

PROCESS FOR THE PRODUCTION OF LUBRICATING OILS

RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 748,979, filed July 31, 1968, now abandoned.

BACKGROUND OF THE INVENTION

This invention relates to the production of lubricating oils. More particularly, it relates to the production of high viscosity index oils by hydrocracking.

Viscosity index (VI) is a measure of the amount of change of viscosity of an oil with temperature. A high viscosity index indicates that the viscosity change is small over a wide range of temperatures. Thus, a high VI oil is one that does not thin out at high temperatures or become viscous at low temperatures. Because of this property, high VI oils are considered premium oils. The best oils are those with VI's above 100, preferably above 110.

Many lubricating oils as produced do not have particularly high VI's. Consequently, a number of processes have been proposed in the art for increasing the VI of oils. These have included processes in which high VI components are added to a low VI oil or in which a low VI oil is hydroprocessed to raise the VI. Solvent extraction has also been used to improve VI; the low VI components are extracted from the oil, leaving only the high VI components. It is apparent that each of these processes has some disadvantageous features: either foreign materials must be added to the oil; or some oil yield is lost through extraction; or additional processing steps are required.

In recent years, hydroprocessing has been actively investigated as a means for producing lubricating oils with high VI's. These investigations have centered around two basic types of hydroprocesses: hydrocracking and hydrogenation. In general, hydrogenation has been used as a finishing step in lubricating oil manufacture. The raw oils, either straight run or produced by solvent extraction or some similar type of separation process, are hydrogenated at relatively mild conditions. A typical such process is disclosed in U.S. Pat. No. 2,967,144, in which oxidation stability of an oil is improved by hydrogenation. Hydrocracking, which has been considerably less prominent in the lubricating oil area, has been used primarily to produce certain types of lubricating oils. A typical single-stage process is disclosed in U.S. Pat. No. 2,960,458. Occasionally the two processes have been combined with the hydrogenation step being used to upgrade the oil produced by hydrocracking. Typical examples of this combination will be found in U.S. Pat. Nos. 2,779,713, 2,787,582, and 2,917,448.

Another problem which has faced manufacturers of lubricating oils is the fact that many hydrocarbon stocks from which lubricating oils are made contain waxy components. Also, in some hydrotreating processes waxes are formed from previously nonwaxy materials. Elimination of these waxes has been the goal of a number of dewaxing processes. Most of these involve some form of solvent dewaxing. In each of these processes, however, the wax is recovered as a product and must be disposed of as wax in some manner. This has been rather difficult in many cases, for this wax has a fairly low value.

Faced with this problem of disposing of unwanted wax, some researchers have suggested methods of converting the wax into more desirable products. One such method is disclosed in U.S. Pat. No. 3,046,218, in which a hydrocarbon wax and a specifically described type of deasphalted residuum are hydrocracked to produce lubricating oils. As with some other suggested processes, however, this process requires a narrowly defined feed and, therefore, is of no use as a process of general application. Further, since the process involves the use of only one hydrocracking reactor, it inherently has little flexibility for making good lubricating oil products from a variety of feeds.

STATEMENT OF INVENTION

In accordance with the present invention, there is provided a process for the simultaneous production of high viscosity index lubricating oils and conversion of wax to desirable products which comprises:

- a. Hydrocracking in a first hydrocracking zone in the presence of hydrogen and hydrocracking catalyst comprising an active cracking catalyst support comprising silica and alumina and containing by weight more alumina than silica, at a temperature of 700°-850° F. a first hydrocarbon oil feed boiling in the range 800°-1,200° F. and containing less than 5 weight percent asphaltenes, at a conversion of at least 20 volume percent to materials boiling below the initial boiling point of said feed, and with a net hydrogen consumption of at least 500 s.c.f. of hydrogen per barrel of said feed;
- b. Separating from the effluent of said first zone a wax-containing hydrocarbon fraction boiling in the range 750°-1,100° F.;
- c. Hydrocracking in a second hydrocracking zone in the presence of hydrogen and a hydrocracking catalyst comprising an active cracking catalyst support comprising silica and alumina and containing by weight more alumina than silica, at a conversion of at least 20 volume percent to materials boiling below the feed boiling range and at a temperature of 650°-830° F., and with a net hydrogen consumption of at least 500 s.c.f. of hydrogen per barrel of hydrocarbon feed, said wax-containing hydrocarbon fraction and a second hydrocarbon oil boiling in the range 700°-1,100° F., said second hydrocarbon oil having an average boiling point no higher than the average boiling point of said first hydrocarbon oil feed and containing less than 5 weight percent asphaltenes; and
- d. Recovering from the effluent of said second zone at least one light neutral oil having a viscosity index above 100. Preferably said hydrocarbon oil feeds contain less than 1 weight percent asphaltenes, because oils with high asphaltene contents tend to foul the hydrocracking catalysts. The lubricating oil products may be stabilized to ultraviolet light either prior to or following dewaxing. Said wax-containing hydrocarbon fraction may be separated from the effluent from said first zone by solvent dewaxing. Preferably, in each of said zones the hydrocarbon feed thereto is hydrocracked at a conversion of at least 50 volume percent to products boiling below the initial boiling point of said feed. Preferably the catalyst in each of said zones comprises an acidic cracking component and a hydrogenating component selected from Group VI and Group VIII metals and compounds of said metals.

