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12/20/2001 - 11:06:21

(12) **Patent:**

(11) **CA 965030**

(54) PREPARATION OF HIGH VISCOSITY INDEX LUBRICATING OILS

(54)

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(45)		**Mar. 25, 1975**
(22)		
(43)		
(52)		**196/54**
(51)		**N/A**
		No
(30)		**None**
		N/A
		Unknown

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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This invention relates to the preparation of high V.I. lubricating oils by two-stage hydroprocessing.

The characteristics of satisfactory lubricating oils and specific types of lubricating oils are known in the art. To provide lubricating oils which can be used for known and ever-changing specific purposes and have acceptable characteristics, the refining processes generally require a careful selection of the crude base stock and an elaborate combination of refining steps sufficient to produce the desired product.

It is desirable therefore to be able to supply the demands of the consumer by utilizing as broad a feed spectrum as possible and particularly less desirable feeds in a refining process which minimizes the refining steps necessary to obtain a desired valuable product such as lubricating oil of high V.I. in good yields.

It is known that improved lubricating oils can be prepared by a plural stage hydrogenation process in which lubricating oil fractions are subjected to hydrogenation under different conditions prior to the hydrogenation designed to open the naphthene rings in polycyclic naphthenes. Such a process is taught by U.S. Patent 2,915,452 issued December 1, 1959, to Fear which uses any suitable metallic hydrogenating catalyst in each stage, although cobalt molybdate is preferred.

This process is limited in that its feedstocks are restricted to lubricating oil fractions and the catalysts used in the second stage are insufficiently selective to give a large yield of high V.I. oil.

In accordance with the invention, a two-stage hydrocracking process is employed to produce a high quality lubricating oil characterized by high V.I. The process comprises contacting a petroleum feedstock having an initial boiling point

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above 340°C. at atmospheric pressure in a first stage with hydrogen and a catalyst comprising a hydrogenation component selected from the group consisting of metals of Group VIB and non-noble metals of Group VIII of the Periodic Table, their oxides and sulfides and mixtures thereof, and an amorphous component at a temperature ranging from about 340°C. to about 450°C. at a pressure range from about 1500 by 5000 psig and at a liquid hourly space velocity ranging from about 0.1 to about 10.0 V/V/Hr., contacting at least a portion of the first stage effluent in a second stage under less severe conditions of temperature and space velocity with hydrogen and a catalyst different from the first stage catalyst and comprising a crystalline aluminosilicate zeolite component said zeolite having a silica to alumina ratio ranging from 2.5 to 10, and a hydrogenation component selected from the group consisting of the metals of Groups VIB and VIII of the Periodic Table, their oxides and sulfides and mixtures thereof, said second stage contacting being conducted at a temperature ranging from about 230° to about 370°C., at a pressure ranging from about 1500 to about 5000 psig, and at a liquid hourly space velocity ranging from about 0.1 to about 10.0 V/V/Hr., and recovering a lubricating oil.

The first stage effluent is contacted in the second stage with hydrogen and a catalyst comprising a crystalline aluminosilicate zeolite component and a hydrogenation component under conditions for selectively converting a substantial portion of the polycyclic naphthenes present in the feedstock to single ring naphthenes and isomerizing a substantial portion of the isomerizable paraffins present in the feedstock. The second stage conditions are selected so that less than about 15 wt. %, preferably less than about 10 wt. %, conversion, based on feed to the second stage, at 340°C. and light products

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occurs.

Suitable process feedstocks include hydrocarbons, mixtures of hydrocarbons and, particularly, hydrocarbon fractions, the predominant portions of which exhibit initial boiling points above about 340°C. Preferably less than about 5 volume percent of the charge oil has a boiling point below about 370°C. Unless otherwise indicated, boiling points are taken at atmospheric pressure. Nonlimiting examples of useful process feedstocks include crude oil vacuum distillates from paraffinic or naphthenic crudes, i.e. waxy crudes, 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. In general the feedstock has a Saybolt Universal viscosity at 38°C. of at least about 50 seconds and more preferably at least about 100 seconds. Usually the feedstock will have a viscosity of not more than about 300 Saybolt Universal seconds at 100°C.

The first stage hydrogenation is conducted at a temperature ranging from about 340°C. to about 450°C., preferably from about 340°C. to about 412°C. The pressure ranges from about 1500 to about 5000 psig. The liquid hourly space velocity (V/V/Hr.) ranges from about 0.1 to 10.0, preferably from about 0.2 to 2.0. The hydrogen feed rate is between about 1000 and 10,000 SCF/bbl., preferably between about 2000 and 10,000 SCF/bbl. While the first stage reaction mechanism is not well-defined, it is postulated that conversion of a substantial portion of the aromatic compounds present in the feed, which would otherwise form undesirable products in the subsequent hydrogenation, into compounds which do not form undesirable products in the subsequent step, e.g., polynuclear naphthenes and the like occurs.

The catalyst in the first stage comprises one or more Group VIB or VIII metals of the Periodic Table such as cobalt, molybdenum, nickel, tungsten and the like, preferably in the combined state as the sulfide or oxide or mixtures thereof. The Periodic Table referred to herein is that described in "The Encyclopedia of Chemistry," Reinhold Publishing Corporation, 2nd Edition (1966) at 793. Thus, catalysts such as the sulfides of Ni-W, Ni-Mo, Co-Mo, Co-W or mixtures thereof on a suitable carrier such as bauxite, alumina, silica, silica-alumina and the like are contemplated as first stage catalysts. Preferably, the carrier will be a nonzeolite, which may further comprise minor amounts of a crystalline aluminosilicate zeolite, for example, less than 20 wt. %, preferably less than 9 wt. %, most preferably less than 5 wt. %, based on the total weight of the catalyst. A preferred catalyst comprises the sulfide of Ni-W on Al_2O_3.

The second stage of the process is conducted at less severe conditions than the first stage. The temperature ranges between about 230°C. and about 340°C., although temperatures as high as about 370°C. may be used. The feed rate is generally higher than the first stage feed rate ranging between about 0.1 and 10 V/V/Hr., preferably between about 0.5 and 5 V/V/Hr. Pressure and recycle gas rate are about the same as in the first stage.

