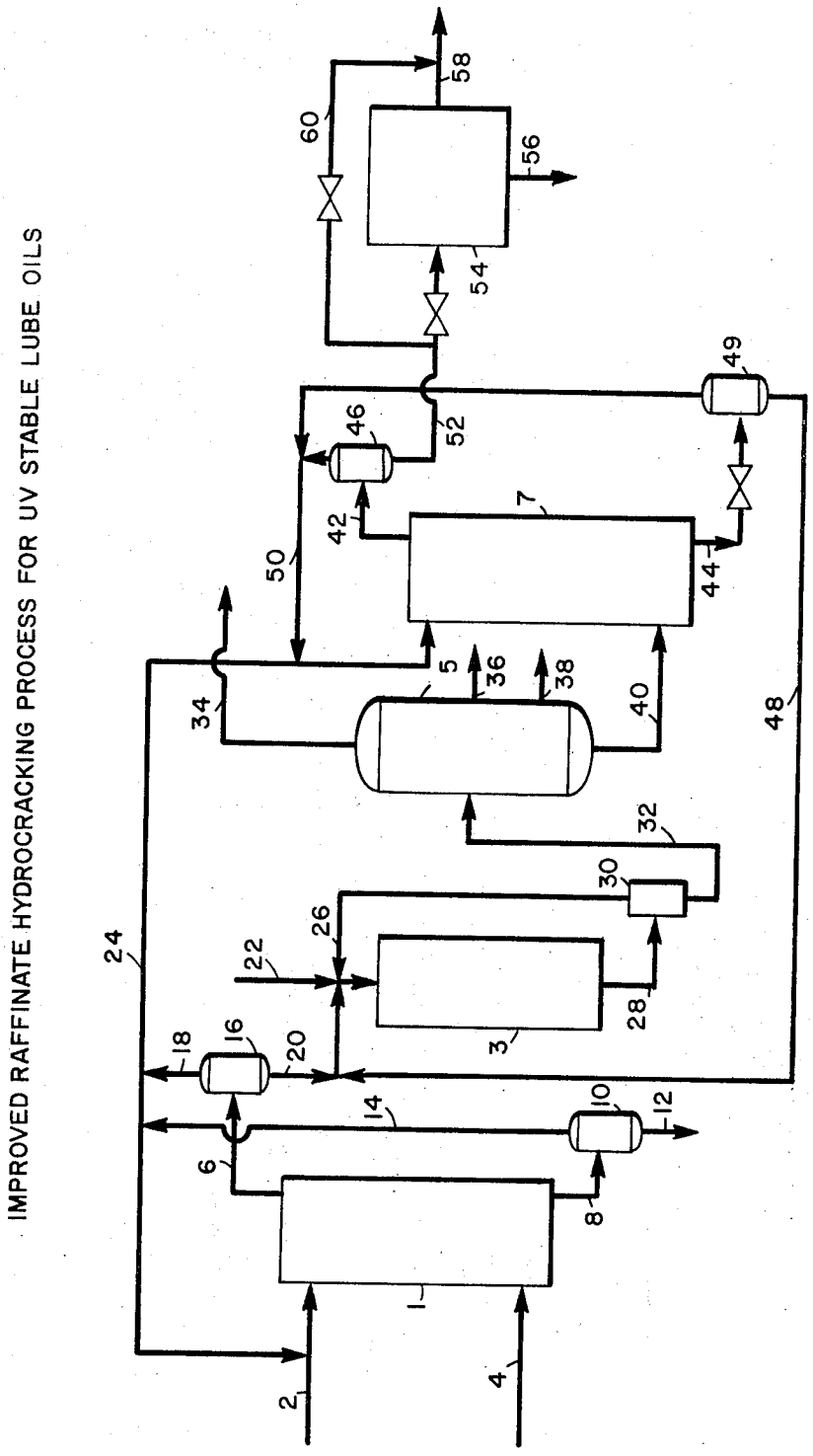
April 23, 1974 H. C. HENRY ET AL 3,806,445

RAFFINATE HYDROCRACKING PROCESS FOR UV STABLE LUBRICATING OILS

Filed Aug. 31, 1972

IMPROVED RAFFINATE HYDROCRACKING PROCESS FOR UV STABLE LUBE OILS



United States Patent Office 3,806,445
Patented Apr. 23, 1974

3,806,445

RAFFINATE HYDROCRACKING PROCESS FOR UV STABLE LUBRICATING OILS

H. Clarke Henry and John B. Gilbert, Sarnia, Ontario, Canada, assignors to Esso Research Engineering Company

Filed Aug. 31, 1972, Ser. No. 285,208
Int. Cl. C10g 13/00, 37/00
U.S. Cl. 208—87 12 Claims

ABSTRACT OF THE DISCLOSURE

High quality UV stable lubricating oil stocks are prepared by solvent extracting a hydrocarbon feedstock with a solvent having preferential solubility for aromatics, thereby reducing the aromatic content thereof and recovering a raffinate phase therefrom. The raffinate is stripped of solvent and subsequently hydrocracked under mild conditions to increase the viscosity index of the raffinate. The hydrocrackate product is then solvent extracted with a solvent having preferential solubility for aromatics, which solvent may be the same or different than the solvent used in the first extraction, thereby forming a second extract phase and a second raffinate phase. The extract and raffinate phases are separated and the extract phase stripped of solvent and recycled to the hydrocracker.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a process for the upgrading of lubricating oil stocks. More specifically, the process relates to improvements in the viscosity index and UV stability of lubricating oil stocks.

