treatment in the process of the invention are those which contain relatively large amounts of sulfur compounds, organometallic compounds, and high molecular weight coke forming hydrocarbons. A number of Latin American crude oils have these characteristics. Distillation in tower 2 can be operated at atmospheric pressure or under a vacuum. For simplicity the drawing shows a single overhead fraction recovered by line 3.

Any number of fractions can be recovered from the distillation zone for further refining. A bottoms fraction or petroleum residuum having an initial boiling point in the range of 500—1000° F. is removed by line 4 and passed to a conventional deasphalting tower 5. If desired, the distillation bottoms can be blended with other heavy fractions derived from petroleum refining operations. Generally speaking, from 30—90% of the material in line 4 boils above 900° F. The material will have a gravity of 5—25° API, a sulfur content of 1—8 wt. percent, a Conradson carbon of 5—25 wt. percent and a metals content of 100—2000 p.p.m. The metals include vanadium, nickel, copper, iron and others.

Deasphalting is carried out in the conventional manner employing a non-polar light aliphatic hydrocarbon solvent containing 3 to 8 carbon atoms in the molecule. Specifically, propane, butane, pentane, hexane or mixtures thereof are used. When propane is used as the solvent, conditions in tower 5 include a temperature in the range of 120 to 195° F., a pressure in the range of 500 to 900 p.s.i.g. and a solvent to oil ratio of 0.5 to 8.0. Deasphalted oil and solvent are passed overhead by line 6, cooled in cooler 7 and fed into flash drum 8. Propane is flashed overhead and recycled via line 9, cooler 10 and pump 11 to tower 5. A low metals oil containing less than about 100 p.p.m. metals, preferably less than about 50 p.p.m. metals, is recovered by line 12. This oil may be subjected to catalytic hydrodesulfurization since the metals content is now below the quantity of metals which causes rapid poisoning of hydrodesulfurization catalysts such as cobalt molybdate on alumina.

The bottoms or raffinate from the deasphalter is passed by line 13 containing pump 14 to supercritical separation unit (SCS Unit) 15.

In supercritical separation, the separation of the fraction(s) is primarily by molecular weight of the components and this is similar to distillation. In addition some influences of compound type are evident resulting in separation effects like those of solvent extraction.

A requirement of supercritical separation is that at least two phases must be formed by the solvent-feed mixture. If the properties of the feed are too similar to those of the solvent, the mutual solubility of the two will be so great that the formation of two phases will be impossible. Generally, it is preferred that the initial boiling point of the feed should be about 200° F. above the critical temperature of the solvent.

The mode of operation of supercritical separation and the processing equipment used are similar to those used in solvent extraction. In one embodiment, the solvent or carrier gas is mixed with the fraction or oil-solid slurry to be separated at supercritical conditions and two fluid phases are formed. In a preferred embodiment shown in the drawings of this disclosure the feed and solvent are passed through a countercurrent contacting tower at supercritical conditions. This unit may be either single stage or multistage. A light oil phase containing an intermediate quantity of metals is recovered overhead and a high metals asphalt phase is recovered as bottoms. The solvent is recovered from the separated fractions and recycled. The tower can have shed trays, rotating disc mixers, disc and donut trays, or the like as internals. In multistage
Referring to the drawing, dimethyl ether solvent is passed by line 16 into tower 15. A light extract phase comprising oil having an intermediate metals content of about 100-500 p.p.m. and solvent is recovered overhead by line 17. The light phase is passed through heater 16 into flash drum 19. The solvent is flashed overhead into line 16. The solvent is cooled in cooler 29 and repressed by pump 21 for recycle to the SCS Unit. Make-up solvent is added by line 22. The intermediate metals oil is recovered by line 23. In a preferred embodiment a portion of the oil in line 23 is pumped via line 24 and pump 25 as reflux to the SCS Unit. In another preferred embodiment a portion of the oil is recycled by lines 23 and 26 to the inlet line 4 of the desalting tower for further treatment. Another portion of the oil, i.e. 25-90% is recovered from the process by line 27. This oil is a suitable fuel oil. High metals asphalt is recovered by line 28.

When the process of the invention is applied to typical Latin American feeds the following exemplary results will be obtained.

Table III shows that only 10% of the crude oil is rejected as high metals asphalt. Supercritical separation thus provides an additional 15-20% oil which can be blended with low metals oil, recycled to desalting for further metals reduction, or refined in suitable processes such as slurry hydrosulfurization, coking, etc.

What is claimed is:
1. A process for the demetalization of a petroleum residuum fraction comprising the steps of
   (a) Contacting the residuum with a non-polar solvent at desalting conditions,
   (b) Recovering a low metals desalting oil extract,
   (c) Contacting the asphalt with a polar solvent collected from the group consisting of ammonia, mono-methyl amine, dimethyl amine, nitrous oxide, sulfur dioxide, methyl chloride, dimethyl ether, methyl alcohol, formaldehyde, acetone, HCl, HBr and mixtures thereof at supercritical conditions in which the initial boiling point of the feed is about 200°F above the critical temperature of the polar solvent, and the pressure is above the critical pressure of the polar solvent,
   (d) Recovering an intermediate metals extract of low metals content, and
   (e) Recovering a high metals asphalt.
2. A process according to claim 1 in which said residuum fraction contains at least 100 p.p.m. metals.
3. A process for the demetalization of a petroleum residuum fraction containing at least 100 p.p.m. metals comprising the steps of
   (a) Countercurrently contacting said feed in a desalting zone with a process solvent at a temperature in the range of 120 to 195°F, and
   (b) Recovering an extract phase containing less than about 50 p.p.m. metals,
(c) Countercurrently contacting the raffinate from step 1 in a supercritical contacting zone with a polar solvent selected from the group consisting of ammonia, monomethyl amine, dimethyl amine, nitrous oxide, sulfur dioxide, methyl chloride, dimethyl ether, methyl alcohol, formaldehyde, acetone, HCl, HBr and mixtures thereof at a (CT+) temperature of 5–50° F. above the critical temperature and a (CP+) pressure of 300–1000 p.s.i.g. above the critical pressure,

(d) Recovering an extract oil containing less than 500 p.p.m. metals, and

(e) Blending the extract phases of steps 2 and 4.

4. Process according to claim 3 in which the polar solvent is dimethyl ether.

5. Process according to claim 3 in which the polar solvent is dimethyl amine.