

[54]	TREATMENT OF HEAVY PETROLEUM OILS	2,825,678	3/1958	Jahnig et al.....	208/187
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[57]

ABSTRACT

Metal and asphaltene-containing heavy petroleum oils are subjected to high temperature steam treatment and then contacted with a deasphalting solvent. The product is particularly suited for further catalytic treatment.

12 Claims, No Drawings

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[57] ABSTRACT

Metal and asphaltene-containing heavy petroleum oils are subjected to high temperature steam treatment and then contacted with a deasphalting solvent. The product is particularly suited for further catalytic treatment.

12 Claims, No Drawings

TREATMENT OF HEAVY PETROLEUM OILS

This invention is concerned with the treatment of heavy petroleum oils. More particularly it is concerned with the removal of contaminants from residue-containing oils. In one of its more specific aspects it is concerned with the removal of metals and asphaltenes from heavy hydrocarbon oils.

In the refining of petroleum it is conventional to distill a crude oil to remove valuable lighter boiling fractions such as naphtha, kerosine and light and heavy gas oils. The still residue is a heavy oil containing higher boiling hydrocarbons and is contaminated with asphaltenes and compounds containing sulfur, nitrogen and metals which make such an oil undesirable as a fuel. In order to remove the sulfur or nitrogen or to convert the heavy residue into lighter more valuable products, the oil is ordinarily subjected to a catalytic treatment. This is conventionally done by contacting the oil at elevated temperature with a particulate catalyst. Unfortunately, unlike distillate stocks which are substantially free from asphaltenes and metals, the presence of asphaltenes and metal-containing compounds in the heavy oil leads to a relatively rapid reduction in the activity of the catalyst to below a practical level. The presence of these materials in the charge stock results in the deposition of metal-containing coke on the catalyst particles which prevents the charge from coming in contact with the catalyst and thereby in effect, reduces the catalyst activity. Eventually, the on-stream period must be interrupted and the catalyst regenerated.

Regeneration of the catalyst is accomplished by sweeping the reaction zone with an inert gas to remove combustible vapors and then introducing an oxygen-containing gas under carefully controlled conditions to oxidize the deposited carbon or coke without subjecting the catalyst to extremely high temperatures. This treatment results in the removal of the carbon deposit from the surface of the catalyst, and the on-stream period may be resumed with a catalyst of restored activity. However, the metals deposited on the catalyst are not removed by the combustion and gradually the metal buildup on the catalyst is sufficient to deactivate the catalyst to an unsatisfactory level. When this stage is reached the catalyst activity cannot be restored by ordinary methods and it becomes necessary to remove the catalyst from the reaction zone and replace it with fresh catalyst.

It is therefore an object of this invention to remove asphaltenes and metal containing compounds from heavy petroleum oils. Another object is to convert heavy petroleum oils into more valuable products such as fuel oils or oils suitable as charge stocks for catalytic processes. Another object is to prolong the on-stream periods of catalytic treatment of heavy petroleum oils. These and other objects will be obvious to those skilled in the art from the following disclosure.

According to our invention, a process is provided for the removal of asphaltene contaminants from heavy petroleum fractions containing same which comprises forming a dispersion of said fraction with H_2O at a temperature between $750^\circ F.$ and $850^\circ F.$ cooling the reaction product and contacting the H_2O treated fraction with a member of the group consisting of low molecular weight paraffins containing 3-10 carbon atoms, N-methyl-2-pyrrolidone and furfural.

The charge stocks used in the process of this invention are residue-containing oils such as crude petroleum oils, atmospheric residua, vacuum residua, shale oil, tar sand oil and the like, of which asphaltenes and metal-containing compounds comprise a significant portion.