Description of the prior art

Several processes have been used in the past for upgrading lubricating oil stocks. These processes have generally included either solvent extraction and/or hydrogenation including hydrocracking. Generally, the combination solvent extraction-hydrocracking processes have involved subjecting raffinates from solvent extraction operations to hydrocracking at temperatures on the order of about 650° F. in the presence of a catalyst and at relatively high partial pressures of hydrogen. Recent developments in hydrocracking processes have led to increased interest in commercial utilization of such processes as a method for upgrading lubricating oil stocks in order to obtain lubricating oil with increased viscosity index. This has been due in part to a decline in the availability of high quality feedstocks from which high VI, UV stable lubricating oils could be derived by conventional operations such as solvent extraction. This in turn has led to the perfection and utilization of solvent extraction/hydrotreatment combination processes on poorer grades of feedstocks to obtain the high grade lubricating oils that are demanded in today's market.

One such combination process is described in U.S. 3,579,437, issued May 18, 1971 and assigned to Sun Oil Company, Philadelphia, Pa. The process described therein comprises solvent-extracting a lubricating oil fraction with a solvent having preferential solubility for polycyclic aromatics and wherein raffinate derived therefrom is hydrocracked under conditions sufficient to increase the viscosity index of the so-formed lubricating oil product. The hydrocrackate is then subjected to solvent extraction

with a solvent having preferential solubility for polycyclic aromatics and raffinate and extract phases are recovered. The extract phase, containing adulterated solvent, is separated from the raffinate product and recycled to the initial extraction operation wherein it is combined with charge stock to be used in the first extraction stage. The process described therein suffers from several disadvantages including the use of relatively high hydrocracking pressures. Specifically, pressures above 1500 pounds per square inch and preferably above 2000 pounds per square inch are employed. This is undesirable from an economic standpoint and methods by which lower hydrocracking pressures could be used would be desirable. In addition, other disadvantages such as high hydrogen consumption rates have been noted in prior art processes particularly in the '437 process.

In U.S. Pat. 3,652,448, patented Mar. 28, 1972, an extraction/hydrocracking/extraction process, similar to that described in U.S. Pat. 3,579,437, supra, is disclosed. Although, it is indicated that pressures below 1500 p.s.i.g. can be used, the process still suffers from disadvantages such as overall low lube oil yields.

In summary then it would be economically desirable to provide a process for the upgrading of low quality crude sources to high quality lubricating oil products wherein low pressures were used in the hydrocracking step, where there was minimum hydrogen consumption in the hydrocracking step and overall high lube oil yields.

SUMMARY OF THE INVENTION

In accordance with this invention, it has now been discovered that an economically feasible process for the production of high VI, UV stable lubricating oil products can be achieved. Specifically, the process comprises (a) solvent extracting a lubricating oil stock with a solvent having preferential solubility for aromatics thereby forming an extract phase and a raffinate phase, (b) hydrocracking at least a portion of the raffinate phase with hydrogen in the presence of a hydrocracking catalyst, at mild hydracracking conditions, thereby forming a hydrocrackate product, (c) solvent extracting at least a portion of the hydrocrackate product with a solvent having preferential solubility for aromatics thereby forming an extract phase and a raffinate phase and (d) recycling at least a portion of the substantially solvent-free extract phase from step (c) to step (b), wherein it is introduced into the hydrocracking operation either separately or in combination with the raffinate from step (a).

Feedstocks that are suitable for use in the subject process include hydrocarbons, mixtures of hydrocarbons, and, particularly, hydrocarbon fractions, the predominant portions of which exhibit initial boiling points above about 650° F. Unless otherwise iudicated, boiling points are taken at atmospheric pressure. Non-limiting examples of useful process feedstocks include crude oil vacuum distillates from paraffinic or naphthenic crudes, i.e., deasphalted residual oils, the heaviest fractions of catalytic cracking cycle oils, coker distillates and/or thermally cracked oils, heavy vacuum gas oils and the like. These fractions may be derived from petroleum crude oils, shale oils, tar sand oils, coal hydrogenation products and the like. Preferred feedstocks include deasphalted petroleum oils that exhibit initial boiling points in the range of from about 930–1050° F. and a Conradson carbon residue number less than about 3 and heavy gas oils that boil predominantly

between about 650° and 1050° F. and exhibit viscosities ranging from about 35–200, preferably 40–100 SUS at 210° F.

With the exception of those lubricating oil stocks which are of sufficiently low asphalt and metal content, the high viscosity lubricating oil stock feeds to the first extraction step are preferably deasphalted. Any conventional deasphalting operation may be used which fulfills these objectives.

The instant process produces high quality lubricating oils from both good quality lube crudes (e.g., Light Arabian and North Louisiana) and low quality non-lube crudes (e.g., South Louisiana and West Texas Sour). The non-lube crudes are generally characterized by having low VI ceilings, high sulfur content, e.g., greater than 2 wt. percent sulfur, based on feed, and producing low yields of the desired lubricating oil products by solvent refining. It is further noted that process feedstocks may not only be derived from high sulfur content crudes, but may themselves be of high sulfur content, e.g., greater than about 2 wt. percent, based on total feed. The feedstock to the process preferably has a viscosity index above 0 and most preferably above about 30. In each case, the viscosity index referred to in this disclosure is the extended viscosity index (VI_E) (ASTM D2270–64).