CATALYSTS

The cracking component of the catalysts used in the process of the present invention comprises silica and alumina in an amount of at least 10 weight percent, and has an alumina-to-silica weight ratio greater than unity. Such weight ratios result in lower catalyst fouling rates in the presently claimed type of operation than are achieved with catalysts having cracking components containing more silica than alumina. The cracking component may be prepared by any convenient method, preferably cogelation or coprecipitation. The cracking component also may contain materials such as zirconia, titania or boria. Preferred Group VIII components are nickel, cobalt, platinum and palladium, and the oxides and sulfides of nickel and cobalt. Preferred Group VI components are molybdenum and tungsten, and the oxides and sulfides thereof. Examples of preferred combinations are nickel-tungsten-silica-alumina and nickel-molybdenum-silica-alumina.

REACTORS AND OPERATION THEREOF

The first stage reactor in the present process may be operated by preheating the oil feed and hydrogen underpres-

sure and then passing them downwardly through one or more stationary beds of catalyst particles contained in that 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. The second-stage reactor may be operated in a similar manner. Hydrogen consumption in each stage, or zone, is in excess of 500 standard cubic feet per barrel of fresh feed, and a particularly preferred range of hydrogen consumption is 600-3,000 standard cubic feet of hydrogen per barrel of fresh feed. If desired, excess hydrogen from the first zone may be passed into the second zone.

HYDROCARBON OIL FEEDSTOCKS

The hydrocarbon oil feed to the first zone, referred to as the "first feed," is a wax-producing hydrocarbon oil boiling in the range 800°-1,200° F. It may be a heavy straight run gas oil, a deasphalted oil, or the like. It may previously have been desulfurized and/or denitrified. Its wax-producing characteristics may be due to waxes already present and suspended or dissolved in the oil stock; or, alternatively, it may contain oil molecules which, when contacted with hydrocracking catalysts, are converted into wax molecules. Preferred first feeds are those boiling at 900° F. or higher.

The hydrocarbon oil feed to the second reaction zone, referred to as the "second feed," is a hydrocarbon oil boiling in the range 700°-1,100° F. and is no heavier than the first feed (i.e., has an average boiling point no higher than the average boiling point of the first feed.) Preferably, the second feed is somewhat lighter than the first feed, for the former is primarily intended to be a source of the lighter oils while the latter is primarily intended to be a source of the heavier oils. The second feed may also be a straight-run gas oil or any other hydrocarbon oil boiling within the proper range. It is preferred that the second feed have considerably less wax-producing characteristics than the first feed. Because of poisoning effects on the catalysts caused by cracking of asphaltenes to coke, it is required that the feeds each contain less than 5 weight percent asphaltenes. Preferably, in order to minimize catalyst poisoning, the asphaltene content is below 1 weight percent. The nitrogen content, however, may be more than 10 p.p.m. particularly when a catalyst is used that contains sulfides of nickel, cobalt, molybdenum, or tungsten.

CONDITIONS

Reaction conditions in the first zone are temperatures within the range 700°-850° F., hydrogen pressures between 1,000-5,000 p.s.i.g., and liquid hourly space velocities between 0.1-10.0. Under these conditions, a variety of reaction products will be formed as the high-boiling first feed is cracked to lower-boiling products and waxes are formed. The effluent from this zone will contain, among other products, a hydrocarbon wax boiling in the range 750°-1,100° F. This wax is separated from the effluent from the first zone and passed to the second zone for further hydrocracking, together with the hydrocarbon oil feed to the second zone.

It is an unexpected advantage of the process of this invention that the presence of the wax from the hydrocracking of the first feed permits the second zone reaction condition to be maintained at a less severe level for a given LHSV than would otherwise be expected for hydrocracking the second feed alone at the same LHSV. Consequently, the reaction conditions in the second zone include temperatures within the range 650°-830° F., hydrogen pressures between 1,000-5,000 p.s.i.g., and space velocities between 0.1 and 10.0

PRODUCTS AND PRODUCT SEPARATION

The various reaction products are separated from the two hydrocracking zone effluents. Generally, a number of different hydrocarbon materials are recovered. These include

light gases, some materials boiling in the naphtha boiling range, and, of course, lubricating oils, including at least one light neutral oil with a viscosity index of at least 100. Generally, in the process of the present invention said light neutral oil will have a viscosity index of at least 110.

