

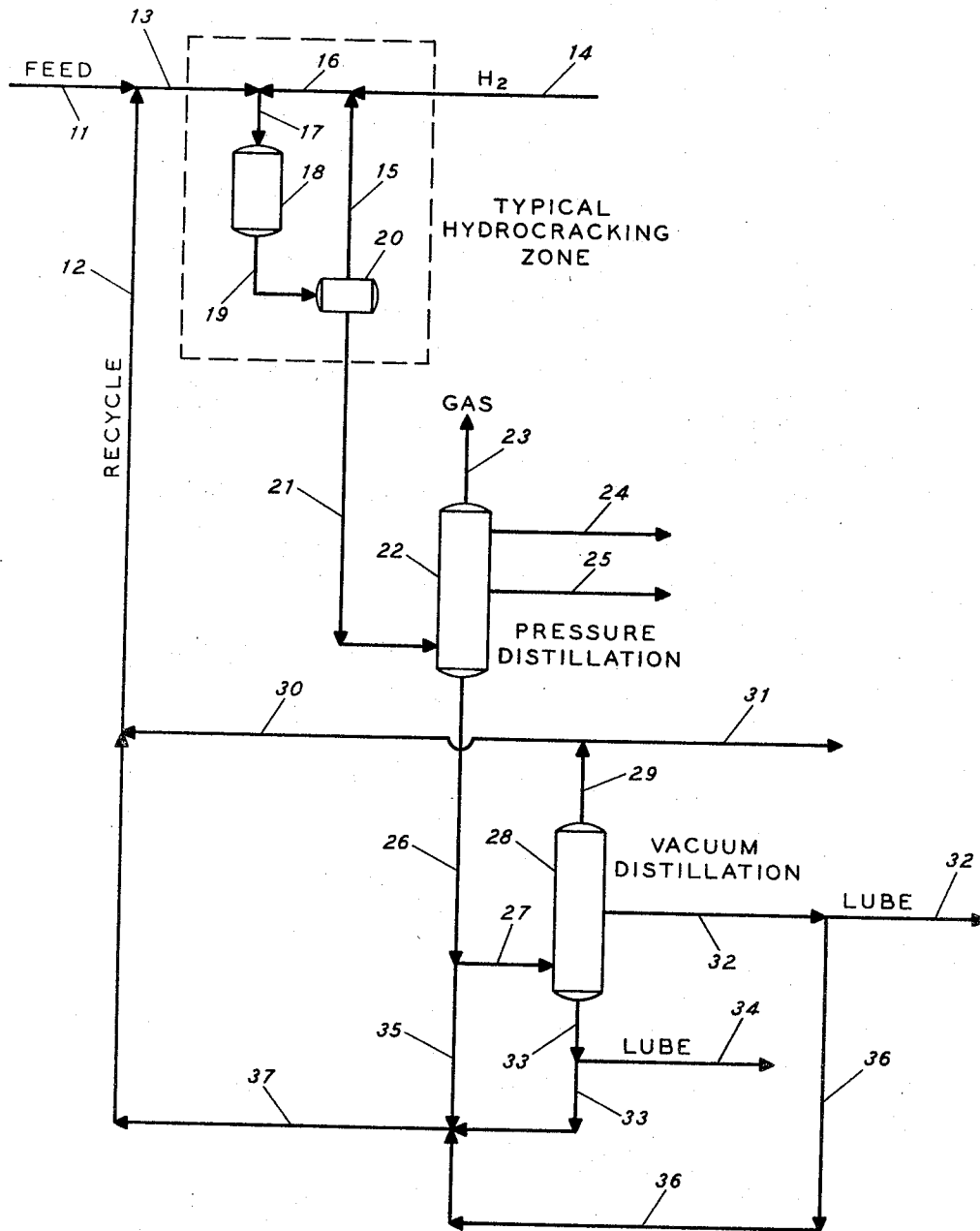
March 7, 1967

R. H. KOZLOWSKI

3,308,055

HYDROCRACKING PROCESS PRODUCING LUBRICATING OIL

Filed April 13, 1964



INVENTOR
ROBERT H. KOZLOWSKI
BY C. J. Zuckin
John M. Whitney
ATTORNEYS

1

3,308,055

HYDROCRACKING PROCESS PRODUCING LUBRICATING OIL

Robert H. Kozlowski, Berkeley, Calif., assignor to Chevron Research Company, a corporation of Delaware
Filed Apr. 13, 1964, Ser. No. 359,057
7 Claims. (Cl. 208—111)

This invention relates to catalytic hydroconversion processes for upgrading hydrocarbon oils. More particularly, the invention relates to processes for hydrocracking heavy petroleum oils and to processes for producing lubricating oils.

A variety of schemes have been proposed from time to time for producing lubricating oils from less suitable oils by catalytic hydroconversion or hydrotreating processes. In general, such processes involve contacting a selected hydrocarbon oil feed, such as a petroleum fraction, with hydrogen in the presence of a catalyst, at conditions of elevated temperature and pressure found to improve the properties of the oil feed with respect to its use as a lubricant. For example, mild hydrogen treating has been used to improve the stability of lubricating oils by hydrogenating hetero organic compounds, such as sulfur and nitrogen compounds responsible for the poor stability of the feed. More severe destructive hydrogenation, involving both hydrocracking and hydrogenation, has been proposed as a substitute for one or more of the solvent extraction, acid treating, and clay contacting steps conventionally employed in the production of lubricating oils by chemical treatment. The destructive hydrogenation processes remove a portion of the aromatics and condensed ring compounds by ring-scission with limited side chain removal by hydrocracking to lower boiling distillates.