The charge stock is contacted with water at a temperature of at least $750^\circ F.$ preferably 750° to $850^\circ F.$ since, above about $850^\circ F.$ undesirable coke formation takes place. The pressure may be atmospheric or super atmospheric, for example up to about 1,000 psig. The oil and water (steam) are passed through a zone wherein they come into intimate contact to form an oil-steam dispersion. The reaction zone may be either in the form of an elongated tubular zone through which the reactants are passed under conditions of turbulent flow or it may be in the form of a vessel filled with an inert packing such as glass beads or Berl saddles. The reaction mixture is heated to a temperature above $750^\circ F.$ and maintained at that temperature for at least about $\frac{1}{2}$ hour preferably from 1-2 hours so that upon cooling a stable water-asphaltene emulsion is formed. The entire effluent may be subjected to further treatment or the emulsion, which has a grease-like consistency, may be separated from the treated oil by filtration, sedimentation or decantation and the treated oil may then be subjected to stripping to remove residual traces of water. If desired the emulsion may be dried and metals recovered therefrom.

It is important that the H_2O treatment of the oil be effected at a temperature between 750° and $850^\circ F.$ under conditions that a dispersion is formed. The dispersion permits intimate contact of the H_2O and the oil and a temperature of at least $750^\circ F.$ is necessary as, if the treatment takes place below that temperature, the formation of a stable water-asphaltene emulsion does not take place on condensation of the steam.

Pressure in the H_2O treating zone may range between atmospheric and about 1000 psig, a preferred range being atmospheric to 200 psig. The hydrocarbon oil feed may be introduced into the reactor at a rate of 0.5-5.0 volumes of oil per volume of reactor space per hour, preferably 0.5-3.0 v/v/hr. The liquid hourly space velocity of the water should range between 0.1 and 5.0 v/v/hr. preferably 0.2-3.0 v/v/hr.

After cooling the treated oil is subjected to contact with a low molecular weight paraffin containing from 3 to 10 carbon atoms, preferably 3-8 carbon atoms as for example propane or isobutane or with N-methyl-2-pyrrolidone or furfural for the removal of residual asphaltenes. This treatment may be effected in the presence or absence of the water-asphaltene emulsion.

The deasphalting treatment preferably is effected at a temperature between $150^\circ F.$ and $300^\circ F.$ although temperature of $50^\circ F.$ to $400^\circ F.$ may be used. Pressures of from atmospheric to 400 psig may be used, pressures of from 0 to 50 psig being preferred. The solvent, that is the low molecular weight paraffin, N-methyl-2-pyrrolidone or furfural may be used at a solvent to oil ratio of from 0.5 to 10 liquid volumes of solvent per volume of oil, a preferred ratio being from 1.0 to 3.0.

When the deasphalting treatment is carried out after removal of the stable water-asphaltene emulsion, the solvent-oil layer is separated from an asphaltic layer and the solvent is removed from the oil by distillation therefrom. When the deasphalting treatment is carried out on the cooled treated oil in the presence of the wa-

ter-asphaltene emulsion, three layers are formed on settling, a solvent-oil layer, a water layer and an asphaltic layer. As in the case of deasphalting after separation of the water-asphaltene emulsion, the solvent may be removed from the oil by distillation therefrom and recycled to the deasphalting zone. The water may be recycled for admixture with additional fresh feed. If desired, the asphaltic residue may be treated for the recovery of metals therefrom.

The following examples are given for illustrative purposes only.

EXAMPLE I

In this example the feed is an Arabian Atmospheric Reduced Crude having the following characteristics:

TABLE 1

Gravity, °API	13.4
Sulfur, wt. %	3.2
Carbon Residue, wt. %	10.17
Asphaltenes, wt. %	3.22
Nickel, p.p.m.	<5
Vanadium, p.p.m.	25

In Run A, the charge is treated with H₂O in a reactor packed with berl saddles and the treated oil is contacted with n-pentane in the presence of the water-asphaltene emulsion. In Run B, the charge is not subjected to any treatment prior to deasphalting with n-pentane. Data on the runs appear below:

TABLE 2

Run	A	B
Temperature, °F.	800	—
Pressure, psig	0	—
Oil rate, v/v/hr	1.0	—
Water rate, v/v/hr	0.33	—
Liquid yield, wt. % charge	100	—
Deasphalting conditions		
Temperature, °F.	70	70
n-C ₅ /oil ratio	10	10
Yields, Liquid wt. %	87.5	89.4
Solid, wt. %	8.4	9.2
Deasphalted Product Liquid		
Sulfur, wt. %	3.02	3.07
Carbon Residue, wt. %	5.90	6.64
Nickel, ppm	<3	<5
Vanadium, ppm	<5	10
Deasphalted Product Solid		
Sulfur, wt. %	6.33	5.55
Nickel, ppm	89	62
Vanadium, ppm	354	302

The above results show that the high temperature treatment makes the oil more susceptible to improvement than the untreated oil.

EXAMPLE II

The charge in this example is a Lago Medio Atmospheric Reduced Crude having the following characteristics:

TABLE 3

Gravity, °API	19.9
Sulfur, wt. %	2.0
Carbon Residue, wt. %	6.89
Asphaltenes, wt. %	2.94
Nickel, ppm	20
Vanadium, ppm	215

Run C follows the procedure of Run A of Example I. In Run D, the stable water-asphaltene emulsion is separated from the treated oil by filtration prior to deasphalting. Run E is a substantial duplicate of Run B of Example I. Data on the runs appear below:

TABLE 4

Run	C	D	E
Temperature, °F.	800	800	—
Pressure, psig	0	0	—
Oil rate, v/v/hr	1.0	1.0	—
Water rate, v/v/hr	0.33	0.33	—
Yield, wt. % chg			
Oil	100.0	94.7	—
Solid	0	5.3	—
Water treated liquid			
Sulfur, wt. %	—	1.94	—
Carbon residue, wt. %	—	6.55	—
Nickel, ppm	—	14	—
Vanadium, ppm	—	170	—
Water treated solid			
Nickel, ppm	—	118	—
Vanadium, ppm	—	807	—
Deasphalting Conditions			
Temperature, °F.	70	70	70
n-C ₅ /oil ratio	10	10	10
Yields, liquid wt. %	74.0	89.0	89.9
solid, wt. %	9.2	6.8	6.0
Liquid			
Sulfur, wt. %	1.83	1.75	1.82
Carbon residue, wt. %	3.46	3.53	5.03
Nickel, ppm	<5	<5	7
Vanadium, ppm	41	35	101
Solid			
Sulfur, wt. %	3.5	4.4	4.2
Nickel, ppm	127	179	199
Vanadium, ppm	1420	2060	2140

These results show that the process of Run C may be used to reduce the metal content of the oil significantly. Run D shows that a slightly larger amount of metals can be removed if the water-asphaltene emulsion is separated from the treated oil e.g. by filtration prior to solvent deasphalting.

The product oil may be used directly as a fuel or may be subjected to further catalytic treatment for conversion into more valuable products.

One method of converting the oil into more valuable products is by catalytic cracking whereby the oil is contacted with a particulate catalyst in a fluidized system as for example in the apparatus disclosed in U. S. Pat. No. 3,433,733.

Another method for converting the oil is by contacting the oil with hydrogen in the presence of a catalyst. The hydro-catalytic treatment of the treated oil, which may for example be either a hydro-desulfurization or a hydrocracking, is carried out by contacting the treated oil in the presence of added hydrogen having a purity of about 60–95 percent with a catalyst at elevated temperature and pressure. Reaction conditions include temperatures between about 500° and 900° F. and pressures between about 300 and 3,000 psig. Preferred temperatures are from about 650° to 850° F. and preferred pressures range from about 500 to 1500 psig. The oil may be passed through the reaction zone at a space velocity between about 0.2 and 5.0 volumes of oil per volume of catalyst per hour, preferably between about 0.5 and 2 v/v/hr. with a hydrogen rate of between about 500 and 10,000 standard cubic feet per barrel of oil preferably between about 750 and 5000 SCFB.