The particular solvent which is used in the extraction operation depends upon several considerations, such as for example basic economics. While there is no requirement that the solvent used in the first extraction be the same as that used in the second extraction step, it is preferred that the solvents be the same. Any solvent, selective for aromatics, particularly polycyclic aromatics, may be used such as furfural, acetophenone, liquid SO_2, acetonitrile, phenol, nitrobenzene, aniline, 2,2-dichlorodiethyl ether, dimethyl sulfoxide, dimethyl formamide, n-methyl 2-pyrrolidone and mixtures thereof. In addition, any of these solvents in combination with an anti-solvent such as water may be used in the solvent extraction steps. In general, the most preferred solvents are phenol, furfural, and phenol-water. The latter solvent is most preferred and contains between about 0.1 and 15 LV percent water based on the solvent mixture, preferably 3 to 8 LV percent water. Solvent dosages of about 50 to 500%, preferably 75 to 250%, are used in pre- and post-hydrocracking extractions.

In general, the various means customarily utilized in extraction processes to increase the contact area between the oil stock and the solvent can be employed. Thus, the apparatus used in the instant process can comprise a single extraction zone or multiple extraction zones equipped with (a) shed rows or other stationary devices to encourage contacting; (b) orifice mixers; or (c) efficient stirring devices such as mechanical agitators, jets of restricted internal diameter, turbo mixers and the like. The operation may be conducted as a batch or continuous-type operation with the latter being preferred. A continuous countercurrent operation is most preferred. Known techniques for increasing selectivity for aromatics can be employed. Examples of these are the use of small amounts of anti-solvents, e.g., water, during the extraction with the solvent, operating at fairly low temperatures sufficient to carry out the extraction objectives, and using low solvent to oil ratios.

The equipment employed in the operation of the extraction processes of the subject invention are not critical and can comprise rotating disc contactors, podbielniak contactors, countercurrent packed bed extraction columns and countercurrent tray contactors.

The temperature of the extraction and the amount of solvent used are interdependent, and are, in turn, dependent upon the composition of the particular oil stock to be extracted. With this in mind the following extraction process points are noted. First, the temperature of the pre-hydrocracking extraction is preferably maintained at about 40° F. below the temperature of miscibility of the oil and solvent in order to obtain the desired extraction effect and to conduct a highly efficient extraction operation with good yields of oil. The lower temperature limit is controlled in part by the pour point of the hydrocracker feed when it has been dewaxed. If the feed has not been dewaxed, then the minimum temperature of the extraction is controlled by the point at which solids appear. It is noted that if the extraction temperature is too low, the extraction will be too selective and will require application of compensating features, such as additional amounts of solvent and extraction stages. The extraction temperature range is generally between about 0 and 350° F., preferably between about 80° and 250° F., depending on the oil-solvent miscibility temperature. In the case of the preferred phenol-water solvent system, the temperature ranges from about 120° to 200° F.

It is noted that high solvent-oil ratios tend to reduce operational efficiency, producing lower yields of raffinate as hydrocracker feed and are to be avoided. Thus, for the most part solvent-oil ratios (defined as volume of solvent added per volume of oil) range between about 6:1 and about 0.25:1. Particularly preferred ratios range between about 4:1 to about 0.8:1. For feedstocks derived from low lube quality crudes such as heavy vacuum gas oils and deasphalted oils derived from South Louisiana crudes, typical extraction temperatures of 170° F. and 200° F. may be used with solvent to oil ratios of about 2.5:1 to 1.5:1.

Subsequent to the initial extraction step, the resulting raffinate and extract phases are separated and the raffinate phase substantially free of solvent is then introduced into a hydrocracking zone or zones with one or more catalysts present therein. Illustrative but nonlimiting examples of the hydrocracking procedure and modifications used herein are disclosed in U.S. Pats. 3,617,476, 3,242,068 and 3,579,437, the disclosures of which are incorporated herein by reference.

The preferred hydrocracking procedure is characterized by having overall low hydrogen consumption and comprises hydrocracking the raffinate obtained above at temperatures ranging between about 650° and 825° F., preferably between about 700° and 800° F. Pressures which may be employed in the hydrocracking process are generally below about 1500 p.s.i.g., preferably below about 1000 p.s.i.g., and most preferably ranging between about 600 p.s.i.g. and about 1000 p.s.i.g. In addition, liquid hourly space velocities can range between about 0.2 and 4 v./v./hr. and more preferably between about 0.4 and 1.5 v./v./hr.

The hydrocracking operation is conducted, as previously indicated, in the presence of one or more hydrocracking catalysts, i.e., having both aromatic saturation and ring scision activity. The catalyst may be any conventional hydrocracking catalyst, such as, for example, that described in U.S. Pats. 3,535,230 and 3,287,252, the disclosures of which are incorporated herein by reference. Thus, the catalyst comprises a mixture of a major amount of an amorphous component and a minor amount of a hydrogenation component preferably comprising one or more transitional metals selected from Groups VI–B and/or VIII of the Periodic Table and the oxides and sulfides thereof. The catalyst may also contain a minor amount of P_2O_5 which acts to stabilize the catalyst and increase its overall activity.