During the second stage hydrogenation, conversion to products boiling below 340°C. is kept below about 15 wt. % preferably below about 10 wt. %, while the polynuclear naphthenes, including those polynuclear naphthenes which existed in the original feedstock and those formed in the first stage, are converted largely to single-ring naphthenes. The conversion of polynuclear naphthenes to single ring naphthenes results in a large increase of the V.I. of the product. Also in the second stage, the normal paraffins are extensively isomerized to branch chain structures thereby increasing lube yield and V.I. of the product. It is noted that the explanation for the observed V.I. increase is speculative, in view of the fact that the reaction chemistry is not well defined.

The second stage catalyst is a zeolite-base catalyst, preferably a faujasite-base catalyst. The alkali metal atoms, silicon, aluminum and oxygen in the zeolite 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. While both natural and synthetic faujasite can be used, the latter is more readily accessible and is therefore preferred. Methods for their preparation are described in the literature.

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 can then be heated at elevated temperatures to drive off ammonia, thereby producing the hydrogen form of the material. Alternatively, the ammonium ion-exchanged form can be back-exchanged with solutions of the desired salts thereby producing the polyvalent metal form.

The form of the hydrogen aluminosilicate can be employed as such, or can be subjected to a steam treatment at elevated temperatures 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.

Suitably, the exchanged polyvalent metals are transition metals and are selected from Groups VIB and VIII of the Periodic Table. Preferred metals include nickel, molybdenum, tungsten and the like.

In addition to the ion-exchanged polyvalent metals, the aluminosilicate may contain as nonexchanged constituents one or more hydrogenation components comprising the transitional metals, preferably selected from Groups VIB and VIII of the Periodic Table and their oxides and sulfides. Such hydrogenation components may be combined with 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. In one embodiment, the catalyst comprises a faujasite base impregnated with a metallic hydrogenation component comprising Group VIB and/or Group VIII metals and/or the oxides and/or sulfides of said metals such as cobalt, nickel, tungsten, molybdenum, the platinum group metals and mixtures thereof. Thus, mixtures of sulfides of metals such as nickel-tungsten, nickel-molybdenum, cobalt-tungsten and cobalt-molybdenum, are contemplated.

The silica:alumina mole ratio of the second stage catalyst is greater than about 2.5 and preferably ranges between about 2.5 and 10, most preferably between about 3 and 6. The pore diameter size of the crystalline aluminosilicate can range from about 5 to 15 Å, and preferably from about 6 to 13 Å. The alkali metal oxide content of the catalyst should be less than about 2.0 wt. %, preferably less than 0.5 wt. %, based on the total aluminosilicate composition.

In one preferred embodiment the catalyst comprises a noble metal such as palladium or platinum on H-faujasite.

In the most preferred embodiment, the catalyst used in the second stage of the process comprises a mixture of (1) an amorphous component, (2) 10 to 70 wt. % (based on total catalyst) of a crystalline aluminosilicate component and (3) a hydrogenation component. Catalysts of this type are exemplified and described more completely in U.S. patents 3,547,807, 3,304,254 and 3,304,808.

Preferably, the catalyst comprises a mixture of (1) a major component comprising an amorphous support upon which is deposited one or more transitional metal hydrogenation components, preferably selected from Groups VIB and VIII metals of the Periodic Table and/or the oxides and/or sulfides thereof and (2) a minor component comprising a crystalline aluminosilicate zeolite having a silica:alumina mole ratio greater than about 2.5 and an alkali metal content of less than 2.0 wt. % (as alkali metal oxide) based on the final aluminosilicate composition, and containing deposited thereon or exchanged therewith one or more transitional metal hydrogenation components preferably selected from Group VIB and VIII metals of the Periodic Table and/or the oxides and/or sulfides thereof.

The amorphous component (support) of the second stage catalyst can be one or more of a large number of non-crystalline materials having high porosity. The porous support is desirably inorganic; however, it may be an organic composition. Representative porous support materials include diatomaceous earth; sintered glass; firebrick; organic resins; alumina; silica-alumina; zirconia; titania; magnesia metal halides; sulfates; phosphates; silicates; and the like. Preferably, alumina or silica-stabilized alumina (desirably 1-5 wt. % silica based on total support) is employed.

Suitable hydrogenation components that can be added to the porous support are the transitional metals and/or the oxides and/or sulfides thereof. The metals are preferably selected from Groups VIB and VIII of the Periodic Table and are exemplified by chromium, molybdenum, tungsten, cobalt, nickel, palladium, platinum, iron, rhodium, and the like. The metals, metal oxides or sulfides may be added alone or in combination to the support. The preferred hydrogenation components are nickel, tungsten and molybdenum metals and the oxides and/or sulfides thereof. In use the hydrogenation components probably exist in a mixed metal/metal oxide or metal/metal oxide/metal sulfide form. The hydrogenation components are added to the support in minor proportions ranging from about 1 to 25% by weight based on the total amorphous component of the second stage catalyst. The hydrogenation components that are deposited on the porous support can be the same as or different from the hydrogenation components used in the crystalline aluminosilicate component of the second stage catalyst.

The amorphous component of the second stage catalyst can be prepared in any suitable manner. Thus, for example, if silica-alumina is employed, the silica and alumina may be mechanically admixed or, alternatively, chemically composited with the metal oxides such as by cogelation. Either the silica or alumina may, prior to admixture with the other, have deposited thereon one or more of the metal oxides. Alternatively, the silica and alumina may first be admixed and then impregnated with the metal oxides.

A preferred amorphous component of the second stage catalyst comprises alumina containing nickel oxide and tungsten oxide or molybdenum oxide. The weight ratio of nickel oxide to tungsten oxide or molybdenum oxide can range from about 1:25 to 25:1 and preferably from 1:4 to 1:6. Finally, the weight ratio of the support to total metal oxide can range from about 20:1 to 1:20 and preferably from 4:1 to 8:1.

The amorphous component and the crystalline aluminosilicate component of the second stage 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.