The effluent from the first zone will, in addition, contain hydrocarbon wax. In accordance with the process of this invention, however, at least a portion of the wax is not recovered as a product, but is passed to the second-hydrocracking zone for conversion along with the second feed. Preferably the combined hydrocarbon oil plus wax feed to the second zone will contain 1-11 volume percent hydrocarbon wax. While it is preferred to convert in the second zone all the wax in the effluent from the first zone, it may in some cases be desirable to recover as a wax product some portion of the wax from the effluent from the first zone. The wax may be added to the second hydrocracking zone in any convenient manner. It may, for instance, be added to the second feed prior to reaching the second zone. If the second zone comprises a reaction vessel with a plurality of fixed catalyst beds, in a particularly preferred embodiment the wax is added at the inlet end of the vessel (generally the top, in a conventional vertical downflow reactor); and the second feed, which is lighter than the wax, is added between the first and second catalyst beds. This minimizes the total amount of catalyst required to obtain the desired products.

The various lubricating oils are separated according to their "neutral oil rating." A neutral oil rating is simply the viscosity of a given oil at 100° F. Thus an oil with a viscosity of 130 S.U.S. at 100° F. would be labeled a 130 neutral oil. In the process of this invention, various neutral oils will be produced, such as light neutral oils having neutral ratings of 100-200 and heavier neutral oils which may have neutral ratings of about 300-500, up to as high as about 800 or more. In ordinary operation, the effluents from the two zones are combined and the wax is separated and passed to the second zone. The dewaxed material is then separated into the various products, including the neutral lubricating oils. In some cases, however, particularly where a very high viscosity index oil having a neutral rating of about 200-500 is desired, the process of this invention may be run in what is termed "blocked operation." In blocked operation, the two effluents are dewaxed and fractionated separately. Wax from the first zone effluent and any wax which may appear in the second zone effluent are combined and passed to the second zone. The various products from fractionation of the effluents of each zone may be selectively combined, although many products will be recovered individually since the purpose of the blocked operation is to produce unblended materials.

LUBRICATING OIL STABILIZATION

In the past it has been noticed that some oils produced by hydrocracking show a degree of instability in the presence of ultraviolet light. This instability is evidenced by the formation of a dark precipitate when the oil is exposed to natural or artificial ultraviolet light. The light neutral oils tend to show a higher degree of instability (e.g., by forming a precipitate more rapidly) than do the heavier neutral oils. This instability can be overcome by conventional stabilization processes, the most common of which is solvent extraction with a solvent such as phenol, hydrogen fluoride or furfural.

EXAMPLES

Several examples will illustrate the process of this invention:

Example 1

A heavy gas oil was hydrocracked to produce a variety of products, including a 36.2° API gravity, 800°-1,050° F. slack wax. This slack wax was hydrocracked along with a 750° F. + asphaltene-free gas oil. The ratio of oil to wax in the feed was 9:1. The hydrocracking was conducted at 770° F., a hydrogen pressure of 2,300 p.s.i.g., a liquid hourly space velocity of 1.0

and a hydrogen throughput of 7,800 s.c.f./bbl. over a nickel-tungsten on silica-alumina catalyst. The ratio of alumina to silica in the catalyst was greater than unity. The product-lubricating oil yield was 41 volume percent of 147 neutral oil with a VI of 119. Hydrocracking of the same gas oil alone to the same yield of light neutral oil would produce a VI of only 99.

Example 2

A 750°-1,020° F. gas oil was hydrocracked with a hydrocracked slack wax similar to that described in example 1 and a small amount of recycle slack wax. The relative proportions by weight of each of these three components were 90:7:3, respectively. Hydrocracking was conducted over the same type of catalyst as in example 1, that is, a nickel-tungsten on silica-alumina catalyst, wherein the ratio of alumina to silica was greater than unity, at a temperature of 775° F., a hydrogen pressure of 2,300 p.s.i.g., and a liquid hourly space velocity of 1.0. A 36 volume percent yield of 124 neutral oil with a VI of 120 was obtained. Under the same conditions, hydrocracking of the gas oil alone would produce an equal yield of light neutral oil with a VI of only 104.

Example 3

The same oil and wax feed as in example 2 was hydrocracked over the same type of catalyst at a temperature of 790° F., a hydrogen pressure of 2,300 p.s.i.g., and a liquid hourly space velocity of 1.3. A 31 volume percent yield of 113 neutral oil with a VI of 123 was obtained. Without the wax present in the feed a product having only a 108 VI would be obtained.