It is characteristic of such processes that the feedstocks employed are carefully selected, the selection being generally restricted to oils which are already recognized as lubricating oils or as good conventional sources for lubricating oils. For example, to produce lubricating oils of very high viscosity index, it has been necessary to employ as the feed an oil which already has a moderately high viscosity index. Thus, high quality crude oils are segregated for use specifically in preparing lube oils, whether by hydrofining or by chemical treatment. Further, previously known and proposed processes are each designed to be operated for the production of a particular type of lubricating oil product. Accordingly, it has been necessary to size the treating process to handle a quantity of oil corresponding closely to the expected product demand. Since lubricating oils are a small volume product as compared to other petroleum refinery products such as gasoline, kerosene, heating oils, and chemicals, the practical application of many of the proposed processes is seriously limited by economics. Catalytic hydroconversion processes operating at elevated temperature and pressure are quite expensive and difficult to justify economically except for processing large quantities and unless a tremendous upgrading in the value of the products as compared to the value of the feed can be accomplished. Thus, the lube hydrotreating processes are generally re-

2

stricted to mild hydrofining carried out at only moderate temperatures and pressures, with short contact time between the oil feed and catalyst to minimize the size of the equipment. As a further consequence of the economic situation, the processes heretofore proposed strive to obtain the highest possible yield of product lubricating oil from the oil feed. Even in severe destructive hydrogenation processes where distillate fuels of some value are produced as a by-product, it is necessary to control the operation of the process with respect to obtaining the desired quality in the major lubricating oil product, and both the quality and amount of other products be permitted to fall where they may. This is another reason why it has been necessary to select the feedstock carefully, and to design a particular process installation for treating the particular selected feed.

The present invention provides a process whereby good lubricating oils and lubricating oil base stocks can be produced from nearly any heavy hydrocarbon oil feed as a by-product of hydrocracking. In particular, the invention provides a method of producing lubricating oil base stock from a heavy, high-boiling, oil which is normally unsuitable for any use except as an ingredient of heavy fuel oil. In one embodiment the invention provides a hydrocracking process for upgrading heavy fuel oil characterized by always producing a superior lubricating oil by-product. The principal products in terms of volumetric yield are high value distillate fuels, and consequently the invention makes possible the use of a large plant wherein the economics are more favorable. A particular feature of the invention is that it provides a process wherein there is considerable flexibility and latitude permitted in adjusting independently both the yields and the qualities of the lubricating oil and distillate fuel products.

In accordance with the invention, it is found that by hydrocracking a heavy oil feed together with a heavy recycle oil, controlling conditions so as to accomplish only a controlled per pass conversion to distillate fuels, limiting the withdrawal of products boiling in the boiling range of the heavy oil feed, and providing adequate heavy recycle oil, the viscosity index of products boiling in the lubricating oil range can be made to increase far above that which would otherwise be obtained. Furthermore, the conversion, product withdrawal, and recycle ratio can be independently adjusted within substantial limits to compensate for changes in such factors as feed quality and demand for different products, without serious effect on product qualities. In a preferred embodiment of the invention, a heavy fuel oil is converted entirely to lower boiling distillates and improved lubricating oil base stock by hydrocracking the heavy fuel oil and a heavy recycle oil in a volume ratio of heavy recycle to heavy fuel oil between 0.3 and 1.5. The hydrocracking is carried out in a catalytic hydrocracking reaction zone at conditions for converting between 25 and 75% of the combined fuel oil and recycle oil to distillates boiling below 700° F. The entire normally liquid hydrocarbon oil effluent of the hydrocracking reaction zone is distilled to separate said effluent into lower-boiling distillates and a remainder. At least a portion of

this remainder is then further distilled, and there is recovered therefrom a lubricating oil base stock of which an amount corresponding to between 2% and 25% of the heavy fuel oil feed boils within the boiling range of the feed. The aforesaid heavy recycle oil is formed by combining each portion of the aforesaid remainder which was not so distilled with at least each highest-boiling portion of said remainder which was so distilled but not recovered as lubricating oil base stock.

It is found that by processing in accordance with the invention lubricating oils of higher viscosity index can be produced than are produced by known processes applied to similar feeds. More particularly, it is found that by the process of the invention there can be produced oils of acceptable viscosity index for use in lubricating oil from extremely low grade oils, including oils having very low, even negative, viscosity indices. Although the lubricating oil or lubricating oil base stock is obtained in relatively low yield, it is obtained in a process designed for high throughput, and consequently there are adequate production quantities. Thus, the invention avoids the need to segregate special quality crude oils or portions thereof for lubricating oil production.

The attached drawing illustrates an arrangement of flow paths and major process units as they appear schematically in a preferred embodiment of the invention. The following description of the drawing serves particularly to clarify the manner in which the hydrocracking reaction zone effluent may be worked up.

A heavy oil feed in line 11 and a heavy recycle oil in line 12 are both fed to a hydrocracking zone, for example, by combining them in line 13. Hydrogen is also continually supplied to the hydrocracking zone through line 14. In a typical hydrocracking zone, as shown, the makeup hydrogen is combined with a recycle hydrogen-rich stream 15 to form a hydrogen-rich gas in line 16, which is then passed into reactor 18 together with the feed and recycle via line 17. The oil and hydrogen are supplied preheated and at elevated pressure by means of conventional furnaces, heat exchangers, pumps, and compressors not shown. In general, engineering details have been omitted entirely from the drawing because they are subject to being incorporated in innumerable arrangements and permutations, all within the skill of the art. Reactor 18 contains a hydrocracking catalyst in the form of small particles, whereby the oil is in intimate contact with the catalyst and hydrogen during passage of the oil therethrough, the time of contacting and the temperature and pressure conditions being such that between 25 and 75% of the combined feed and recycle are converted to lower boiling distillates. As used herein, the conversion is determined by comparing the volume of distillates produced which boil below 700° F. with the volume of material in the combined feed and recycle which does not boil below 700° F. "Conversion" thus excludes "overlap" material which may appear in the distillates withdrawn.

The entire effluent of reactor 18 passes via line 19, usually being cooled while so passing, to separation zone 20, wherein hydrogen-rich gas is separated for recycling through line 15. The normally-liquid hydrocarbon effluent then passes through line 21 to distillation zone 22.