It is noted that conversion, in the second stage, of hydrocarbon components boiling above 340°C., to materials boiling below 340°C. is preferably maintained below about 15 wt. %,based on second stage feed.

The product effluent of the two-stage process of this invention is separated by conventional techniques such as by distillation into desired fractions, e.g. 160°C. and lighter (if any), 160-290°C., 290-340°C., 340-427°C. and 427°C. and higher. The fraction boiling 340-427°C. may be recycled to the first stage for further V.I. improvement. The 340-427°C. fraction and the 427°C+ fractions are usually combined and dewaxed to produce the desired high V.I. lubricating oil. Removal of the waxy material in desired amounts is accomplished by any of the well-known techniques used to give desired low pour point oils. Dewaxing to obtain exceptionally low pour points is essential for some lubes and may be accomplished using one or more steps of solvent extraction with a solvent such as propane, methyl ethyl ketone, toluene and others with suitable chilling and filtering between steps followed by recovery of the solvent by distillation. This dewaxing step is part of this invention only to the extent required to obtain desired pour point lube oils.

If desired, the combined dewaxed fraction may be further upgraded by treating it with anhydrous HF as described in U.S. 3,463,724 or with any other similar treating agent known in the art.

In carrying out this invention any suitable equipment arrangement may be used for contacting the oil with the catalyst in the presence of excess hydrogen in either stage. For example, the catalyst may be maintained as one or more fluidized beds, gravitating beds, or fixed beds of small particles, through which the oil and hydrogen are passed, upflow or downflow, concurrent or countercurrent. A slurry of catalyst in oil may also be used. Vapor phase, liquid phase, or mixed phase contacting may be used. Usually the catalyst is in the form of small pellets or rod-like extrusions contained in a reactor as a plurality of fixed beds and the oil and hydrogen are passed together downflow through the beds at controlled temperature, pressure and flow rates. The process may be conducted as a batch or continuous operation. The effluent is cooled to separate product oil from hydrogen-rich gas which is recycled.

Contact time of the catalyst and feed in the first and second stages is subject to wide variation, being dependent in part upon the temperature and space velocities employed. In general feed rates in the first stage may range, for example, from 0.1 to 10 V/V/Hr. and preferably from 0.2 to 2 V/V/hr. Contact times in the second stage may range from 15 to 500 minutes and preferably from 60 to 120 minutes.

The invention will be described with reference to the drawing which is a flow diagram of a preferred embodiment.

Referring to the drawing in detail, a feedstock consisting of a blend of 60 wt. % deasphalted oil and 40 wt. % heavy vacuum gas oil each obtained from West Texas crude is introduced by way of line 1 and line 2 into reaction zone 3. Hydrogen is added therein through line 2. The reaction zone contains an amorphous catalyst of the type as hereinbefore described. The molar ratio of hydrogen to feedstock is maintained in the first stage between about 1:1 and 25:1. The temperature in zone 3 is maintained between about 371 and 427°C. The hydrogen partial pressure ranges between about 1000 and 2500 psig and the space velocity of fresh feed ranges between about 0.3 to 1.5 (v/v/hr.). After about 15-500 minutes of contacting in zone 3, the liquid product is removed via line 4 and introduced into high pressure separator 5 wherein excess hydrogen and byproducts such as ammonia and hydrogen sulfide are removed via line 6. It is noted that, alternatively, separator 5 may be removed from the system and the liquid product from reaction zone 3 introduced directly into reaction zone 9 via line 4.

In the present embodiment, the liquid is removed from separator 5 and introduced into zone 9 via line 7. Hydrogen is admitted via line 8 into reaction zone 9 which contains an amorphous base-crystalline aluminosilicate catalyst of the type hereinbefore described.

The reaction conditions within zone 9 include a reaction temperature in the range of about 260 to 316°C., a hydrogen partial pressure in the range of about 1000 to 2500 psig and a liquid hourly space velocity of second stage feed in the range of about 0.3 to 1.5 v/v/hr. After about 15 to 500 minutes of contacting, the liquid product is removed via line 10 and introduced into separator 11 wherein excess hydrogen and byproducts such as ammonia, H_2S and the like are removed via line 12 while the liquid product therefrom is removed via line 13 and introduced into distillation zone 14.

The liquid product is distilled at atmospheric pressure to remove overhead a lower boiling cut with a 5-95% boiling point range of about 93 to 375°C. The bottoms product is removed from zone 14 via line 16 and may be introduced into distillation zone 17 wherein it is distilled in vacuo to recover various lube distillate cuts via lines 18, 19 and 20. The resulting lube distillates comprise a first cut with a 5-95% boiling point range between about 354 to 510°C., a second cut with a 5-95% boiling point range between about 410 to 599°C., and a third cut with an initial boiling point above about 500°C. The lube cuts may be further processed such as by dewaxing in dewaxer 21 if lower pour point products are desired to yield dewaxed fractions through lines 22, 23 and 24.

The invention will be further understood by reference to the following examples which include preferred embodiments of the invention.

EXAMPLE 1

A mixture (boiling 340°C.+) of 60% deasphalted oil and 40% heavy vacuum gas oil both from West Texas sour crude was first processed at nonconversion conditions, 360°C., 2500 psig, 0.25 V/V/Hr. with 4000 $SCFH_2$ per bbl. of feed over a $NiW-Al_2O_3$ catalyst (sulfided) to saturate the aromatics present in the feed. The product was stabilized at atmospheric conditions and the stabilized product was passed over Pd on hydrogen-faujasite catalyst at similar conditions except for temperature and feed rate. The data shown in Table I were obtained.

