

[54] PRODUCTION OF NAPHTHENIC OILS

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[58] Field of Search 208/59, 111

[56] References Cited

UNITED STATES PATENTS

3,663,423	5/1972	Bennett et al.	208/59
3,654,133	4/1972	Olson	208/59
3,663,430	5/1972	Morris	208/111
3,539,498	11/1970	Morris et al.	208/111

3,480,539	11/1969	Voorhies et al.	208/111
3,516,925	6/1970	Lawrence et al.	208/111
2,960,458	11/1960	Beuther et al.	208/19
3,607,723	9/1971	Peck et al.	208/59
3,442,794	5/1969	Van Helden et al.	208/111
3,442,795	5/1969	Kerr et al.	208/120
3,493,493	2/1970	Henke et al.	208/264
3,562,149	2/1971	Bryson et al.	208/143
3,579,435	5/1971	Olenzak et al.	208/59

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[57] ABSTRACT

Naphthenic oils are prepared by hydrocracking a petroleum residuum and catalytically dewaxing the lubricating oil so produced. The dewaxed oil is then subjected to solvent extraction or mild hydrogenation.

12 Claims, No Drawings

PRODUCTION OF NAPHTHENIC OILS

This invention relates to the hydroconversion of petroleum fractions. More particularly, it is concerned with the conversion of low value stocks such as residuum into valuable oils.

Previously it was customary to use naphthenic oils as bases for specialty oils such as turbine oils, torque fluids, transformer oils and the like. However, recently the supply of crudes from which naphthenic oils are obtained has diminished to such an extent that there is a distinct shortage of naphthenic oils. It is therefore an object of this invention to produce naphthenic oils. Another object is to produce valuable naphthenic oils from petroleum fractions of low value such as petroleum residue. These and other objects will be obvious to those skilled in the art from the following disclosure.

According to our invention there is provided a process for the production of naphthenic oils which comprises contacting a residue-containing petroleum fraction having an initial boiling point of at least about 800°F. with a catalyst comprising a Group VI metal and a Group VIII metal or their compounds or mixtures thereof on a support having cracking activity under hydrocracking conditions to convert at least a portion of the charge to a fraction boiling in the lubricating oil range, subjecting the lube oil fraction so produced to catalytic dewaxing by contacting same with a catalyst comprising a Group VI metal and a Group VIII metal or their compounds or mixtures thereof supported on a mordenite having a silica-alumina ratio of at least 20:1 in the presence of hydrogen under dewaxing conditions and recovering a naphthenic oil from the dewaxed product.

The charge stocks used in the process of this invention are heavy residue-containing petroleum fractions having an initial boiling point of at least about 800°F. They may be derived from any suitable crude source such as West Texas-New Mexico Sour, tar sand oil, shale oil and the like. Ordinarily they are obtained by distilling the crude to remove all of the materials boiling below about 800°F. Preferred starting materials are residua having an IBP of at least 900°F. obtained by vacuum distillation of the crude oil.

The charge stock is first subjected to hydrocracking by contact in the presence of hydrogen with a hydrocracking catalyst.

The hydrocracking catalyst comprises a Group VI metal or compound thereof in association with a Group VIII metal or compound thereof. Preferred metals are nickel, iron, cobalt, molybdenum and tungsten. Preferred compounds are the oxides and sulfides. The Group VIII metal may be present in an amount based on the entire catalyst composite of about 1-10 percent by weight preferably 2-8 weight percent. The Group VI metal may be present in an amount between about 5 and 40 percent preferably between 6 and 25 percent by weight. The catalyst support is composed of an amorphous inorganic oxide such as alumina, silica, magnesia, zirconia or the like. Since the charge stock contains asphaltenes, the catalyst should have a surface area of at least 250 m²/g preferably at least 300 m²/g, a pore volume of at least 0.6 cc/g and an average pore diameter of less than 100A., preferably between 50A. and 95A. The pore diameter is calculated from the formula $4V/S$ where V is the pore volume and S is the sur-

face area and is expressed in Angstrom units. As a practical matter, where the catalyst must withstand the rigorous conditions of commercial operation in large units, the surface area should not exceed 800 m²/g and the pore volume should not exceed about 1.0 cc/g. Good results have been obtained using catalysts having a surface area of 280-400 m²/g, a pore volume of 0.6-0.8 cc/g and an average pore diameter of 70-90A.