In distillation zone 22, which may include one or several columns, the effluent is distilled, generally at atmospheric or superatmospheric pressure, to separate light gases and low-boiling hydrocarbons, designated by line 23; distillate fuel fractions such as gasoline, designated by line 24; and distillate fuel fractions such as kerosene or other middle distillates, designated by line 25. In general, all distillate fuels boiling below about 500–550° F. produced by hydrocracking are recovered in this first distillation, leaving a remainder in line 26. The distillates recovered, however, may also include all material in the hydrocracking zone effluent boiling below about 650–700° F., corresponding approximately to the

minimum initial boiling point of lubricating oil produced by the process of this invention. That is to say, the distillates boiling below about 700° F. obtained in the process usually have greater value as distillate fuels, or as intermediate feeds to be further converted to higher value fuels by subsequent processing, than as lubricating oil.

At least a portion of the so-called remainder in line 26 is passed through line 27 to vacuum distillation zone 28, which may comprise one or more columns. Because of the lower pressure, and if the first distillation is carried out so as to leave materials boiling below about 650–700° F. in the remainder, a distillate is obtained overhead in line 29. It is desirable to remove this distillate to control the flash point and/or initial boiling point of the lubricating oil products. This distillate or a portion thereof may be passed via line 30 to form a portion of recycle stream 12. Alternately, however, all or a portion of the distillate in line 29 may be withdrawn via line 31 and recovered as a salable gas oil or heavy middle distillate. The amount of any portion so recovered which boils below 700° F. is included as a part of the distillate fuel products in controlling the hydrocracking so as to convert between 25 and 75% of the combined feed and recycle to said distillate products.

From distillation zone 28 there may be withdrawn cuts of one or more distillate lubricating oils as indicated by line 32. The boiling range of the cut or cuts withdrawn as through line 32 is controlled with reference to the viscosity desired. For example, there may be withdrawn two distillate lubricating oils or lubricating oil base stocks having the properties of, and suitable for use as or in, a 150 neutral and a 480 neutral, boiling respectively from about 700 to about 800° F. and from about 800 to about 900° F. The term "lubricating oil base stock" is used herein as indicating that in some cases it will be desirable to further treat the oil, as by solvent extraction and/or dewaxing, in order to take maximum advantage of the improved oil qualities and produce superior lube oil.

From that portion of the remainder in line 26 which was passed through line 27, and thus distilled in zone 28, there is obtained a highest-boiling portion in line 33. In the case where only a portion of the remainder in line 26 was so distilled, all or a portion of this highest-boiling portion in line 33 may be recovered as a lubricating oil base stock in line 34. For example, when the feed in line 11 is a deasphalted residuum, a 185 bright stock may be recovered in line 34. In the case where all of the remainder in line 26 is passed through line 27 and so distilled, only a portion of this highest-boiling portion in line 33 can be recovered through line 34. Any portion of this highest-boiling portion in line 33 which is not recovered as lubricating oil base stock in line 34, i.e., all the rest, is to be combined with any portion of the remainder which was not vacuum distilled, i.e., the entire portion in line 35, thereby forming line 37, for use in forming the recycle oil in line 12. In order to adjust the properties of lubricating oil recovered in line 34, such as viscosity and initial boiling point, more material may be distilled in zone 28 and taken off by line 32 than it is desired to recover as lubricating oil having the properties of the material in line 32. In that case, a portion of the material in stream 32 is diverted through line 36, which is also used in forming the recycle oil. In many cases the diversion of material through line 36 to help form the recycle oil is necessary in order to avoid withdrawing an amount of total lubricating oil products, boiling in the range of fresh feed in line 11, corresponding to more than 40 volume percent of the fresh feed. Thus, in forming the recycle oil in line 37, there is used any portion of the remainder 26 which is not distilled under vacuum, i.e., any portion in line 35, and also any remaining highest-boiling portion of the material which is so distilled, i.e., the portion of line 33 not recovered

5

as lubricating oil in line 34, and there will also be used any distillate boiling in the feed boiling range which is not recovered as lubricating oil, i.e., the portion in line 36. In combination with the material in line 37 there may also be used in forming the recycle oil in line 12 the distillate in line 30, as mentioned previously.

As feed to the process of this invention there may be employed virtually any high boiling heavy hydrocarbon oil derived from petroleum or similar hydrocarbonaceous materials of ancient origin. By "high-boiling" is meant that a substantial portion of the feed, at least 30%, does not boil below about 800° F. That is, if the feed is distilled, a substantial portion will not yet have boiled over when the temperature has reached 800° F. (corrected to atmospheric pressure distillation). Preferred oil feeds boil substantially entirely above about 650–700° F., disregarding the initial low-boiling 5%, such as heavy vacuum gas oil distillates of crude petroleum having end points in the range 1000–1150° F. The initial boiling point of the preferred feeds may be 900° F., or higher, and the feed may have no definite end boiling point. Thus, for example, the feed may be a solvent decarbonized residuum, such as the oil obtained by propane deasphalting a short residuum. In the case of residuals, the asphaltenes at least should first be removed as by solvent extraction or precipitation to form a suitable feed for this process, to prevent too rapid coking of the hydrocracking catalyst. It will be noted, however, that included within the suitable feeds are materials which would normally be unsuited for any use other than as ingredients of heavy fuel oil. Freedom from asphaltenes is based on the desire to have a long on-stream time between catalyst regenerations, not because they prevent production of improved lubricating oil. Consequently, how completely asphaltenes are to be removed is a matter of degree, affecting the economics, but not the essential nature of the process. Use of the term "oil" in referring to the feed and other streams means that liquid phase conditions exist at the process conditions, and it is not meant to imply that the feed cannot be solid or semisolid at room temperature.