TABLE I

	1st Stage	2nd Stage			
Catalyst	Ni-W-Alumina	Ni-W-Alumina	Pd-H-Faujasite		
Run	1	2	3	4	5*
Process Conditions					
Temperature, °C.	360	410	260	310	300
Pressure, Psi	2500	2500	---------2500---------		
Gas Rate, SCF/Bbl.	4000	4000	---------4000---------		
V/V/Hr.	0.25	0.53	1.6	2.8	3.6
Lube Yield, 650°F.+, Wt.%	95	73.1	93.0	91.7	70.7(68.5)**
Lube Inspections					
340-427°C. Fraction, Wt.%		16.6	9.6	9.7	11.9**
°API		31.3	29.6	29.6	
V.I. (Waxy)		91	------76-----		
427°C.+ Fraction, Wt.%		56.5	83.4	82.0	56.6**
°API	28.1	30.5	29.0	31.0	30.0
V.I. (Waxy)	--	114	102	111	93
V.I. (Est. on DWO)		102	90	99	81
VSU @ 100°F.		620	790	778	1220
VSU @ 210°F.		71.5	89.8	90.0	96.8
N_2, ppm	7	--	--	1.7	--
S, ppm	16		--	1.0	--

* 427°C.+ fraction, from previous 2 runs with Pd on faujasite catalyst, used as feed.

** Original feed basis, only 2.8 wt.% of recycle feed was converted to 340-427°C. lube fraction.

The data of Table I show that very high V.I. oils can be obtained by a two-stage process in which a faujasite-base catalyst is used in the second stage provided the conversion to 340°C. and lighter products be kept under 15 wt. %, based on second stage feed. If a nonzeolitic catalyst is used in the second stage, high V.I. oils can be obtained only at a sacrifice in yield. (Compare column 2 with columns 3 and 4 of Table I). When the conditions in the second stage are set so that substantial cracking to lighter products occurs, both yield and V.I. of the lube oil product decrease (see column 5 as compared to column 2 of Table I). Obviously, the V.I. level of the 340-427°C. fraction can be increased by recycling with the result that the V.I. will be 91 or greater, in which case, dewaxing of the combined fractions gives greater overall lube yield of excellent V.I.

EXAMPLE 2

A blend of 60 liquid volume % deasphalted oil (DAO) having an initial boiling point above about 500°C. and 40 liquid volume % heavy vacuum gas oil (HVGO) with a 5-95% boiling point range between about 410 to 599°C., each secured from West Texas Sour Crude (WTS) was treated in a two-step process as shown in the drawing. Detailed feedstock inspection data is shown in Table II.

The first and second stage reactors were 1.25" in diameter with 0.25" central thermocouple well and contained catalyst beds 44" long. The reactors were operated in a single pass, isothermal, concurrent-downward flow operation.

A catalyst comprising nickel oxide and molybdenum oxide on a silica-alumina support was used in the first stage. The catalyst comprised about 4.5 wt. % of nickel oxide and 13 wt. % of molybdenum oxide based on total catalyst. The molar ratio of silica to alumina was about 1:5. The catalyst was presulfided by conventional techniques prior to use, i.e.

treatment with H_2S.

Reaction conditions in the first stage are shown in Table III. The total liquid product from the first stage reaction zone was passed through a high pressure separator wherein the excess hydrogen and byproducts, i.e. H_2S, ammonia and the like, were separated. Thereafter, the liquid was introduced into the second stage of the process. It is noted that Run 5 was conducted in a "sour" environment, that is, in the presence of H_2S and ammonia.

The second stage catalyst comprised a molecular sieve component and an amorphous component. The sieve component comprised about 20 wt. % of the total catalyst and consisted of a nickel-exchanged synthetic faujasite. The amorphous component comprised an alumina support and the sieve/support combination was believed to have been impregnated, after admixture, with NiO and WO_3. The catalyst was sulfided with H_2S prior to contacting with the first stage effluent, thereby converting at least a portion of the NiO and WO_3 to their respective sulfides. The total amount of nickel present in the complete catalyst prior to sulfiding was 4.9 wt. %, (calculated as nickel oxide), while the total amount of WO_3 present in the catalyst prior to sulfiding was 21.5 wt. %, based on total catalyst.

The second stage was operated at several different temperatures ranging from 260 to 316°C. in order to determine the effect of temperature on the process efficiency. Other operational parameters in the second stage are shown in Table III.

The products from the second stage reactor were subsequently distilled and dewaxed to yield a first fraction with a 5-95% boiling point range of about 371 and 496°C., a second fraction with a 5-95% boiling point range of about 496 and 566°C., and a third fraction with an initial boiling point above about 566°C.

In Tables III and IV is shown the effect of the subject two-stage hydrocracking process on lube oil color and VI_E

distribution.

From the data it is evident that a significant product color improvement was obtained with the use of the second stage treatment. Additionally, it is noted that the VI_E distribution after second stage treatment was not only more uniform but approached higher and more desirable values.

Moreover, it was determined that a second stage temperature of about 316°C. was most desirable in achieving the beneficial results of the subject process.

Silica gel-liquid phase chromatographic separation data on the dewaxed lube products from the above experiment are tabulated in Table V.

It is noted that lube cuts from the first stage reactor contain about 5.3 to 17.8 wt. % aromatic and polar compounds, depending on the boiling point range of the lube cut. The concentration of these compounds is reduced considerably in all lube cuts following second stage treatment. The greatest improvement was obtained in Run 1 wherein the second stage reaction temperature was maintained at approximately 316°C. However, it is noted that there was appreciable improvement even in Runs 2-4 where the reaction conditions were less severe. The substantial conversion of aromatic and polar compounds from the lube cuts accounts for the excellent color and UV stability of the lube oil products.

UV stability data relating to a one-step operation vis-a-vis the two-step operation of the subject invention is summarized in Table VI. The data refer to lube cuts obtained from Example 2. The results are compared to the minimum time requirements established for lubes prepared via conventional processes, i.e. hydrocracking followed by solvent extraction.

It is noted that there was a significant increase in the overall UV stability of lube oils prepared via the two-stage process of the subject invention. Moreover, the results of the two-stage process compare favorably with those of the conventional operation wherein an expensive solvent extraction step is used following a hydrocracking operation.

An unexpected result from use of the instant process involves the formation of significant amounts of jet fuels along with the lube oil products. The process, therefore, allows the flexibility to produce various lube/fuels combinations depending on demand. In this respect Table VII summarizes the composition of the total liquid product from the experiments.

A yield of 17.2 wt. % of jet fuels, i.e. boiling point 177-268°C., based on total feed to the first stage, was obtained in Run 1 at a reaction temperature of approximately 316°C. The results suggest inferentially that higher conversion to jet fuels can be obtained if more severe reaction conditions are employed.