The catalyst may be shaped as pellets or spheres and may be used in the form of a fixed, moving or fluidized bed. In a preferred embodiment the catalyst is pellet-shaped and is used in the form of a fixed bed. The charge stock may be passed upwardly or downwardly through the reactor concurrently with the hydrogen or may be passed downwardly countercurrent to an up-flowing stream of hydrogen. In a specific embodiment, the charge stock is introduced into a fixed bed of catalyst at an intermediate point thereof and hydrogen at the rate of at least 3,000 SCF per barrel of charge sufficient to maintain liquid above the point of introduction is introduced at or near the base of the catalyst bed to flow countercurrent to the downward-flowing heavier components of the charge and cocurrent to the upward flowing lighter components of the charge and the products of the hydrocracking reaction. The heavier materials withdrawn from the bottom of the hydrocracking zone may be recycled to the charge and the overhead removed from the upper end of the hydrocracking zone may be sent in all or in part to the catalytic dewaxing zone. In this embodiment the separation of the unconverted residuum charge takes place in the hydrocracking zone. In the other methods where the product is removed in its entirety from one outlet of the hydrocracking zone, then the entire effluent including hydrogen, hydrocracked product and unconverted charge may be sent to the catalytic dewaxing zone or the effluent may be separated into various components and the lube oil fraction sent to the catalytic dewaxing zone with separated hydrogen or with fresh hydrogen.

The hydrogen need not necessarily be pure hydrogen. Hydrogen having a purity of at least 65 percent preferably 70-95 percent may be used. Suitable sources of hydrogen are catalytic reformer by-product hydrogen, hydrogen obtained by partial oxidation of hydrocarbonaceous material followed by shift conversion and CO₂ removal and electrolytic hydrogen.

Reaction conditions in the hydrocracking zone include a temperature of 650°-950°F., a pressure of 500-5000 psig, a space velocity of 0.1-10 volumes of charge per volume of catalyst per hour and a hydrogen rate of 1000-10,000 SCFB. Preferred conditions are a temperature between 750° and 900°F., a pressure between 1,000 and 3,000 psig, a space velocity between 0.3 and 1.5 v/v/hr and a hydrogen rate between 3,000 and 10,000 SCFB. Conditions are chosen so that there is a substantial conversion, e.g., at least 30 percent to materials boiling below the initial boiling point of the charge. For example, if the temperature is at the lower end of the above range, then the space velocity should also be low but a low temperature should not be combined with a high space velocity. As mentioned above, the entire effluent from the hydrocracking zone or a selected portion thereof may be sent to the catalytic dewaxing zone.

The oil is then subjected to catalytic dewaxing. In this stage the oil is contacted with a catalyst in the presence of hydrogen at elevated temperatures and pressures. The temperature will range from 450°–850°F., preferably 550°–750°F. Pressures of from atmospheric to 5,000 p.s.i.g. and higher may be used although a preferred range is from 300 to 2,000 p.s.i.g. A suitable liquid hourly space velocity is from 0.5 to 3.0 volumes of oil per hour per volume of catalyst although space velocities of from 0.1–10 may be used. Advantageously, hydrogen in an amount ranging up to 20,000 s.c.f.b. (standard cubic feet per barrel) of charge may be present, preferred rates being 500–10,000 s.c.f.b.