The catalyst may be used as a slurry or in the form of a fixed bed, a fluidized bed or a moving bed and the reactant stream may be passed upwardly or downwardly through the reaction zone. Preferably the catalyst is in the form of a fixed bed of pellets, and the reactant stream is passed downwardly through the catalyst bed.

The hydroconversion catalyst generally will comprise a group VIB metal and a group VIII metal usually as the oxide on a support. When the principal hydroconver-

sion reaction is desulfurization or denitrogenation the catalyst support comprises a refractory inorganic oxide such as alumina, magnesia, or zirconia or mixtures thereof. Small, e.g., less than 10 percent, stabilizing amounts of silica may be present. If the principal hydroconversion reaction is hydrocracking the base or support will have cracking activity. Suitable supports comprise silica and alumina mixtures containing at least about 50 percent silica. The hydrocracking catalyst may also contain a modified zeolite such as fau-
 5 site or zeolite Y which has been subjected to a decationization treatment for the removal of alkali metal ion and the introduction into the zeolite structure of hydrogen ion. Advantageously the alkali metal is removed by subjecting the zeolite to ion exchange with a solution of an ammonium compound followed by heating to dry and then calcination. The calcined zeolite is subjected to a second ion exchange with a solution of an ammonium compound and then dried. This treatment results in a zeolite having an alkali metal
 10 content of less than about 1 percent by weight.

The hydroconversion catalyst should contain between about 2 and 10 percent by weight of the group VIB metal and between about 5 and 40 percent by weight of the group VIII metal. Suitable combinations are nickel and molybdenum, nickel and tungsten and cobalt and molybdenum. A particularly suitable catalyst for the hydrocracking of a treated oil which contains more than 100 parts per million nitrogen comprises 3 to 8 percent nickel, 15 to 30 percent tungsten on a support comprising 20 to 25 percent decationized zeolite Y, 50 to 75 percent silica and 5 to 20 percent alumina. Advantageously, the catalyst is sulfided prior to use.

Other modifications and variations of the above invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for the removal of asphaltene contami-

nants from a heavy petroleum fraction containing same which comprises forming a dispersion of said fraction with H₂O at a temperature between 750° F. and 850° F., cooling the product to form an H₂O-treated heavy petroleum fraction of reduced asphaltene content and a stable water-asphaltene emulsion and contacting the H₂O treated fraction with a solvent selected from the group consisting of low molecular weight paraffins containing 3-10 carbon atoms, N-methyl-2-pyrrolidone and furfural.

2. The process of claim 1 in which contact of the treated fraction with the solvent is effected at a temperature between 50° F. and 400° F.

3. The process of claim 1 in which the stable water-asphaltene emulsion is formed on cooling said product to a temperature below 400° F.

4. The process of claim 3 in which the solvent contacting is effected in the presence of said emulsion.

5. The process of claim 3 in which the emulsion is removed prior to contacting the H₂O treated fraction with solvent.

6. The process of claim 1 in which the solvent is N-methyl-2-pyrrolidone.

7. The process of claim 1 in which the solvent is a low molecular weight paraffin containing 3-10 carbon atoms.

8. The process of claim 1 in which the solvent desasphalted oil is subjected to catalytic treatment at a temperature between 700° F. and 950° F.

9. The process of claim 8 in which the catalytic treatment is cracking.

10. The process of claim 8 in which the catalytic treatment is hydrocracking.

11. The process of claim 8 in which the catalytic treatment is hydrosulfurization.

12. The process of claim 1 in which the heavy petroleum fraction is introduced into a dispersing zone at a rate between 0.5 and 5.0 volumes of heavy petroleum fraction per volume of dispersing zone per hour and the H₂O is introduced at a rate between 0.1 and 5.0 v/v/hr.

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