In summary then, the subject process affords the following advantages relative to conventional combination hydrocracking/extraction processes:

1. The preparation of lube oils with low color intensity.

2. The preparation of lube oils with UV stability.

3. The preparation of lube oils with high VI_E and substantially uniform VI_E distribution.

4. The production of substantial amounts of jet fuel as by-product.

EXAMPLE 3

Several experiments were conducted wherein the first and second stage catalysts were varied to determine the effect of catalyst structure on the overall process efficiency. In the first set of experiments the first stage catalyst was identical to that used in Example 2. The second stage catalyst comprised a mixture of 5 wt. % based on total catalyst nickel-exchanged faujasite and 95 wt. % based on total catalyst of P_2O_5 and silica-stabilized alumina, the faujasite/stabilized alumina combination containing NiO and MoO_3 that were believed to have been deposited thereon after admixture of the faujasite and alumina. The results of the experiments along with the reaction conditions under which the experiments were performed are displayed in Tables VIII, IX and X.

Comparing the performance of the second stage catalyst used in Examples 2 and 3, it is clear that the 20 wt. % sieve catalyst is superior vis-a-vis the low sieve-content catalyst in providing (1) lube products of high uniform viscosity index distribution and (2) lube products of low color intensity. Specifically, comparing Runs 3 and 4 in Table IX with Run 1 in Table III, the following points are noted:

1. Lower second stage reaction temperatures, i.e. 316°C. versus 372°C., were required in Example 2 to attain high uniform viscosity index distributions.

2. Color intensities of the lube oil products obtained by use of the low sieve-content catalyst were quite high vis-a-vis the 20 wt. % sieve catalyst.

3. Although not shown, UV stabilities of the lube oil products derived from use of the low sieve-content catalyst were quite poor vis-a-vis the 20 wt. % sieve catalyst. Thus, the former lube oil products rapidly discolored and precipitated sludge in 2 to 4 days as compared with 6 to 26 days for the latter prepared lube oil products.

4. The yield of jet fuel products with boiling points ranging between 177 and 268°C. was generally quite low when the low sieve-content catalyst was used in the second stage of the process vis-a-vis the 20% sieve-containing

TABLE II

Feedstock Inspection Data

Feedstock	Blend[1]
V_{210}, SUS	159.1
Gravity, °API	19.6
RI at 60°C.	1.5054
C, wt. %	85.9
H, wt. %	12.2
S, wt. %	1.37
N, ppm	1100
Fe, ppm	1.7
Ni, ppm	0.7
V, ppm	1.0
Dewaxed Oil	
Dry Wax, wt. %	9.2
V_{100}, SUS	6035
V_{210}, SUS	194
VI_E	60
Distillation Cuts - Inspection Data	
Initial - 496°C. wt. %	9.6
Dry Wax, wt. %	8.4
V_{100}, SUS	928
V_{210}, SUS	67.0
VI_E	25
Color, ASTM	D8
496°C - 566°C., wt. %	45.2
Dry Wax, wt. %	9.6
V_{100}, SUS	3475
V_{210}, SUS	131.8
VI_E	42
Color, ASTM	D8
566°C.+, wt. %	45.2
Dry Wax, wt. %	9.6
V_{100}, SUS	17673
V_{210}, SUS	402
VI_E	77
Color, ASTM	D8

(1) Blend of 40 LV% WTS-HVGO and 60 LV% DAO.

TABLE III

TWO-STAGE LUBE HYDROCRACKING

TOTAL LIQUID PRODUCT INSPECTIONS

Stage	Feed(1)	1st	2nd				
Operation		Pure H_2					
Run No.	--	--	1	2	3	4	5(2)
Reaction Temp. °C.	--	388	316	260	288	288	318
Space Velocity, v/v/hr.	--	0.5	0.5	0.5	0.5	0.5	0.49
Pressure, psig H_2	--	2500	2500	2500	2500	1500	2500
Gas Rate, SCF H_2/B	--	5000	5000	5000	5000	5000	5000
Average Catalyst Age, Hr.	--	394	105	154	194	231	619
Total Liquid Product							
Recovery on Feed, wt. % (first or second stage)	100	98	98	99	99	100	102
Gravity, °API	19.9	29.8	35.1	29.8	30.8	30.5	30.3
RI at 60°C.	1.5054	1.4675	1.4508	1.4655	1.4625	1.4641	1.4645
371°C. - Conversion(3) wt. %	--	17.3	38.0	18.9	20.6	19.0	16.6
Nitrogen, ppm	1900	6.1	<1	<1	--	--	--
Sulphur, wt. %	1.37	0.06	<0.06	<0.06	--	0.09	--
TLP Colour, ASTM(4)	D8.0	4.0	0.0	0.0	0.0	0.0	0.0

(1) WTS-3 feedstock (West Texas Sour 60% DAO Blend/40% HVGO).
(2) (Run in the presence of H_2 + NH_3 + H_2S, i.e. sour conditions) - 408 cc t-butyl mercaptan and 58 cc n-butylamine added/gal. feed to 2nd stage.
(3) Based on WTS-3 feed to first stage.
(4) Determined by method as described in ASTM Standards, 17, p. 567, Jan. 1967.