The process of this invention may be advantageously combined with the process disclosed and claimed in U.S. application Ser. No. 748,978 now U.S. Pat. No. 3,503,565. The following examples illustrate how the processes of these two inventions may be combined:

Example 4

In the first reaction zone, a heavy gas oil feed is hydrocracked to produce a variety of oils and wax. A 750°-930° F. hydrocracked oil and a slack wax are both separated from the effluent of the first reactor and passed to the second reactor, where they are hydrocracked along with a lighter gas oil of type described in examples 1-3. Hydrocracking is conducted over a catalyst of the type used in examples 1-3 at a temperature of 761° F., a pressure of 2,300 p.s.i.g., and a liquid hourly space velocity of 1.3. A 53 percent yield of 184 neutral oil having a VI of 109 was obtained. Under the same conditions, hydrocracking of the gas oil feed and wax alone would produce a similar oil having a VI of 103 and hydrocracking of this gas oil alone would produce an oil having a VI of only 87.

Example 5

The same feed as that described in example 4 was hydrocracked under equivalent conditions, with the same type of catalyst as used in example 4, with the sole exception that the temperature was raised to 782° F. Under these conditions, a 38 volume percent yield of 131 neutral oil having VI of 120 was obtained. Hydrocracking the gas oil and wax feed alone would produce an equivalent oil having a VI of 119, while hydrocracking a gas oil alone under these conditions would produce an oil having a VI of only 102.

It is apparent from the above data that addition of

hydrocracked slack wax, from a reactor wherein a heavy oil feed is hydrocracked, to a reactor wherein a generally lighter oil feed is being hydrocracked materially increases the viscosity index of the oil produced. The results are superior to those obtained by recycling the slack wax back to the reactor from which it came, instead of passing it to a different reactor together with a hydrocarbon oil feedstock. One can thus eliminate undesirable slack wax while substantially increasing the value of the product lubricating oil obtained.

What is claimed is:

1. A process for the simultaneous production of high viscosity index lubricating oils and conversion of wax to desirable products which comprises:

a. Hydrocracking in a first hydrocracking zone in the presence of hydrogen and a hydrocracking catalyst comprising an active cracking catalyst support comprising silica and alumina and containing by weight more alumina than silica, at a temperature of 700°-850° F. a first hydrocarbon oil feed boiling in the range 800°-1,200° F. and containing less than 5 weight percent asphaltenes, at a conversion of at least 20 volume percent to materials boiling below the initial boiling point of said feed, and with a net hydrogen consumption of at least 500 s.c.f. of hydrogen per barrel of said feed;

b. Separating from the effluent of said first zone a wax-containing hydrocarbon fraction boiling in the range 750°-1,100° F.

c. Hydrocracking in a second hydrocracking zone in the presence of hydrogen and a hydrocracking catalyst comprising an active cracking catalyst support comprising silica and alumina and containing by weight more alumina than silica, at a conversion of at least 20 volume percent to materials boiling below the feed-boiling range and at a temperature of 650°-830° F. and with a net hydrogen consumption of at least 500 s.c.f. of hydrogen per barrel of hydrocarbon feed, said wax-containing hydrocarbon fraction and a second hydrocarbon oil boiling in the range 700°-1,100° F., said second hydrocarbon oil having an average boiling point no higher than the average boiling point of said first hydrocarbon oil feed and containing less than 5 weight percent asphaltenes; and

d. Recovering from the effluent of said second zone at least one light neutral oil having a viscosity index above 100.

2. The process of claim 1 wherein said wax is removed from the effluent of said first zone by solvent dewaxing.

3. The process of claim 2 wherein following said dewaxing the wax-free portion of said effluent of said first zone is stabilized to ultraviolet light.

4. The process of claim 1 wherein said light neutral oil recovered from the effluent of said second zone is stabilized to ultraviolet light.

5. The process of claim 1 wherein the asphaltene content of the hydrocarbon feeds to each of said zones is less than 1 weight percent.

6. The process of claim 5 wherein said second oil feed has an average boiling point below the average boiling point of said first oil feed.

7. The process of claim 6 wherein in each of said zones at least 50 volume percent of the hydrocarbon feed to the zone is hydrocracked to materials boiling below the initial boiling point of said hydrocarbon feed.

8. The process of claim 7 wherein said hydrocracking catalyst in each of said zones comprises a hydrogenating component selected from Group VI and Group VIII metals and compounds of said metals.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,617,482 Dated November 2, 1971

Inventor(s) Clark J. Egan

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the Abstract, line 4, "then" should read -- than -- .
Column 5, line 35, "3,503,565" should read -- 3,506,565 -- .

Signed and sealed this 10th day of October 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
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Commissioner of Patents