Representative of these metals are molybdenum, chromium, tungsten, nickel, cobalt, palladium, iron, rhodium and the like, as well as combinations of these metals and/or their oxides and/or sulfides. Preferred metals are nickel, molybdenum and mixtures thereof. One or more of the metals, metal oxides or sulfides, alone or in combination, may be added to the support in minor proportions ranging from 1 to 25 wt. percent based on the total catalyst.

The amorphous compnent, i.e., support, can be one or more of a large number of non-crystalline materials having high porosity. The porous material is preferably inorganic but can be organic in nature if desired. Representative porous materials that can be employed include metals and metal alloys; sintered glass, firebrick; diatomaceous earth; inorganic refractory oxides; organic resins, such as polyesters, phenolics and the like; metal phosphates such as boron phosphate, calcium phosphate and zirconium phosphate; metal sulfides such as iron sulfide and nickel sulfide; inorganic oxide gels and the like. Preferred inorganic oxide support materials include one or more oxides of metals selected from Groups II–A, III–A and IV of the Periodic Table. Non-limiting examples of such oxides include aluminum oxide, titania, zirconia, magnesium oxide, silicon oxide, titanium oxide, silica-stabilized alumina and the like.

Preferably, the starting catalyst composition comprises a silica/alumina support containing molybdenum trioxide and nickel oxide hydrogenation components. The silica: alumina weight ratio in the amorphous support can range from 20:1 to 1:20 and preferably from 1:4 to 1:6. The molybdenum trioxide: nickel oxide weight ratio in the amorphous support can range from about 1:25 to 25:1 and preferably from 2:1 to 4:1. Finally the weight ratio of the support to the hydrogenation component can range from about 20:1 to 1:20 and preferably from 4:1 to 6:1. A particularly preferred starting catalyst composition comprises:

	Wt. percent
NiO	4.5
MoO_3	13.0
SiO_2	14.0
Al_2O_3	68.4

The catalyst is preferably pre-sulfided by conventional methods such as by treatment with hydrogen sulfide or carbon disulfide prior to use. The precise chemical identity of the hydrogenation constituents present on the support during the course of the hydrocracking operation is not known. However, the hydrogenation components probably exist in a mixed elemental metal/metal oxide/metal sulfide form.

Additionally, low sieve-content catalysts consisting of a mixture of a major amount of an amorphous component and minor amounts of (1) a crystalline aluminosilicate component comprising less than about 25 wt. percent, preferably less than about 5 wt. percent of the total catalyst and (2) a hydrogenation component, can be used as hydrocracking catalysts. The catalyst may also contain a small amount of P_2O_5, which acts to stabilize the catalyst against decomposition. The amorphous component (support) is similar to that described above. The hydrogenation component is preferably a transitional metal selected from Groups VI–B and VIII of the Periodic Table and/or the oxides and/or sulfides thereof. Useful catalyst metals include chromium, molybdenum, tungsten, platinum, palladium, cobalt, nickel, etc. One such catalyst comprises 95 wt. percent based on total catalyst of NiO/MoO_3 on a SiO_2/Al_2O_3 base (stabilized with P_2O_5) and 5 wt. percent based on total catalyst of nickel-exchanged faujasite.

The crystalline aluminosilicate (sieve component) employed in the preparation of the crystalline component of the catalyst comprises one or more natural or synthetic zeolites. Representative examples of particularly preferred zeolites are zeolite X, zeolite Y, zeolite L, faujasite and mordenite. Synthetic zeolites have been generally described in U.S. Pats. 2,882,244, 3,130,007 and 3,216,789, the disclosures of which are incorporated herein by reference.

The silica:alumina mole ratio of useful alumino-silicates is greater than 2.5 and preferably ranges from about 2.5 to 10. Most preferably this ratio ranges between about 3 and 6. These materials are essentially the dehydrated forms of crystalline hydrous siliceous zeolites containing varying quantities of alkali metal and aluminum with or without other metals. The alkali metal atoms, silicon, aluminum and oxygen in the zeolites are arranged in the form of an aluminosilicate salt in a definite and consistent crystalline structure. The structure contains a large number of small cavities, interconnected by a number of still smaller holes or channels. These cavities and channels are uniform in size. The pore diameter size of the crystalline aluminosilicate can range from 5 to 15 A. and preferably from 5 to 10 A.

The aluminosilicate component may comprise a sieve of one specific pore diameter size or, alternatively, mixtures of sieves of varying pore diameter size. Thus, for example, mixtures of 5 A. and 13 A. sieves may be employed as the aluminosilicate component. Synthetic zeolites such as type-Y faujasites are preferred and are prepared by well-known methods such as those described in U.S. 3,130,007.

The aluminosilicate can be in the hydrogen form, in the polyvalent metal form, or in the mixed hydrogen-polyvalent metal form. The polyvalent metal or hydrogen form of the aluminosilicate component can be prepared by any of the well-known methods described in the literature. Representative of such methods is ion-exchange of the alkali metal cations contained in the aluminosilicate with ammonium ions or other easily decomposable cations such as methyl-substituted quaternary ammonium ions. The exchanged aluminosilicate is then heated at elevated temperatures of about 570°–1112° F. to drive off ammonia, thereby producing the hydrogen form of the material. The degree of polyvalent-metal or hydrogen exchange should be at least about 20%, and preferably at least about 40% of the maximum theoretically possible. In any event, the crystalline aluminosilicate composition should contain less than about 6.0 wt. percent of the alkali metal oxide based on the final aluminosilicate composition and, preferably, less than 2.0 wt. percent, i.e., about 0.3 wt. percent to 0.5 wt. percent or less.