The heavy recycle oil, having been prepared as previously described, will contain no substantial amount of materials boiling below the end boiling point of kerosene or jet fuel, i.e. 500–550° F., and usually will contain no substantial amount of materials boiling below 650–700° F. The recycle will always contain at least some of the highest-boiling materials fed to or produced in the process. The initial boiling point of the recycle may, however, be below, the same as, or above the initial boiling point of the feed, depending on whether any lubricating oil product is withdrawn which contains material boiling below the initial boiling point of the feed, and depending on whether "salable gas oil" (line 31 in the drawing) is recovered. It is also possible for the recycle oil to have a "vacancy" in its distillation curve, if all of the remainder from the first atmospheric or pressure distillation is distilled under vacuum and there is recovered a lubricating oil product comprising all materials boiling in a particular narrow boiling range, for example, from 800° to 900° F. It will be appreciated, however, that the many possible variations in recycle properties, and in recovery of products, are restricted by the need to provide recycle oil in a ratio to fresh feed of between 0.3 and 1.5 volumes of recycle per volume of feed. Also, equivalent results are not obtained in all such permissible variations. Thus, it is preferred for optimum lube oil properties to recover lube oil in a yield of only 2–20% and to provide heavy recycle in a ratio to fresh feed between 0.5 and 1.25.

The heavy oil feed and heavy recycle oil are hydrocracked by passing them and hydrogen through a catalytic hydrocracking reaction zone at elevated temperature and pressure to contact therein a hydrocracking catalyst. Suitable hydrocracking catalysts for use in the process of

6

this invention are those solid contact materials having the properties of accelerating scission of carbon-carbon bonds and of accelerating hydrogenation of cracked hydrocarbon fragments so produced. Also, since the feeds to be processed are generally oils containing hetero organic compounds of nitrogen, sulfur, oxygen, and even metals in some cases, the catalyst must be one whose cracking and hydrogenation activities are not rapidly or permanently impaired by such compounds or their decomposition products. Thus, in particular, the catalyst must be one which is relatively insensitive to nitrogen contaminants. Also, for purposes of the present invention in its preferred aspects, it is highly advantageous to employ a catalyst which maintains high activity throughout continuous operation for long periods of time of at least 600 hours, and more preferably in the neighborhood of from two to several thousand hours, without regeneration. These requirements are met by many known catalysts, which usually are composed of a refractory oxide in combination with an active hydrogenating metal component of Group VIII of the Periodic Table and a hydrogenating metal component of Group VI of the Periodic Table. It is generally desirable to convert the metal components to the sulfides to develop their maximum catalytic activity for hydrocracking oils containing nitrogen compounds.

Particularly good refractory oxides are the high surface area porous oxide cogs or coprecipitates of silica with alumina or magnesia, wherein the silica and the alumina or magnesia are each present to the extent of at least 10%. Other high surface area cogs with materials such as zirconia, titania, or boria can also be used. The single ingredients alumina, silica, or magnesia do not themselves appear to have sufficient cracking activity to be considered within the preferred refractory oxides. Preferred Group VIII components are the oxides and sulfides of the iron group and noble metals, cobalt, nickel, platinum, and palladium, but specially nickel. Preferred Group VI components are the oxides and sulfides of molybdenum and tungsten. Thus, examples of hydrocracking catalysts which would be preferred for use in the process are the combinations nickel-tungsten-silica-magnesia, nickel-tungsten-silica-alumina, nickel-molybdenum-silica-alumina, and nickel-molybdenum-silica-magnesia. Such catalysts may vary greatly in their activities for hydrogenation and for cracking and in their ability to sustain high activity during long periods of use depending on their compositions and methods of preparation. Obviously, the best proven catalyst available is selected, taking into consideration all of the above factors and also price.

Numerous schemes can be devised for bringing together the oils, hydrogen, and the catalyst at the temperature and pressure conditions for catalytic hydrocracking. Thus, the catalyst may be suspended in the oil as finely divided particles, or it may gravitate through the oil as relatively large particles. The oil and hydrogen may be passed upwards or downwards concurrently or countercurrently in one or more parallel or series-connected reaction chambers. Probably the most suitable commercial method for carrying out the process continuously, however, comprises preheating the oil and hydrogen under pressure and then passing them downward through one or more stationary beds of catalyst particles contained in a high pressure reactor. The amount of hydrogen passed through the reactor is in substantial excess of the amount consumed in hydrogenation reactions occurring therein, and the gas used is sufficiently pure, so that the hydrogen partial pressure at all times constitutes the major portion of the total pressure. In some cases hydrogen consumption may exceed 1700 standard cubic feet per barrel of fresh feed, and accordingly there should be provided at least 2000 standard cubic feet of hydrogen per barrel and most preferably 4000 standard cubic feet or more.

Hydrocracking reaction conditions are preferably controlled in the ranges 700–850° F., 1000–4000 p.s.i.g., and flow rate of 0.3–3 volumes of combined feed and recycle per hour per volume of catalyst so as to thereby convert between 25% and 75% of the combined heavy oil feed and heavy recycle oil which does not boil below 700° F. to distillate fuels which boil below 700° F. Thus, for example, if 10% of the combined fresh feed and recycle boils below 700° F., that portion is ignored in calculating the conversion, which is arrived at by comparing the volume of net products boiling below 700° F. with the volume of combined fresh feed and recycle which does not boil below 700° F., i.e., the 90%. Likewise, if the combined feed and recycle has an initial boiling point above 700° F., for example 800° F., materials formed in the boiling range 700–800° F. are not included in calculating the conversion even though a product stream may be withdrawn comprising materials boiling in the range 700–800° F. Since materials would not be included in the measurement of distillate fuels boiling entirely below 700° F., nor would they be included in the measurement of lubricating oil product boiling above the initial boiling point of the feed. This amount does not escape accounting in the process of the invention, however, because in addition to the requirement of between 25% and 70% of the combined feed and recycle which does not boil below 700 being converted to distillate fuels boiling below 700° F., and the requirement that an amount of lubricating oil boiling within the feed boiling range corresponding to between 2 and 40 volume percent of the feed be withdrawn, there is the further requirement that an amount of heavy recycle oil be provided in a ratio between 0.3 and 1.5 volumes per volume of fresh feed. It is characteristic of the hydrocracking reactions that in order for the conversion as defined herein to be at or near the lower limit of 25% the ratio of recycle to feed will be near the upper limit of 1.5; for conversion near 75%, the ratio will be near the lower limit of 0.3. Consequently, the amount of distillate boiling above 700° F. and below the initial boiling point of the feed which can be withdrawn will generally be limited to less than the difference between the amount of higher-boiling lubricating oil actually withdrawn and the 40% yield which might have been withdrawn. That is, such a distillate product displaces lube oil product.