TABLE IV
TWO-STAGE LUBE HYDROCRACKING
LUBE INSPECTIONS

Stage	Feed(1)	1st	2nd				
Run No.			1	2	3	4	5(2)
371-496° Cut							
Yield on WTS-3 Feed, wt. %	9.6	28.3	18.7	23.2	23.9	24.4	25.8
Waxy Color, ASTM	-	<1.5	<0.0	-	-	-	-
Dry Wax on Lube Cut, wt. %	8.4	8.2	12.0	8.9	8.3	9.6	9.2
Dewaxed Oil: Yield on WTS-3, wt.%	8.8	26.0	16.5	21.2	22.0	22.1	23.4
Visc. 100°F., SUS	928	233	172	242	217	213	236
Visc. 210°F., SUS	67.0	46.9	44.6	42.5	46.5	46.0	47.1
VI_E(3)	25	76	98	77	83	80	77
Color, ASTM(4)	-	2.5	<0.5	<1.0	<0.5	<1.5	<1.5
496-566°C. Cut							
Yield on WTS-3 Feed, wt. %	45.2	28.3	22.7	32.8	31.3	30.2	33.2
Waxy Color, ASTM	D8	2.5	<0.5	-	-	-	-
Dry Wax on Lube Cut, wt. %	9.6	15.2	19.7	15.7	16.5	15.3	14.8
Dewaxed Oil: Yield on WTS-3, wt.%	40.9	24.0	18.2	27.6	26.1	25.6	28.3
Visc. 100°F., SUS	3475	947	768	910	883	846	921
Visc. 210°F., SUS	131.8	81.4	76.6	79.6	79.2	76.7	80.9
VI_E(3)	42	85	94	84	87	84	87
Color, ASTM(4)	D8.0	<4.5	1.0	<1.0	<1.0	<2.0	<2.5
566°C.+ Cut							
Yield on WTS-3 Feed, wt. %	45.2	26.1	20.6	25.1	24.2	28.1	24.4
Waxy Color, ASTM	D8	<6.5	<1.0	-	-	-	-
Dry Wax on Lube Cut, wt. %	9.6	18.8	21.9	22.5	19.8	19.5	19.3
Dewaxed Oil: Yield on WTS-3, wt. %	40.9	21.2	16.1	19.4	19.4	22.6	19.7
Visc. 100°F., SUS	17673	3005	2874	3133	3150	2820	3248
Visc. 210°F., SUS	402	171.5	172.9	176.8	178.6	165.0	179.4
VI_E(3)	77	97	101	97	98	97	97
Color, ASTM(4)	D8.0	<8.0	<1.5	<2.0	<2.5	2.5	<4.0

FOOTNOTES TO TABLE IV

(1) WTS-3 Feedstock (West Texas Sour 60% DAO Blend/40% HVGO).

(2) Run in the presence of $H_2 + NH_3 + H_2S$, i.e. sour conditions - 408cc t-butyl mercaptan and 58 cc n-butylamine added/gal. feed to 2nd stage.

(3) Determined by method as described in ASTM Standards, 17, p. 810, Jan. 1967, i.e. D 2270-64.

(4) Determined by method as described in ASTM Standards, 17, p. 565, Jan. 1967.

TABLE V

TWO-STAGE LUBE HYDROCRACKING

SILICA GEL SEPARATION OF DEWAXED LUBE PRODUCTS

1	Stage	1st. Stage	2nd Stage				
2	Feedstock	WTS-3	Total Liquid Product from 1st Stage				
3	Run No.		1(1)	2(1)	3(1)	4(1)	5(2)
4	Dewaxed 371-496°C. Cut (wt.%)						
5	Saturates	82.2	98.7	88.5	95.5	90.9	89.6
6	Aromatics	16.8	0.9	10.9	4.2	8.7	10.1
7	Polars	1.0	0.4	0.6	0.3	0.4	0.3
8	Dewaxed 496-566°C. Cut (wt.%)						
9	Saturates	89.2	98.7	92.4	95.8	93.2	93.1
10	Aromatics	10.1	1.1	7.1	3.9	6.4	6.5
11	Polars	0.7	0.2	0.5	0.3	0.4	0.4
12	Dewaxed 566°C.+ Cut (wt.%)						
13	Saturates	94.7	99.0	96.0	97.0	96.0	96.6
14	Aromatics	4.8	0.8	3.5	2.6	3.5	3.2
15	Polars	0.5	0.2	0.5	0.4	0.5	0.2

16 (1) In the presence of pure hydrogen.
17 (2) Run in the presence of $H_2 + NH_3 + H_2S$, i.e. sour conditions.

TABLE VI

UV STABILITY DATA[1]

Dewaxed Lube	1st. Stage	1st Stage/ 2nd Stage	Conventional Hydrocracking followed by Solvent Extraction[4]
371-496°C. cut	3[2]	6[3]	7
496-566°C. cut	3[2]	8[3]	10
566°C.+ cut	2[2]	26+	20

(1) 10 ml of the lube fractions was placed in a vial with 40 ml capacity, lightly stoppered (preferably with a cotton plug), and placed in a southern exposure window. The numbers refer to days in the window till appearance of sludge deposit.

(2) Heavy dark sludge.

(3) Trace pale sludge.

(4) Minimum acceptable times considered satisfactory for high UV stable lube oils.

TABLE VII

TWO-STAGE LUBE HYDROCRACKING PROCESS

FUELS YIELDS BY HIGH VACUUM DISTILLATION

Stage	Feed[1]	1st	2nd				
Operation			Pure H_2				
Run No.			1	2	3	4	5[2]
Yield on WTS-3 Feed, Wt. %							
IBP - 94°C.	--	0.5	0.2	0.2	0.2	0.2	0.2
Naphtha, 94-177°C.	--	3.0	5.8	1.5	2.0	2.5	2.0
Jet Fuel, 177-268°C.	--	2.5	17.2	4.5	5.4	2.4	5.5
Heating Oil, 268-344°C.	--	6.0	8.1	6.4	8.0	8.5	6.1
Cat. Feed, 344-372°C.	--	3.1	2.5	3.4	2.2	2.9	2.5
Waxy Lube, 372°C.+	100	82.7	62.1	79.4	79.3	81.4	83.4

(1) WTS-3 Feedstock (West Texas Sour 60% DAO Blend/40% HVGO).

(2) Run in the presence of $H_2 + NH_3 + H_2S$, i.e. sour conditions, -- 408 cc t-butyl mercaptan and 58 cc n-butylamine added/gal. feed to second stage.