The catalyst used in the dewaxing stage of the process comprises a hydrogenating component supported on a low sodium mordenite. Synthetic mordenite is usually prepared as the alkali metal aluminosilicate which for the purpose of the present invention is an inactive form. To convert the synthetic mordenite to a form active for the hydrocracking of the waxy components of the oil, it is converted to the hydrogen form by removal of the alkali metal ion, usually sodium. The removal of the sodium ion is accomplished by contacting the synthetic mordenite with ammonia or a compound thereof usually in the form of a water solution to incorporate the ammonium ion in the mordenite. Subsequent calcination converts the mordenite to the active or acid form. The mordenite may also be converted to the low sodium or acid form by contact with a dilute acid such as 3N or 6N HCl. However, in addition to converting the mordenite to the acid form, the mordenite is additionally treated with acid to leach out a portion of the alumina thereby to increase the silica-alumina ratio to at least 20:1 and preferably to at least 40:1.

Of the various natural and synthetic zeolites now available in the industry only the low sodium or acid form of mordenite is satisfactory for the purposes of the present invention. Other crystalline zeolites such as zeolite A, faujasite, zeolite X and zeolite Y are unsatisfactory whether or not they have a low alkali metal content. This is attributed to the combination of pore size and unusual catalytic activity of the mordenite. Whereas zeolite A and faujasite have pore openings of 5 Å. and zeolites X and Y have uniform pore openings of 10–13 Å., the catalyst support used in our process has sorption channels which are parallel to the C-axis of the crystal and are elliptical in cross-section. The dimensions of the sorption channels of sodium mordenite based on crystallographic studies have been reported as a minor diameter of 5.8–5.9 Å., a major diameter of 7.0–7.1 Å. and an average diameter of 6.6 Å. The hydrogen form of the mordenite appears to have somewhat larger pore openings with a minor diameter of not less than 5.8 Å. and a major diameter less than 8 Å. The effective working pore diameter of the hydrogen mordenite prepared by acid treating synthetic mordenite appears to be in the range of 8 Å. to 10 Å. as indicated by the absorption of aromatic hydrocarbons.

Supported on the hydrogen form of the mordenite is a hydrogenating component which comprises a Group VIII metal or compound thereof, for example the oxide or sulfide, which may be associated with a Group VI

metal or compound thereof. Noble metals such as platinum, palladium and rhodium have been found especially useful and may be used in amounts of 0.1–5 percent based on the total catalyst weight with a range of 0.5–2.5 being preferred. Other suitable hydrogenating components comprise nickel, cobalt and iron, particularly when used in conjunction with a Group VI metal such as molybdenum or tungsten. Suitable combinations include cobalt molybdenum, nickel molybdenum and nickel tungsten. The latter type of hydrogenating component may be present in an amount ranging from 5–40 percent by weight, preferably 10–25 percent. The hydrogenating component may be incorporated into the support by ion exchange or by impregnation, each of these methods being well known in the art.

In the catalytic dewaxing stage of the process, the waxy components are cracked to lighter components having a boiling point considerably lower than the desired lube oil fraction and therefore are easily separated therefrom. The principal byproducts of our catalytic dewaxing process are light hydrocarbons such as ethane, propane, butane and the corresponding olefins.

The following example is submitted for illustrative purposes only.

EXAMPLE

In this example the charge is a mixture containing 90 percent West Texas-New Mexico Sour and 10 percent Lafitte Paradis Vacuum Residua having the following characteristics:

Gravity, °API	11.7
Kinematic Viscosity, 100°F.	6030
at 210°F.	1117
Conradson Carbon Residue, wt. %	19.7
n-Pentane Insolubles, wt. %	10.2
Pour Point, 20 F.	120.+
Sulfur, wt. %	2.88
Total nitrogen, ppm	4615
Metals, ppm	
Nickel	46
Vanadium	52
Iron	79
Initial boiling point, °F. (approximate)	1000

The hydrocracking catalyst is in the form of a fixed bed of pelleted cobalt molybdate on alumina catalyst having the following characteristics:

Surface area, m ² /g	290
Pore volume, cc/g	0.63
*Average pore diameter, Å	86.9
Cobalt, wt. %	2.0
Molybdenum, wt. %	9.0
Silica, wt. %	3.9
Alumina, wt. %	78.9
* $d = 4 V_g / S_g$ where d = average pore diameter V_g = pore volume per unit mass and S_g = surface area per unit mass.	