The higher the total conversion, the greater the proportion of light products, i.e., boiling below 400° F. It is frequently desired, however, to produce a greater proportion of middle distillate products, i.e., boiling between 400° F. and 700° F. Preferably the hydrocracking conditions are such as to convert an amount between 20% and 40% of that portion of the combined feed and recycle which does not boil below 700° F. into hydrocarbon oil which boils between 400° F. and 700° F., and to convert no more than an equal amount but at least about 10% of said portion into normally liquid (C₅+) hydrocarbon oil which boils below 400° F. The above description of the preferred conversion ratios does not imply that there must actually be recovered one product boiling from just above the boiling point of butane to 400° F. and another product boiling from 400° F. to 700° F., but that the amounts of such materials which are formed can be ascertained by sampling and distillation of the samples. Description of the conversion in these terms defines a situation wherein the amount of middle distillate produced equals or exceeds the amount of gasoline produced, and thereby defines a preferred controlled type of hydrocracking wherein primarily only the largest and most complex molecules in the oils are acted upon, and over-cracking of the intermediate-boiling-range product is avoided. In this way, superior lubricating oil and superior distillate fuels are produced in the process of the invention.

If conversion to 400–700° F. distillate is much less than 20%, as may occur either by the total conversion

to distillates boiling below about 700° F. being too low or by the conversion to gasoline by overcracking being high, the improved results may not be obtained. If conversion is too low, there will not be enough hydrocracking occurring to increase the viscosity index appreciably above that obtainable without the process of the invention. Likewise, if the conversions are too high, as by use of a high temperature, product quality suffers particularly in the 320–550° F. boiling range, where increased aromaticity renders the product less desirable for jet fuel.

In the fixed bed process the reactor effluent comprising the reaction products and excess hydrogen is cooled, and excess hydrogen-rich gas is separated for recycling. The distillate fuel products are then separated from a higher boiling remainder by distillation. The distillate fuel fractions thus separated and recovered include all normally liquid oil in the hydrocarbon effluent boiling in and below the kerosene boiling range. This first distillation may be carried out in a series of columns designed to segregate specific products such as normally gaseous hydrocarbons, propane, butanes, light gasoline, heavy gasoline, jet fuel or kerosene, and middle distillates such as furnace oil and diesel oil. Characteristically these distillations are carried out at at least slightly superatmospheric pressure and in some cases at substantially superatmospheric pressure. The maximum initial boiling point of the remainder is thus desirably limited to not over about 700° F. to avoid thermal degradation of the higher boiling constituents.

At least a portion of this remainder from the first, superatmospheric, distillation is further distilled to recover therefrom at least one lubricating oil base stock. The total amount of lubricating oil base stock recovered is limited in yield such that an amount thereof corresponding to a yield of between 2% and 40% from the heavy oil feed boils within the boiling range of the heavy oil feed. That is to say, some of the lubricating oil recovered may boil below the initial boiling point of the fresh feed, in which case that portion is not considered in computing whether there is recovered lubricating oil in a yield between 2% and 40% by volume of the feed. The withdrawal, or not, of such a portion does, however, provide another measure of flexibility by which product qualities can be maintained at desired levels in both the distillate fuels and the lubricating oil when feed quality or other factors change. Similarly, if several lubricating oil products of different boiling range are recovered, the amount of each of which boils within the boiling range of the fresh feed must be considered in determining the net yield. By so limiting the yield of lubricating oil it is found that the viscosity index of a recovered lubricating oil can be maximized, and it is further found that the viscosity index is remarkably increased as compared to the viscosity index of the feed and as compared to the amount of viscosity index increase obtainable when the yield is not so limited, and as compared to the amount of viscosity index increase obtainable by previously known processes. Thus, although there may be other processes which appear capable of producing oils of much higher viscosity index than are obtained generally in the process of this invention, such other processes accomplish that result by employing as the feed an oil which already has a moderately high viscosity index. By the process of this invention a much greater increase in viscosity index, to acceptably high levels, is obtainable when processing feeds of very low viscosity index as compared to the increase in viscosity index obtained by known processes with either high or low viscosity index feeds.

The following examples serve to illustrate the practice of the invention in certain embodiments, the importance of certain features therein, and some of the advantages obtainable thereby as contrasted with previously known processes. To simplify the description and dis-

cussion, the properties of heavy oil feeds employed in the examples are set forth below:

FEED INSPECTIONS

	A	B	C	D
	Heavy California Gas Oil	Propane Deasphalted Oil from California Residua	Heavy Gulf Coast Gas Oil	Heavy Arabian Gas Oil
Gravity, ° API.....	16.2	16.6	23.9	26.7
Aniline Point, ° F.....	152.7	192.3	183.1	172.0
Nitrogen, p.p.m.....	5,650	5,600	785	490
Sulfur, wt. percent.....	0.97	1.08	0.35	2.3
Oxygen, p.p.m.....	5,500	4,070	1,900	500
Pour Point, ° F.....	-5	+120		
ASTM Distillation, percent:				
5.....	700	786	588	632
10.....	744	841	619	646
30.....	809	958	726	689
50.....	844	1,006 at 47%	806	719
70.....	878		873	769
90.....	931		987	850
95.....	967		1,020	900
End Point.....	1,000		1,077	960
Viscosity, SSU at 210° F.....	86.73	255.9	46.83	37.92
Viscosity Index.....	-67	*-5	*35	*87

*Dewaxed

The following example illustrates the high viscosity index obtainable by the process of this invention from a very low viscosity index feed.