The resulting hydrogen aluminosilicates can be employed as such, or can be subjected to a steam treatment at elevated temperatures, e.g. 800° to 1300° F. for example, to effect stabilization, thereof, against hydrothermal degradation. The steam treatment, in many cases, also appears to effect a desirable alteration in crystal structures resulting in improved selectivity.

The mixed hydrogen-polyvalent metal forms of the aluminosilicates are also contemplated. In one embodiment the metal form of the aluminosilicate is ion-exchanged with ammonium cations and then partially back-exchanged with solutions of the desired metal salts until the desired degree of exchange is achieved. The remaining ammonium ions are decomposed later to hydrogen ions during thermal activation. Here again, it is preferred that at least about 40% of the monovalent metal cations be replaced with hydrogen and polyvalent metal ions.

Suitably, the exchanged polyvalent metals are transition metals and are preferably selected from Groups VI–B and VIII of the Periodic Table. Preferred metals include nickel, molybdenum, tungsten and the like. The most preferred metal is nickel. The amount of nickel (or other metal) present in the aluminosilicate, as ion-exchanged metal) can range from about 0.1 to 20% by weight based on the final aluminosilicate composition.

In addition to the ion-exchanged polyvalent metals, the aluminosilicate may contain as non-exchanged constituents one or more hydrogenation components comprising the transitional metals, preferably selected from Groups VI–B and VIII of the Periodic Table and their oxides and sulfides. Such hydrogenation components may be combined with the aluminosilicate by any method which gives a suitably intimate admixture, such as by impregnation. Examples of suitable hydrogenation metals, for use herein, include nickel, tungsten, molybdenum, platinum, and the like and/or the oxides and/or sulfides

thereof. Mixtures of any two or more of such components may also be employed. Particularly preferred metals are tungsten and nickel. Most preferably, the metals are used in the form of their oxides. The total amount of hydrogenation components present in the final aluminosilicate composition can range from about 1 to 50 wt. percent, preferably from 10 to 25 wt. percent based on the final aluminosilicate composition.

The amorphous component and the crystalline aluminosilicate component of the low sieve content catalyst may be brought together by any suitable method, such as by mechanical mixing of the particles thereby producing a particle form composite that is subsequently dried and calcined. The catalyst may also be prepared by extrusion of wet plastic mixtures of the powdered components followed by drying and calcination. Preferably the complete catalyst is prepared by mixing the metal-exchanged zeolite component with alumina or silica-stabilized alumina and extruding the mixture to form catalyst pellets. The pellets are thereafter impregnated with an aqueous solution of nickel and molybdenum or tungsten materials to form the final catalyst.

At least a portion of the hydrocrackate is solvent extracted, the procedure being similar to that hereinabove described for the first extraction operation. It is noted that the hydrocrackate product may first be separated into various lube fractions followed by individual extraction of each fraction; alternatively, the hydrocrackate product may be first extracted as a broad cut fraction, containing substantially all of the lube oil components in said hydrocrackate, say, for example, the 650° F.+ fraction, followed by separation of the raffinate into the individual lube fractions. More specifically, for the aqueous phenol extraction system, the extraction temperature and phenol water content may have to be slightly altered compared to the first extraction stage conditions in order to compensate for lower oil viscosity and increased oil-phenol immiscibility resulting from the hydrocracking operation.

The resultant raffinate and extract phases are separated and at least a portion of the extract phase is further treated so as to substantially remove the solvent contained therein. The solvent-free extract can then be recycled to the hydrocracking operation to be additionally hydrocracked therein.

It is speculated that the extract phase comprises a small amount of UV unstable components formed in the hydrocracking operation, which are believed to be partially hydrogenated polycyclic aromatic compounds, together with a larger amount of other components, chiefly aromatics and naphthenes which are of fairly good quality in terms of VI, color, stability, etc. Recycle of this extract to the hydrocracking stage enables a large part of this fraction to be recovered as lube oil product, thus increasing the overall lube oil yield.

BRIEF DESCRIPTION OF THE DRAWING

The figure is a flow diagram of the overall process for the production of high quality lubricating oils.

Turning to the drawing in detail, fresh feed such as a heavy vacuum gas oil boiling between about 850° and 1100° F. and/or a deasphalted oil boiling above about 1000° F. is introduced into extraction zone **1** via line **4**. Make-up solvent is introduced into the extraction zone via line **2**. Extract phase and raffinate phase are formed and are removed from the extraction zone via lines **8** and **6** respectively. The extract phase is then introduced into stripper **10** wherein solvent is removed and preferably recycle to the extraction zone **1** via lines **14** and **24** and **2** or to extraction zone **7** via line **24**. The extract phase is removed from the separator **10** via line **12**. The raffinate phase is removed from the extraction zone **1** as indicated supra via line **6** and introduced into separator **16** wherein solvent and raffinate product are separated and removed therefrom via lines **18** and **20** respectively. The solvent can then be recycled via line **24** to extraction zones **1** and/or **7** respectively.

The raffinate product is introduced via line **20** into the hydrocracking zone **3**. Make-up hydrogen can be added through line **22**. After a time sufficient to bring about the desired conversion, the hydrocrackate product is removed via line **28** and passed to separator **30** where gaseous materials are removed. Recovered hydrogen can then be recycled via line **26** and **22** to the hydrocracking zone.