Hydrocracking is effected under the following conditions with the yields listed below:

Average Operating Conditions	
Space velocity, v/v/hr	0.4
Pressure, psig	2000
Hydrogen rate, SCFB	7710
Temperature, °F.	815
Hydrogen purity, vol. %	88
Hydrogen consumption, SCFB	1575
1000°F.+ conversion, vol. % of feed	61.8

Product yield	Volume %	Weight %
Ammonia		0.31
Hydrogen Sulfide		2.65
Dry Gas (C ₁ -C ₃)		2.20
Butanes	1.7	1.0
Pentanes	1.5	0.9
Naphtha (C ₆ -410°F.)	11.3	8.9
Light Gas Oil (410°F.-600°F.)	15.4	13.3
Lube Fraction (600°F.-1000°F.)	37.9	35.2
Residuum (1000°F.+)	38.2	38.1

The 600°-1000°F. lube oil cut is separated into four fractions, (1) a heavy gas oil, (2) a spindle oil, (3) a light lube fraction and (4) a heavy lube fraction. They have the following properties:

Fraction	1	2	3	4
Gravity, °A.I.	29.9		23.9	21.1
Viscosity, SUS,				
100°F.	52.4	67.5	165.0	830
210°F.	33.5	35.6	43.2	72.1
Pourpoint, °F.	+5	+45	+85	+115
Carbon Residue, wt. %	0.20	0.06	0.05	0.74
Sulfur, Wt. %	0.06	0.06	0.10	0.18
Viscosity Index	78	71	74	69

The four fractions are then catalytically dewaxed by being passed with hydrogen through a fixed bed of particulate dewaxing catalyst composed of 2 weight percent palladium on an acid-leached mordenite having a silica:alumina mole ratio of 53:1. Operating conditions and results are as follows:

Operating Conditions	1	2	3	4
Temperature, °F.	650	650	650	650
Pressure, psig	300	300	300	850
Hydrogen rate, SCFB	2000	2000	2000	2000
Space Velocity, v/v/hr	1.0	1.0	0.5	0.5
Yield, vol. %	60	88	75	55
Product				
Gravity, °API	29.9	29.7	26.1	23.5
Viscosity, SUS,				
100°F.	305	345	380	500
210°F.	53.5	77.3	177	1200
Viscosity Index	64	70	75	50
Pourpoint, °F.	-70	+10	+5	+15

To improve the properties of the dewaxed oil such as color and viscosity index the oil may be subjected to a mild hydrogenation or hydrorefining or may be subjected to solvent extraction.

For the hydrorefining, the catalytically dewaxed oil is introduced into the hydrorefining stage and brought into contact with the hydrogenating catalyst at elevated temperatures and pressures in the presence of hydrogen. Suitable catalysts comprise the oxides and/or sulfides of metals such as cobalt, molybdenum, nickel, tungsten, chromium, iron, manganese, vanadium and mixtures thereof. The catalytic materials may be used alone or may be deposited on or mixed with a support such as alumina, magnesia, silica, zinc oxide, natural and synthetic zeolites or the like. Particularly suitable catalysts are nickel tungsten sulfide, molybdenum oxide on alumina, a mixture of cobalt oxide and molybdenum oxide generally referred to as cobalt molybdate on alumina, molybdenum oxide and nickel oxide on alumina, molybdenum oxide, nickel oxide and cobalt oxide on alumina, nickel sulfide on alumina, molybdenum sulfide, cobalt sulfide and nickel sulfide on alumina.

In the hydrorefining zone, pressures and temperatures may range broadly between 500-5,000 p.s.i.g. and 500°-900°F., preferred ranges being 800-3,000 p.s.i.g. and 600°-800°F., respectively. Space velocities of 0.25-3.0 may be used although a rate between 0.5

and 1.5 is preferred. The hydrogen rate may range between 200 and 10,000 s.c.f.b. although suitable results are obtained at hydrogen rates between 2,000 and 6,000 s.c.f.b. The hydrorefining treatment conditions are selected so that it results in a hydrogenated product having substantially the same boiling range as the charge to the hydrorefining zone and is termed non-destructive hydrogenation as distinguished from destructive hydrogenation in which a substantial portion of the product boils at a temperature below that of the charge.