Example 1

The heavy California gas oil boiling from 600° F. to 1000° F. and having a viscosity index of -67 (Feed A) was combined with 0.57 volume of a heavy recycle oil, boiling entirely about 700° F., per volume of heavy gas oil feed, and passed with 5000 standard cubic feet of hydrogen per barrel of combined oils at a liquid hourly space velocity of 0.5, temperature of 780° F., and pressure of 1800 p.s.i.a. hydrogen through a reactor containing a sulfided nickel-tungsten on silica-magnesia catalyst. The catalyst was prepared by impregnating a silica-magnesia cracking catalyst, with nickel nitrate and ammonium tungstate, calcining, and sulfiding. The conditions were chosen to effect approximately 58% conversion of the combined feed and recycle to distillate fuels boiling below 700° F. The reactor effluent was given a simple distillation at atmospheric pressure to take off the light gasoline fuels, and the remainder was then given a simple distillation using stripping gas, equivalent to a vacuum distillation, to take overhead the heavier distillate fuels boiling up to an end point of 700° F. From the stripper distillation about 13% of the highest-boiling portion was withdrawn, and the rest of the highest-boiling portion not so recovered formed the aforesaid heavy recycle oil. There was thus obtained in a yield of 8.4% based on the fresh feed a lubricating oil having the following properties:

Gravity, ° API.....	32.1
Aniline point, ° F.....	224.6
Pour point, ° F.....	+15
Viscosity, SSU at 100° F.....	171.4
Viscosity, SSU at 210° F.....	44.5
Viscosity index.....	101.5

In a commercial installation to produce 2,000 barrels per day of lubricating oil having the above properties, there would be employed 24,000 barrels per day of the heavy California gas oil feed, 13,700 barrels per day of the heavy recycle oil, and there would also be obtained as products 5,000 barrels per day of a C₅-300° F. gasoline and 20,000 barrels per day of a 300-700° F. low sulfur diesel fuel with 51 cetane number and below -30° F. pour point.

In contrast to the above, when the recycle operation is not employed (based on laboratory data similarly obtained), to produce 2,000 barrels per day of lubricating

oil boiling entirely above 700° F., there is employed 3,500 barrels per day of the heavy California gas oil, which is

passed with 6000 standard cubic feet of hydrogen per barrel into contact with the same nickel-tungsten-silica-magnesia catalyst at a space velocity of 0.5 LHSV, 780° F., and 1800 p.s.i.a. hydrogen. Distillate fuels in a yield of about 43% are obtained, amounting to only 1600 barrels per day, and the 2000 barrels per day of lubricating oil has a viscosity index of only 72.0.

The following examples illustrate the manner in which the invention may be used to produce high quality lubricating oil from deasphalted residuum.

Example 2

One volume of deasphalted residual oil boiling substantially entirely above 800° F. (Feed B), obtained in 55% yield from propane deasphalting a California short residuum, is passed together with 0.9 volume of heavy recycle oil boiling entirely above 900° F. and 5000 s.c.f. hydrogen per barrel into contact with the sulfided nickel-tungsten-silica-magnesia catalyst at 0.5 LHSV, 810° F., and 1800 p.s.i.a. hydrogen pressure (2300 p.s.i.g. total). From 20,000 barrels per day of deasphalted oil there is obtained by two-stage distillation of the products 3,000 barrels per day of C₅-300° F. gasoline, 3,700 barrels per day of 300-500° F. distillate, 5,300 barrels per day of 500-700° F. distillate, and 6,400 barrels per day of 700-900° F. distillate. Of the remaining 900° F.+ material, 2,800 barrels per day is recovered, and the rest recycled. After dewaxing, the 700-900° F. distillate has a viscosity index of 68 and the 900° F.+ product has a viscosity index of 112. Products boiling within the feed boiling range are recovered in a yield of about 35%. (Only a portion of the 700-900° F. distillate boils within the feed boiling range.) In the lower boiling distillates the ratio of middle distillate to gasoline (400-700° F./C₅-400° F.) is about 1.4. Conversion of combined fresh feed and recycle to such lower boiling distillates, as conversion has been defined herein, is about 32%. Thus, this example represents operation near maximum yield of lube oil and minimum conversion to lower boiling distillates within the practice of the invention.

In contrast, however, if the deasphalted oil is passed once-through the reaction zone at the same temperature, pressure, and space velocity, 50% of the product oil still boils above 900° F. and has a viscosity index dewaxed of only 58 and the 700-900° F. distillate has a viscosity index of only 21.

Example 3

The deasphalted residual oil (Feed B) is passed together with 1.1 volumes per volume of heavy recycle oil boiling entirely above 900° F. and 5000 standard cubic

feet of hydrogen per barrel into contact with the sulfided nickel-tungsten-silica-magnesia catalyst at 0.5 LHSV, 775° F., and 1800 p.s.i.a. hydrogen. From 20,000 barrels per day of deasphalted oil feed there is obtained by two-stage distillation of the products 14,500 barrels per day of distillate fuels boiling up to 700° F. A distillate lubricating oil cut boiling between 700° F. and 900° F. is recovered in the same yield as in the preceding example, but all the 900° F.+ material is recycled. Less than two-thirds of this distillate lubricating oil boils within the feed boiling range, and consequently the withdrawal of lubricating oil as defined herein is 21 volume percent. The viscosity index dewaxed is 108. Included in the distillate fuels is a jet fuel boiling from 300° F. to 500° F. having the following properties:

Gravity, API	39.5
Aniline point, ° F.	130.3
ASTM smoke point, mm.	20
Freeze point, ° F.	-85

The middle distillate to gasoline ratio is about 1.7. Thus, at the lower temperature and smaller withdrawal of lube oil in this example, as compared to Example 2, there is obtained a higher middle distillate to gasoline ratio and a higher viscosity index product.