The stripped hydrocrackate product is introduced into pipestill **5** via line **32** wherein it is fractionated into a fuels fraction line **34**, lube side stream fractions exiting through lines **36** and **38** and a bottoms fraction exiting through line **40**. The lube fractions exiting through lines **36**, **38** and **40** are then introduced into extraction zone **7** either individually or as a blend, where they are extracted thereby forming a second extract phase and a second raffinate phase. The raffinate phase is removed from extraction zone **7** via line **42** and stripped of solvent in stripper **46**. The solvent can be recycled via line **50** to extraction zone **7** and the raffinate product can be further processed such as by dewaxing in dewaxing zone **54**.

The extract phase from extraction zone **7** is removed via line **44** and passed through stripper **49** wherein it is stripped of solvent which may be recycled via line **50** to extraction zone **7**. The extraction product is then recycled via line **48** to line **20** wherein it is mixed with raffinate from extraction zone **1** and introduced into the hydrocracking zone **3**. Although not shown, in another embodiment, the extract product in line **48** can be introduced into hydrocracking zone **3** separately, i.e., not mixed with raffinate from extraction zone **1**.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will be more clearly understood by reference to the following non-limiting examples.

A series of tests were performed to illustrate the raffinate hydrocracking process conducted at 1000 p.s.i.g. with a heavy vacuum gas oil (HVGO) and deasphalted oil (DAO) from South Louisiana crude. Using this feedback the advantages of the instant process are further demonstrated since lubes of 95–105 VI cannot be made from the South Louisiana HVGO by extraction alone at practical solvent treat levels. The properties of the HVGO and DAO feedstocks are as follows:

Feedstock	HVGO	DAO
Boiling range, ° F	850–1,100	1,000+
Gravity, °API	21.7	21.4
Refractive index at 60° C	1.4975	1.4988
Viscosity 210° F., SUS	102.5	262
Wax, wt. percent	9.4	12.0
Sulfur, wt. percent	0.5	0.5
Dewaxed gravity, °API	20.2	19.8
Viscosity 210° F. SUS	120	341
VI_E	47	71

In each of the following examples the solvent used in the countercurrent extraction stages was aqueous phenol and the catalyst used in the hydrocracking stage a conventional sulfided hydrocracking catalyst having the following composition:

Composition:

Nio	wt. percent	3–4
MoO_3	do	14–16
P_2O_5	do	Trace
SiO_2	do	4–6
Faujasite	do	5
Al_2O_3	do	Balance

Properties:

Surface area, $m.^2/g.$	173
Pore volume, ml./g.	0.41
Bulk density, gm./gl.	0.77

In each case the isothermal hydrocracker operated at 1000 p.s.i.g. total hydrogen pressure and at a liquid hourly space velocity of 0.5 v./v./hr. The hydrogen gas rate was maintained constant at 1500 s.c.f./b.

In Examples 1 and 2 the second extraction operation (post-hydrocracking) followed vacuum distillation of the hydrocracker products into the required lube cuts. Intermediate tankage savings result from extracting the broad cut lube from the hydrocracker before vacuum distillation. Examples 3 and 4 illustrate such a broad cut extraction processing sequence.

EXAMPLE 1

Operating conditions and products inspections for upgrading South Louisiana HVGO in the raffinate hydrotreating processing sequence are presented in Table I. In this example the hydrocrackate was vacuum distilled into the required lube cuts before the post-hydrocracking extraction operation. These relatively mild extraction and hydrocracking severities were adequate to produce a slate of UV stable neutral lubes (133 to 751 SUS viscosity at 100° F.) of 102 and 113 viscosity index with overall lube yields of 44 vol. percent and 29 vol. percent based on hydrocracker feed and HVGO respectively. This yield of high viscosity index lube oil product is remarkable considering that lubes higher than 95 VI_E cannot be produced from this crude by extraction alone at practical treat levels.

TABLE I

Feedstock	HVGO				
Pre-hydrocracking extraction:					
Water in phenol, vol. percent	6				
Temperature, ° F	190				
Treat, vol. percent	220				
Raffinate yield on HVGO, vol. percent	66.5				
DWO viscosity 210° F. SUS	87.1				
VI_E	80				
Hydrocracking:					
Temperature, ° F	740				
H_2 consumption, s.c.f./b	100				
Hydrocrackate boiling range, ° F	IBP-700	700-925	700-975	925-975	975+
Yield on hydrocracking, vol. percent	40.0	23.3	39.2	15.9	21.5
DWO viscosity 210° F., SUS		43.2	48.5	60.9	84.4
VI_E		105	106	101	100
Post-hydrocracking extraction:					
Water in phenol, vol. percent		3	3	3	3
Temperature, ° F		140	140	140	170
Treat, vol. percent		75	75	75	360
Raffinate yield on extraction, vol. percent		87.7	89.6	96.2	80.4
DWO Yield on HVGO, vol. percent		11.8	19.9	8.4	9.0
Viscosity 100° F. SUS		146.3	223	435	751
Viscosity 210° F. SUS		43.6	49.1	60.7	79.4
VI_E		113	113	102	104
Color, ASTM		1.0	1.0	L1.5	
U.V. stability		Pass		Pass	
Extract yield on HVGO, vol. percent		1.9	2.7	0.4	2.8
DWO viscosity 210° F. SUS		42.9	47.0	68.7	81.9
VI_E		61	75	57	80

The extract from the post-hydrocracking extraction exhibits a viscosity index of 57 to 80 compared to 47 for the raw HVGO. Recycling this high quality extract to the hydrocracker feed will increase the overall yield of lubes and fuels by 0.4 to 2.8 vol. percent on HVGO depending on the lube cut being considered with very little extra demand on the hydrocracking operation. It is estimated that about one-half of this yield gain will appear as high viscosity index lube.