TABLE VIII

TWO-STAGE HYDROCRACKING OVER AMORPHOUS AND LOW SIEVE-CONTENT CATALYSTS

FEED AND TOTAL LIQUID PRODUCT INSPECTIONS

Stage	WTS-3 Feed(1)	1st(2)	2nd(3)			
Run No.			1	2	3	4
Reaction Temperature, °C.	--	388	316	344	372	372
Space Velocity, v/v/hr.	--	0.5	0.41	0.48	0.52	0.50
Pressure, psig H_2	--	2500	2500	2500	2500	1500
Gas Rate, SCF/B	--	5000	5000	5000	5000	5000
Average Cat. Age, Hrs.	--	395	470	505	549	589
Total Liquid Product						
Recovery, wt. %	100	98	102	100(5)	98	99
Gravity, °API	19.9	29.8	30.0	30.5	33.9	33.3
RI at 60°C.	1.5054	1.4675	1.4648	1.4634	1.4550	1.4586
Conversion, wt. %(4)	0	17.3	13.3	15.0	29.8	27.7
T.L.P. Colour, ASTM	D8.0	4.0	<0.5	<1.0	<1.0	2.5

(1) WTS-3 feedstock (West Texas Sour (60% DAO Blend/40% HVGO)).
(2) 4.5 wt. % NiO, 13.0 wt. % MoO_3 on silica-alumina support.
(3) 95 wt. % (NiO, MoO_3/P_2O_5 on silica-alumina support and 5 wt. % Ni-exchanged faujasite, based on total catalyst.
(4) 100-wt. % yield 372°C+ based on feed to first stage or second stage respectively.
(5) Estimated.

TABLE IX

TWO-STAGE HYDROCRACKING OVER AMORPHOUS AND LOW SIEVE-CONTENT CATALYSTS

LUBE INSPECTIONS

Stage	WTS-3 Feed	1st(1)	2nd(2)			
Run No.	--	--	1	2	3	4
371-496°C. Cut						
Yield on Feed to R-1(3) or R-2(3), wt.%	9.6	28.3	27.8	26.3	25.5	27.3
Dry Wax on Lube Cut, wt.%	8.4	8.2	8.5	9.8	9.4	8.7
Dewaxed Oil: Yield on Feed, wt.%	8.8	26.0	25.4	23.7	23.1	24.9
Visc. 100°F., SUS	928	233	239	217	177	149
Visc. 210°F., SUS	67.0	46.9	47.3	46.4	44.8	43.3
VI_E	25	76	78	82	96	102
Color, ASTM	--	2.5	<1.5	1.5	<2.0	2.0
496-566°C. Cut						
Yield on Feed to R-1(3) or R-2(3), wt.%	45.2	28.3	31.8	33.0	24.9	25.7
Dry Wax on Lube Cut, wt.%	9.6	15.2	14.5	15.2	17.8	17.2
Dewaxed Oil: Yield on Feed, wt.%	40.9	24.0	27.2	28.0	20.5	21.3
Visc. 100°F., SUS	3475	947	908	826	657	586
Visc. 210°F., SUS	131.8	81.4	79.5	76.0	71.5	68.4
VI_E	42	85	84	85	96	98
Color, ASTM	D8.0	<4.5	<2.0	<3.0	<3.0	<5.0
566°C.+ Cut						
Yield on Feed to R-1(3) or R-2(3), wt.%	45.2	26.1	27.2	25.7	19.8	19.3
Dry Wax on Lube Cut, wt.%	9.6	18.8	19.8	20.7	21.7	19.6
Dewaxed Oil: Yield on Feed, wt.%	40.9	21.2	21.8	20.4	15.5	15.5
Visc. 100°F., SUS	17673	3005	3003	4226	2088	1944
Visc. 210°F., SUS	402	171.5	172.2	167.1	145.3	140.5
VI_E	77	97	98	98	105	107
Color, ASTM	D8.0	<8.0	<3.5	<4.5	<5.0	D8.0

(1) 4.5 wt. % NiO, 13.0 wt. % MoO_3 on silica-alumina support.
(2) 95 wt. % (NiO, MoO_3)/P_2O_5 on silica-alumina support and 5 wt. % Ni-exchanged faujasite based on total catalyst.
(3) First and second stage, respectively.

TABLE X.

TWO-STAGE HYDROCRACKING OVER AMORPHOUS AND LOW SIEVE-CONTENT CATALYSTS

FUELS YIELDS BY DISTILLATION

Stage	WTS-3 Feed	1st(1)	2nd(2)			
Run No.	--	--	1	2	3	4
Yield on Feed to 1st Stage or Second Stage, wt. %						
IBP - 94°C.	--	0.5	0.2	0.2	--	--
Naphtha, 94-177°C.	--	3.0	2.0	1.0	4.5(3)	3.1(3)
Jet Fuel, 177-268°C.	--	2.5	3.3	3.7	10.9	10.4
Heating Oil, 268-344°C.	--	6.0	7.1	6.6	8.3	8.8
Cat. Feed, 344-372°C.	--	3.1	2.7	2.6	3.9	4.0
Waxy Lube, 372°C.+	100	82.7	86.7	85.0	70.4	72.7

(1) 4.5 wt. % NiO, 13.0 wt. % MoO_3 on silica-alumina support.

(2) 95% (NiO, MoO_3)/P_2O_5 on silica-alumina support and 5% Ni-exchanged faujasite.

(3) Initial Boiling Point - 177°C.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for producing high viscosity index lubricating oils comprising contacting a petroleum feedstock having an initial boiling point above 340°C. at atmospheric pressure in a first stage with hydrogen and a catalyst comprising a hydrogenation component selected from the group consisting of metals of Group VIB and non-noble metals of Group VIII of the Periodic Table, their oxides and sulfides and mixtures thereof, and an amorphous component at a temperature ranging from about 340°C. to about 450°C. at a pressure range from about 1500 by 5000 psig and at a liquid hourly space velocity ranging from about 0.1 to about 10.0 V/V/Hr., contacting at least a portion of the first stage effluent in a second stage under less severe conditions of temperature and space velocity with hydrogen and a catalyst different from the first stage catalyst and comprising a crystalline aluminosilicate zeolite component said zeolite having a silica to alumina ratio ranging from 2.5 to 10, and a hydrogenation component selected from the group consisting of the metals of Groups VIB and VIII of the Periodic Table, their oxides and sulfides and mixtures thereof, said second stage contacting being conducted at a temperature ranging from about 230° to about 370°C., at a pressure ranging from about 1500 to about 5000 psig, and at a liquid hourly space velocity ranging from about 0.1 to about 10.0 V/V/Hr., and recovering a lubricating oil.