When the deasphalted oil is treated at the same conditions of temperature, pressure, and space velocity without the recycle stream, 8,000 barrels per day of distillate fuels boiling up to 700° F. are obtained per 20,000 per day of feed. 3,800 barrels per day of a 700-900° F. lube oil cut can be distilled from the remaining material, but the lube oil so obtained has a viscosity index of only 55. The distillate in the jet fuel boiling range has a lower smoke point and higher freezing point.

The following examples illustrate the production of high viscosity index oil from straight run waxy distillates.

Example 4

The gulf coast heavy gas oil (Feed C) and 0.54 volume of recycle oil boiling entirely above 700° F., per volume of gas oil, are passed with hydrogen-rich gas into contact with another Ni-W-Si-Mg catalyst, containing slightly more nickel and less tungsten than the catalyst in the preceding examples and prepared using a silica-magnesia powder pressed into pellets, at 778° F., 1900 p.s.i.a. hydrogen, and 1.1 LHSV. Of the normally liquid oil reaction effluent 59 volume percent boils below 700° F. Since the gas oil feed includes about 25% of material boiling below 700° F., the conversion as defined herein is about 54%. About 28% of the combined feed and recycle boiling above 700° F. has been converted to 400-700° F. distillate and about 26% has been converted to C₅-400 distillate. A portion of the reaction effluent boiling above 700° F. amounting to a yield of 11.4% based on gas oil feed is withdrawn as product, and the remainder forms the recycle oil. The withdrawn portion has a viscosity index of 118 dewaxed. The distillate boiling below 700° F. can be separated into 18% C₅-300° F. gasoline, 42% 300-550° F. jet fuel with -63° F. freeze point and 22 smoke point, and 40% 34.6° API distillate fuel with 60 cetane number, -5° F. pour point, and less than 0.01 weight percent sulfur.

In a once-through operation at the above temperature, pressure, and space velocity the conversion effluent boiling above 700° F. has a viscosity index of only 89.5.

Example 5

The Arabian gas oil (Feed D) and 0.8 volume of recycle oil boiling entirely above 650° F. are contacted with a sulfided nickel-molybdenum-silica-alumina catalyst at 822° F., 1760 p.s.i.a. hydrogen, and 1.0 LHSV. This catalyst promotes the same reactions as the nickel-tungsten catalysts used in previous examples, though its activity is not quite as high. Excluding overlap of distillate contained in the feed, the conversion of oil in the combined gas oil and recycle oil boiling above 700° F. to

oil boiling below 700° F. is about 50%, 34% to C₅-400 gasoline and 15% to 400-700° F. distillate. When the distillates boiling up to 650° F. are withdrawn as product, and the remaining 650° F.+ material separated into lube oil product, amounting to 9% yield from gas oil feed, and recycle oil, the lube oil has a viscosity index of 119 dewaxed. This, however, is little better than can be obtained at the operating conditions without recycle. It will be noted that the gas oil feed employed contains more material boiling below 700° F., and less material boiling above 800° F., than preferred for use in practicing the invention, i.e., as previously mentioned, at least 30% of the feed should boil above 800° F. in practicing the invention, but only about 20% of Feed D boils above 800° F. Also, at the conditions of this example the relative conversion to gasoline exceeds conversion to middle distillate, whereas the reverse situation is desired.

To recapitulate the foregoing examples, it is seen that the greatest upgrading of very low viscosity index oil to high viscosity index oil occurs in Example 1, where the recovery of lube oil base stock is limited to below 10% yield, the feed boils substantially entirely above 700° F. and about 70% above 800° F., and conversion to 400-700° F. distillate is about 1.5 times conversion to C₅-400° F. distillate. A large improvement is obtained in Example 2 with the very heavy feed even though the yield of lube oil is higher, when the conversion to 400-700° F. distillate is twice the conversion to C₅-400° F. distillate. Example 3 shows that a greater viscosity index increase is obtained in a narrow boiling range by recycling a greater amount of the highest boiling remainder. In Example 4 a higher viscosity index product is obtained when limited to low yield, but the upgrading of the feed is not as great. The high viscosity index product obtained in Example 5 reflects the high viscosity index of the feed, as in prior art processes.

In an embodiment similar to Example 3, a lubricating oil of maximum viscosity index can be obtained in a narrow boiling range having an initial boiling point above the initial point of the feed, e.g. 800° F., and an end boiling point below the end boiling point of the feed, e.g. 900° F. In a preferred embodiment of the invention maximum advantage is taken of this situation by withdrawing primarily, or only, that narrow boiling range portion as product lubricating oil, using all of the highest boiling portion from vacuum distillation in forming the recycle oil, and using all of the lower boiling, e.g. 700-800° F. cut, also in forming the heavy recycle oil.

In such a situation it is found advantageous to distill under vacuum only a portion of the remainder from atmospheric distillation of the reaction effluent so as to obtain just the desired amount of the intermediate boiling range product without the necessity of distilling the larger amounts of material which are to be reprocessed. Thus, for example, it is calculated that less than half of the remainder from a first distillation to 550° F. end point could be subjected to vacuum distillation, to obtain a 550-700° F. distillate, a 700-800° F. distillate which is all used in forming the heavy recycle oil, an 800-900° F. distillate withdrawn as the sole lubricating oil product, and a highest-boiling portion which is also used in forming the heavy recycle oil in combination with the 700-800° F. distillate and with the portion of 550° F.+ remainder not distilled under vacuum. In such a case there would be a build-up of 550-700° F. distillate in the recycle (because present in the portion of remainder not vacuum distilled), so that the amount of recycle oil would be increased.

To avoid increasing the recycle, a preferred arrangement is to take off the 550-700° F. distillate, or a 550-650° F. distillate, in the first distillation, and then to distill under vacuum only about one-third of the remainder to separate the 800-900° F. lube oil cut from the 700-800° F. distillate and the highest boiling portion, which latter are recycled. The ratio of heavy recycle to heavy

oil feed and the conversion then remain substantially unchanged. It would be preferred to take off a 550–650° F. distillate in the atmospheric pressure distillation, to avoid heating the remainder too hot, in which case the recycle would increase, but only slightly.