EXAMPLE 2

The processing sequence described in Example I was applied for upgrading South Louisiana DAO to high quality UV stable lubes as shown in Table II. In this case high viscosity index lube yields of 60 vol. percent and 49 vol. percent on hydrocracker feed and DAO resulted from the combination process. Again, lube and fuels yield advantages would result from recycling the extract from the post-hydrocracker extraction to the hydrocracker feed. For the case of recycling the 700–1000° F. extract, the lube yield advantage over the non-recycle process would be approximately 3 vol. percent.

TABLE II

Feedstock	DAO		
Pre-hydrocracking extraction:			
Water in phenol, vol. percent	6		
Temperature, ° F	190		
Treat, vol. percent	240		
Raffinate yield on DAO, vol. percent	81.6		
DWO viscosity 210° F. SUS	249		
VI_E	83		
Hydrocracking:			
Temperature, ° F	835		
H_2 consumption, s.c.f./b	220		
Hydrocrackate boiling range, ° F	IBP-700	700-1,000	1,000+
Yield on hydrocracking, vol. percent	15.9	21.1	66.0
DWO viscosity 210° F. SUS		49.2	152.9
VI_E		92	95
Post-hydrocracking extraction:			
Water phenol, vol. percent		3	3
Temperature, ° F		150	200
Treat, vol. percent		300	75
Raffinate yield on extraction, vol. percent		58.1	95.4
DWO yield on DAO, vol. percent		8.6	40.8
Viscosity 100° F. SUS		280	2,454
Viscosity 210° F. SUS		52.0	151.5
VI_E		106	97
Color, ASTM		L1.5	L5.5
U.V. stability		Pass	Pass
Extract yield on DAO, vol. percent		7.2	2.5
DWO viscosity 210° F. SUS		50.0	137.7
VI_E		53	23

EXAMPLE 3

The pre-hydrocracking extraction and hydrocracking operations in this example are identical to those described in Example 1. In this case the hydrocrackate was extracted as a broad cut lube rather than extracting the vacuum distillates separately as in Example 1. As was described hereinabove, such a broad cut processing sequence reduces intermediate tankage requirements and production losses due to transient operation. This process produced 38 vol. percent and 26 vol. percent based on hydrocracker feed and HVGO, of 102 to 112 viscosity index UV stable lubes (Table III). In this case the post-hydrocracker extract was of higher quality (84 VI_E) than the feed to the hydrocracker (80 VI_E) and lube yield advantages of about 5 vol. percent would result from recycling this extract to the hydrocracker feed.

TABLE III

Feedstock	HVGO	
Pre-hydrocracking extraction:		
Water in phenol, vol. percent	6	
Temperature, ° F	190	
Treat, vol. percent	220	
Raffinate yield on HVGO, vol. percent	66.5	
DWO viscosity 210° F. SUS	87.1	
VI_E	80	
Hydrocracking:		
Temperature, ° F	740	
H_2 consumption, s.c.f./b	100	
700° F. plus yield on hydrocracking, vol. percent	60.8	
DWO viscosity 210° F. SUS	50.9	
VI_E	107	
Post-hydrocracking extraction:		
Water in phenol, vol. percent	1	
Temperature, ° F	170	
Treat, vol. percent	150	
700° F. plus raffinate yield on extraction, vol. percent.	78.2	
DWO viscosity 210° F. SUS	61.1	
VI_E	109	
700° F. plus extract yield on HVGO, volume percent.	8.8	
DWO viscosity 210° F. SUS	57.0	
VI_E	84	
Lube product boiling range, ° F	700-900	900+
DWO yield on HVGO, vol. percent	5.2	20.3
Viscosity 100° F. SUS	138	657
Viscosity 210° F. SUS	43.0	73.2
VI_E	112	102
Color, ASTM	1.0	L5.0
U.V. Stability	Pass	Pass

EXAMPLE 4

In this example (Table IV) the post-hydrocracking broad cut extraction processing sequence has been demonstrated for upgrading South Louisiana DAO to 98–104 VI_E. Lube yields of 59 vol. percent and 48 vol. percent on hydrocracker feed and DAO result from the combination process. As was also illustrated in Example 3, the broad cut extraction processing produces a lube slate of desirable VI-viscosity distribution in a single-pass operation.