2. The process of claim 1, wherein the hydrogenation component of the first stage catalyst comprises metals, oxides or sulfides of metals selected from the group consisting of cobalt, molybdenum, nickel, tungsten or mixtures thereof.

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3. The process of claim 1, wherein said zeolite is a faujasite.

4. The process of claim 1, wherein the first stage catalyst additionally comprises a crystalline aluminosilicate zeolite component.

5. The process of claim 1, wherein said amorphous component is alumina or silica-alumina.

6. The process of claim 1, wherein the first stage catalyst comprises a mixture of a nickel exchanged faujasite and at least about 95 wt. % (based on total catalyst) of a mixture of molybdenum oxide and nickel oxide deposited on a P_2O_5 stabilized silica-alumina carrier.

7. The process of claim 1, wherein the first stage catalyst comprises a sulfided nickel-tungsten on alumina.

8. The process of claim 1, wherein the hydrogenation component of the second stage catalyst comprises metals selected from the group consisting of cobalt, nickel, molybdenum, tungsten, the platinum group metals and mixtures thereof.

9. The process of claim 8, wherein the second stage catalyst comprises a crystalline aluminosilicate component impregnated with said hydrogenation component.

10. The process of claim 8, wherein the hydrogenation component of the second stage catalyst is palladium and said second stage zeolite is the hydrogen form of a faujasite.

11. The process of claim 1, wherein the second stage catalyst additionally comprises an amorphous component.

12. The process of claim 11, wherein said amorphous component is alumina or silica-alumina.

13. The process of claim 1, wherein the second stage catalyst comprises a mixture of (1) an amorphous component, (2) a crystalline aluminosilicate zeolite component comprising 10-70 wt. % of the total catalyst, said zeolite having a $SiO_2:Al_2O_3$ ratio of at least 2.5 and an alkali metal content of less than 2 wt. % (an alkali oxide), based on the metal zeolite component and (3) a hydrogenation component.

14. The process of claim 1, wherein the second stage catalyst comprises a mixture of about 20 wt. % (based on the total catalyst) of a nickel exchanged faujasite, alumina and a hydrogenation component selected from the group consisting of oxides and sulfides of nickel, tungsten, molybdenum and mixtures thereof.

15. The process of claim 1, wherein the first stage contacting temperature ranges from about 340° to about 412°C. and the first stage space velocity ranges from about 0.2 to about 2.0 V/V/Hr.

16. The process of claim 1, wherein the second stage contacting temperature ranges from about 230° to about 340°C. and the second stage space velocity ranges from about 0.5 to about 5.0 V/V/Hr.

17. The process of claim 1, wherein the amount of conversion to products boiling below about 340°C. in the second stage is below 15 wt. % based on the weight of the second stage feed.

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18. The process of claim 1, wherein said petroleum oil feedstock is characterized in that less than 5 volume % of the oil has a boiling point below about 370°C. as well as having a Saybolt Universal Viscosity at 38°C. of at least 50 seconds.

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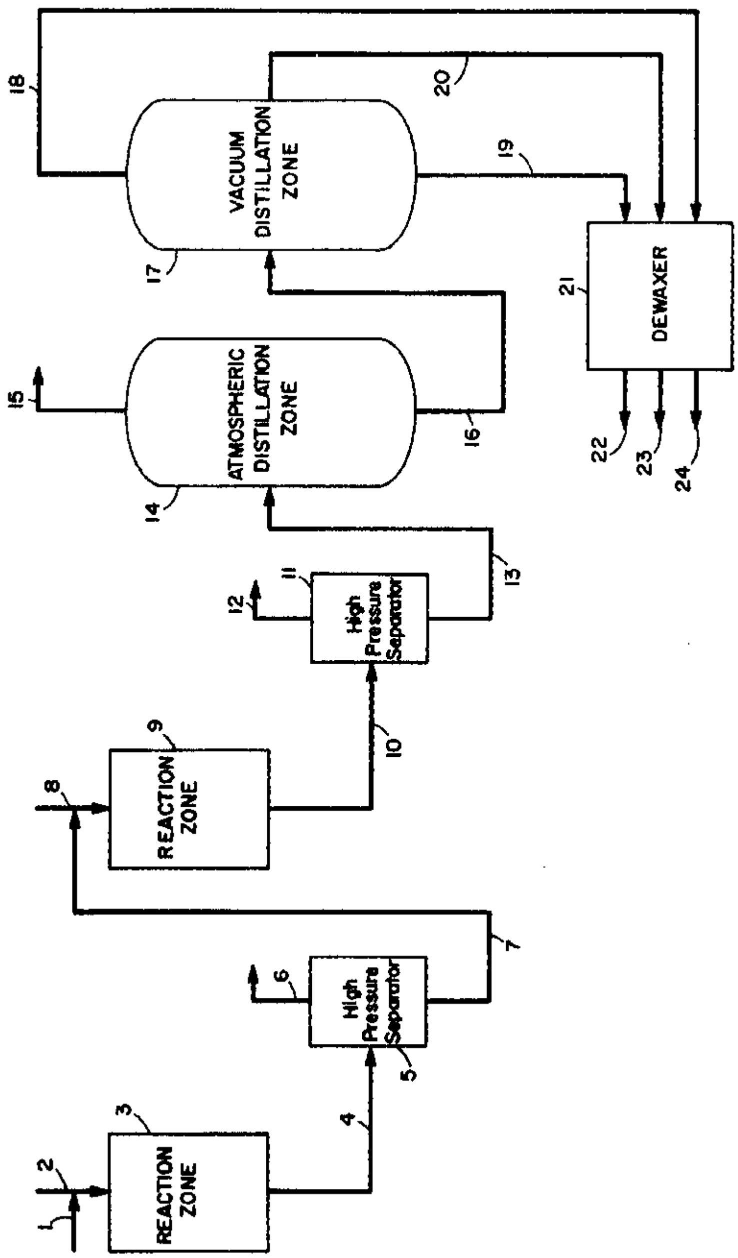

PATENT AGENTS