Because of the built-in flexibility of the process, any other desired lubricating oil cut could be similarly obtained, and its viscosity index maximized, without adversely affecting the quality of the primary, distillate fuel, products. A particularly advantageous procedure is to thus withdraw desired narrow boiling range lube oil cuts individually, at different times, thereby facilitating their individual further treatment as by solvent extraction and/or dewaxing, at the different treating conditions indicated as most advantageous in each case, in a single treating plant of small size.

I claim:

1. A process for substantially entirely converting a heavy oil feed which has (a) a viscosity index of not more than 35, (b) an end boiling point of not less than 1000° F. and (c) of which at least 30% boils above 800° F. to (i) distillates boiling below about 700° F. and (ii) improved lubricating oil base stock boiling substantially entirely above 700° F.,

which process comprises hydrocracking said heavy oil feed in admixture with a heavy recycle oil boiling substantially entirely above 700° F. and containing at least a substantial portion of the highest boiling components of said heavy oil feed

in a catalytic hydrocracking reaction zone at conditions for converting between 20 and 40% of the combined feed and recycle oil which does not boil below 700° F. to distillates boiling between 400° and 700° F. and no more than an equal amount but at least 10% of the combined feed and recycle oil which does not boil below 700° F. to distillates boiling below 400° F.,

said recycle oil being supplied in a volume ratio to heavy oil feed between 0.3 and 1.5,

distilling the normally liquid hydrocarbon effluent of said hydrocracking reaction zone to separate said effluent into distillates boiling below about 700° F. and a remainder boiling higher than said distillates, further distilling at least a portion of said remainder to separate it at least into a distillate lubricating oil fraction and a residual lubricating oil fraction and recovering from said lubricating oil fractions at least one lubricating oil base stock in a limited yield such that the portion of said total lubricating oil base stock recovered which boils within the boiling range of said heavy oil feed is equal in amount to between 2% and 40% of said heavy oil feed,

and forming said heavy recycle oil by combining each portion of said remainder boiling substantially entirely above 700° F. which was not so further distilled with each portion of the remainder which was so further distilled and boils substantially entirely above 700° F. but was not recovered as lubricating oil base stock, including a substantial portion of said remainder boiling over the same boiling range as a portion recovered as lubricating oil base stock.

2. The process of claim 1 wherein the amount of lubricating oil base stock recovered which boils within the feed boiling range is between 2% and 20% by volume of said feed, and the volume ratio of heavy recycle oil to feed is between 0.5 and 1.25.

3. The process of claim 1 wherein all of said remainder is distilled to obtain a gas oil distillate boiling substantially entirely above 700° F., a distillate lubricating oil base stock, and a highest-boiling portion, a substantial amount less than all of said gas oil distillate and a minor portion of said distillate lubricating oil are withdrawn as products, and the rest of said gas oil distillate and the rest of said distillate lubricating oil are combined with

said highest-boiling portion to form the heavy recycle oil.

4. The process of claim 1 wherein only a portion of said remainder is distilled to separate an amount of highest-boiling lubricating oil base stock which is withdrawn as product, from distillate boiling in the feed boiling range, and the portion of said remainder not so distilled is combined with said distillate to form the heavy recycle oil.

5. A process for making an improved lubricating oil base stock having a viscosity index of at least about 101.5 from a low-grade heavy oil feed, which process comprises passing through a hydrocracking zone containing a nitrogen insensitive hydrocracking catalyst (1) hydrogen, (2) a heavy oil feed which as a viscosity index of not more than 35, boils substantially entirely above 700° F. and at least 30% above 800° F., has an end point of not less than 1000° F. and is substantially free of asphaltenes, and (3) a heavy recycle oil boiling substantially entirely above 700° F. obtained as hereinafter specified;

therein subjecting said feed and recycle to hydrocracking reaction conditions controlled in the ranges 700–850° F., 1000–4000 p.s.i.g., and flow rate of 0.3–3 volumes of combined feed and recycle per hour per volume of nitrogen insensitive hydrocracking catalyst so as to thereby convert an amount between 30% and 75% of that portion of the combined feed and recycle which does not boil below 700° F. to distillates boiling below 700° F.;

distilling the liquid oil effluent of said hydrocracking zone to separate said effluent into distillate fuel fractions including all normally liquid oil therein boiling in and below the kerosene boiling range, and a higher boiling remainder boiling substantially entirely above 700° F.;

distilling a portion of said remainder to obtain a distillate fraction including hydrocarbons boiling below the initial boiling point of said feed, a distillate fraction suitable for use as lubricating oil base stock containing hydrocarbons boiling above the initial boiling point of said feed, and another fraction suitable for use as lubricating oil base stock boiling entirely above the initial boiling point of said feed;

withdrawing an amount of said fractions limited such that the amount of material withdrawn which boils above the initial boiling point of said feed is between 2% and 20% by volume of said feed;

and combining the portion of said remainder not so distilled with the portions of said fractions containing material boiling above the initial boiling point of said feed which are not so withdrawn, to thereby form the aforesaid heavy recycle oil in a volume ratio to feed between 0.3 and 1.5.

6. The process of claim 5 wherein the entire liquid oil effluent of said hydrocracking zone is distilled at superatmospheric pressure, the entire remainder from said superatmospheric distillation is distilled under vacuum to separate distillate boiling below the initial boiling point of said feed, and only a portion of the remainder from this vacuum distillation is further distilled under vacuum to separate fractions boiling above the initial boiling point of said feed.

7. The process of claim 6 wherein said distillate boiling below the initial boiling point of said feed is withdrawn as a net product.

References Cited by the Examiner

UNITED STATES PATENTS

3,142,634	7/1964	Ireland et al. _____	208—94
3,142,635	7/1964	Coonradt et al. _____	208—111
3,174,925	3/1965	Claussen et al. _____	208—111

DELBERT E. GANTZ, *Primary Examiner.*

75 R. RIMENS, *Assistant Examiner.*