In the solvent refining operation the oil undergoing treatment is subjected to liquid-liquid contact with a selective solvent which preferentially dissolves the more aromatic constituents from the oil undergoing treatment. It is a characteristic of the selective solvent employed that it is partially miscible with the oil undergoing treatment so that during the solvent refining operation there are formed two phases, a raffinate phase containing substantially only a solvent refined oil having a reduced amount or proportion of aromatic hydrocarbons as compared to the oil charged to the solvent refining operation, and an extract phase or mix comprising selective solvent and dissolved therein extract or extracted oil having a relatively increased proportion or amount of more aromatic hydrocarbons as compared with the charge oil. The aforesaid solvent refining operation may be carried out stagewise (combinations or mixer-settler) or continuously in a suitable contacting apparatus, e.g., packed or plate tower, rotating disc contactor, either concurrently or counter-currently. Selective solvents which are suitably employed include furfural, phenols, liquid sulfur dioxide, nitrobenzene, β,β' -dichloroethylether, dimethyl-formamide, diethylene glycol, N-methyl pyrrolidine and the like.

If stability to ultraviolet light is not important then the catalytically-dewaxed oil may be finished by the hydrorefining treatment. However, if it is desired to produce an oil which is stable to ultraviolet light, then the catalytically dewaxed oil should be finished with a solvent extraction treatment preferably using furfural or N-methyl pyrrolidone as the solvent.

When mild hydrogenation is used as the finishing step, the entire effluent from the catalytic dewaxing zone may be sent to the hydrorefining zone unless it is desired to recover the low boiling olefins such as ethylene and propylene present in which case these products are removed from the catalytic dewaxing zone effluent prior to the hydrorefining.

I claim:

1. A process for the production of naphthenic oils which comprises contacting an asphaltene-and residue-containing petroleum fraction having an initial boiling point of at least about 800°F. with a catalyst comprising a Group VI metal and a Group VIII metal or their compounds or mixtures thereof on an amorphous support having cracking activity and having a surface area of at least 250 m²/g, a pore volume of at least 0.6 cc/g and an average pore diameter of 50-95Å., under hydrocracking conditions to convert at least a portion of the charge to a fraction boiling in the lubricating oil range, subjecting the lube oil fraction so produced to catalytic dewaxing by contacting same with a catalyst comprising a Group VI metal and a Group VIII metal

or their compounds or mixtures thereof supported on a mordenite having a silica-alumina ratio of at least 20:1 in the presence of hydrogen under dewaxing conditions and recovering a naphthenic oil from the dewaxed product.

2. The process of claim 1 in which the charge is a vacuum residuum.

3. The process of claim 1 in which the dewaxing catalyst has a silica:alumina ratio of at least 40.

4. The process of claim 1 in which the surface area is between 280 and 400 m²/g, the pore volume is between 0.6 and 1.0 cc/g and the average pore diameter is between 70 and 90A.

5. The process of claim 1 in which the catalytically dewaxed oil is mildly hydrogenated.

6. The process of claim 1 in which the catalytically dewaxed oil is subjected to a solvent extraction treatment.

7. The process of claim 6 in which the solvent is furfural.

8. The process of claim 6 in which the solvent is N-

methyl pyrrolidone.

9. The process of claim 5 in which the entire effluent of the dewaxing zone is introduced into the mild hydrogenation zone.

10. The process of claim 1 in which the charge is introduced into a fixed bed of hydrocracking catalyst at an intermediate point thereof and at least 3,000 SCF hydrogen per barrel of charge is introduced at the lower end of said bed to flow countercurrently to downwardly flowing heavier components of said charge and concurrently with upwardly flowing lighter components of said charge and the products of the hydrocracking reaction and removing from the hydrocracking zone an overhead product containing a lube oil fraction.

11. The process of claim 10 in which the entire overhead is introduced into the dewaxing zone.

12. The process of claim 11 in which the entire dewaxing zone effluent is introduced into a mild hydrogenation zone.

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