TABLE IV

Feedstock	DAO			
Pre-hydrocracking extraction:				
Water in phenol, vol. percent	66			
Temperature, °F	190			
Treat, vol. percent	240			
Raffinate yield on DAO, vol. percent	81.6			
DWO viscosity 210° F. SUS	249			
VI_E	83			
Hydrocracking:				
Temperature, ° F	735			
H_2 Consumption, s.c.f./b	220			
700° F. plus yield on hydrocracking, vol. percent	87.1			
DWO viscosity 210° F. SUS	154.2			
VI_E	97			
Post-hydrocracking extraction:				
Water in phenol, vol. percent	1			
Temperature, ° F	170			
Treat, vol. percent	200			
700° F. plus raffinate yield on extraction, vol. percent	84.8			
DWO viscosity 210° F. SUS	113.1			
VI_E	101			
700° F. plus extract yield on DAO, vol. percent	10.8			
DWO viscosity 210° F. SUS				
VI_E				
Lube product boiling range, ° F	700-925	700-1,000	925-1,000	1,000+
DWO yield on DAO, vol. percent	3.9	8.2	4.3	40.0
Viscosity 100° F. SUS	165.8	220	462	2300
Viscosity 210° F SUS	44.8	48.1	61.6	147
VI_E	100	102	101	98
Color, ASTM	L2.0	L2.5	L2.0	5.0
U.V. Stability	Pass			Pass

EXAMPLE 5

For hydrocracking 83 VI_E South Louisiana DAO raffinate over a conventional commercial sulfided nickel-molybdenum on silica-alumina base catalyst, hydrogen consumption can be minimized in the hydrocracking step with no lube yield or viscosity index deficit resulting from lowering the reaction pressure. As shown in Table V, for fixed hydrocracking temperature and space velocity, hydrogen consumption is reduced from 220 s.c.f./b. to 50 s.c.f./b. by reducing the reaction pressure from 1500 p.s.i.g. to 600 p.s.i.g.; the viscosity index of the product boiling above 1050° F. remaining constant at 90.

TABLE V

Hydrocracking conditions:			
Temperature, ° F	721	720	723
Liquid space velocity, v./v./hr	0.5	0.5	0.5
Pressure, p.s.i.g	600	1,000	1,500
H_2 consumption, s.c.f./b	50	152	220
Dewaxed oil inspections: 1,050° F. plus yield on DAO, wt. percent	45	46	47
Viscosity 210° F., SUS	227	213	211
VI_E	90	90	90

What is claimed is:

1. In a process for the production of high VI, UV stable lubricating oils, the steps in combination of:

(a) solvent extracting a lubricating oil stock with a solvent having preferential solubility for aromatics, thereby forming extract and raffinate phases;

(b) hydrocracking at least a portion of said raffinate phase, in a hydrocracking zone at mild hydrocracking conditions, with hydrogen in the presence of a hydrocracking catalysts, thereby forming a hydrocrackate product containing lube oil components;

(c) solvent extracting at least a portion of said hydrocrackate with a solvent having preferential solubility for aromatics thereby forming extract and raffinate phases, and

(d) recycling the extract phase, substantially free of solvent, from step (c) to step (b) wherein it is introduced into the hydrocracking zone either separately or in combination with the raffinate from step (a).

2. The process of claim **1** wherein the solvent used in step (a) is the same as that used in step (c) and is selected from the group consisting of furfural, acetophenone, liquid SO_2, acetonitrile, phenol, n-methyl-2-pyrrolidine, dimethyl formamide and mixtures thereof.

3. The process of claim **2** wherein the solvent is phenol or furfural.

4. The process of claim **3** wherein the solvent is phenol and wherein the phenol is admixed with a minor amount of water ranging between about 0.1 and 15 LV percent, based on solvent mixture.

5. The process of claim **4** wherein the solvent extraction temperature in step (a) ranges between about 120 and 200° F.

6. The process of claim **1** wherein the hydrocracking operation is conducted at a temperature ranging between about 650° and 825° F., at a pressure below about 1500 p.s.i.g. and at a liquid hourly space velocity ranging be-

tween about 0.2 and 4 v./v./hr. and where the catalyst comprises a major amount of an amorphous component and a minor amount of a hydrogenation component selected from the group consisting of the Group VI—B and VIII transition metals, their oxides and sulfides and mixtures thereof

7. The process of claim 6 wherein the catalyst contains, in addition to the amorphous component and the hydrogenation component, less than about 25 wt. percent based on total catalyst of a crystalline aluminosilicate component.

8. The process of claim 1 wherein the solvent extraction temperature in steps (a) and (c) range between about 0° and 350° F.

9. The process of claim 1 wherein the solvent/oil liquid volume ratios in step (a) and (c) range between about 6:1 and 0.25:1.

10. The process of claim 1 wherein the hydrocrackate is separated into a broad cut fraction boiling above about 650° F., said fraction containing substantially all of the lube oil components in said hydrocrackate and, thereafter, solvent extracting said fraction in step (c).

11. The process of claim 1 wherein the catalyst comprises a major amount of an amorphous component and

minor amounts of (1) a hydrogenation component selected from the group consisting of the Group VI–B and VIII transition metals, their oxides and sulfides and mixtures thereof and (2) P_2O_5.

12. The process of claim 1 wherein the catalyst comprises a major amount of an amorphous component and minor amounts of (1) a hydrogenation component selected from the group consisting of the Group VI–B and VIII transition metals, their oxides and sulfides and mixtures thereof, (2) a crystalline aluminosilicate component and (3) P_2O_5.

References Cited

UNITED STATES PATENTS

3,579,437	5/1971	Wentzheimer et al.	208—18
3,256,175	6/1966	Kozlowski et al.	208—87
3,652,448	3/1972	Cummins	208—87

HERBERT LEVINE, Primary Examiner

U.S. Cl. X.R.

208—18