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MULTIZONE HYDROCRACKING PROCESS FOR HVI LUBRICATING OILS

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ABSTRACT OF THE DISCLOSURE

High viscosity index lubricating base oils are produced from a deasphalted oil in a multizone hydrocracking process in which a sulfided nonacidic catalyst comprising one or more metals of the Group VI-B, VII-B or VIII metals is used in each reaction zone. Preferably, hydrogen sulfide and/or ammonia are removed from the first-zone effluent before introducing it into the second zone. The first reaction zone temperature is at least 750° F. while the second reaction zone temperature is at least 700° F.

BACKGROUND OF THE INVENTION

Field of the invention

The invention relates to a multizone hydrocracking process for the preparation of lubricating oils having a high viscosity index. It particularly relates to a process in which deasphalted oils are hydrocracked at specific temperatures and pressures to produce a lubricating oil base having a high viscosity at 210° F. and a viscosity index greater than 120.

Description of prior art

Lubricating oils, in particular oils used for the lubrication of combustion engines such as gasoline and diesel engines, should meet certain requirements both as regards their viscosity at certain standard temperatures and their viscosity-temperature relationship. As is known, this relation is expressed by the viscosity index as proposed by Dean and Davis. As a result of the introduction of so-called multigrade lubricating oils there is an increasing need for lubricating base oils which show a high viscosity at 210° F. as well as a high viscosity index. In this connection desirable lubricating base oils will have a viscosity of more than 8 centistokes at 210° F. and a viscosity index higher than 110.

The Society of Automotive Engineers has introduced a classification scheme for lubricating oils for combustion engines which is based on viscosity ranges at 210° F. and at 0° F. Multigrade lubricating oils are oils which meet viscosity requirements at 210° F. as well as at 0° F., thus ensuring that in winter these oils are sufficiently thin to present no difficulties in the cold start of the engine and are sufficiently thick at the engine temperatures to perform a lubricating action. Such multigrade oils are designated as 5W/20, 10W/20, 5W/30, 10W/30, 20W/30, 5W/40, 10W/40, 20W/40, etc. oils. Here 5W, 10W and 20W indicate the maximum viscosity at 0° F., the so-called winter grades, while the numbers after the stroke refer to the SAE viscosity range at 210° F.

As a rule mineral lubricating base oils which are obtained by a refining treatment from crude lubricating oil base materials do not meet the SAE specifications for multigrade oils. In general the viscosity index of these mineral lubricating base oils will not be higher than 100 to 105. Therefore, it is customary in the preparation of multigrade lubricating oils to add to the lubricating base

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oils both additives which increase the viscosity of the oil (thickeners) and additives which improve the viscosity-temperature relationship (VI-improvers). In addition, various other additives are incorporated which impart other desired properties to the oil. A multigrade lubricating oil is therefore in general a formulation. Preferred oil formulations are, for example, a 10W/30 or a 10W/40 multigrade oil.

Research on formulated lubricating oils in engines has shown, however, that a lubricating oil deteriorates in the long run through many causes, one being gradual decomposition of the thickener and the VI-improver as a result of shear in the engine. This decomposition of the said compounds (which are in general high-molecular compounds) leads to a permanent decrease in viscosity index and viscosity. In the end the multigrade oil has to be replaced. In addition, the fresh oils show a temporary viscosity loss because as a result of the said shear stresses the polymers in the oil align themselves, as a result of which an apparent viscosity decrease occurs on account of a decrease of the internal friction in the oil itself.

The foregoing shows that there is a need for oils which meet the SAE multigrade specifications without the addition of dopes or at most with only a very slight addition. Such oils will last much longer, while in addition an apparent viscosity loss does not occur. Preferably, lubricating base oils will meet the 10W/30 specification, that is a viscosity at 210° F. of at least 9.6 centistokes (cs.) and a viscosity index of at least 132.

SUMMARY OF THE INVENTION

The present invention provides a process for the preparation of lubricating base oils meeting the 10W/30 multigrade specification without addition of a thickener and/or VI-improver. The process yields lubricating base oils with a viscosity at 210° F. of at least 9.6 cs. and a viscosity index of 125 to 135. These lubricating oils can be formulated to 10W/30 or 10W/40 multigrade oils by addition of small amounts of thickener and/or VI-improver.

A lubricating oil base having the desired properties is produced by treating a deasphalted oil with hydrogen in two reaction zones in the presence of a sulfided non-acidic catalyst. A substantially non-acidic catalyst carrier and one or more metals belonging to Groups VI-B, VII-B and VIII of the Periodic System of Elements is employed in a first reaction zone at a temperature of 760 to 830° F. and a pressure of more than 2100 p.s.i.g., after which the liquid product of the first reaction zone is subsequently passed over a sulfided catalyst of the type described in a second reaction zone, in the presence of hydrogen, at a temperature of 715 to 885° F. and a pressure of more than 2100 p.s.i.g. A lubricating base oil having a viscosity at 210° F. of 9.6 to 14.0 centistokes and a viscosity index of 125-140 is recovered from the liquid product of the second reaction zone.

It is preferred that the liquid product of the first zone is substantially freed from hydrogen sulfide and/or ammonia which are formed from sulfur- and/or nitrogen-containing organic compounds which are usually present in the lubricating oil base material. The simplest way to remove this hydrogen sulfide and/or ammonia is by reduction of the pressure. Other methods, such as stripping with an inert gas, for example, hydrogen or nitrogen, at the pressure prevailing at the reactor outlet or at reduced pressure, can also be applied.

DETAILED DESCRIPTION

It appears that in particular the removal of hydrogen sulfide from the reaction product of the first zone has a very favorable effect on the selectivity and the activity of the sulfided catalyst applied in the second zone. Selec-

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tivity should be taken to include here the selectivity towards the production of a lubricating base oil with the desired properties as defined hereinbefore. As a result of this increased selectivity a higher yield of lubricating base oil with the desired properties is obtained. The activity has also increased so that lower temperatures may be employed in the second zone than in the case where no hydrogen sulfide removal has taken place.

As, however, a sulfided catalyst is applied in the second zone, small quantities of a sulfur compound should be present in the feed to the second zone to keep the catalyst in a sulfided state. The feed to the second zone should preferably contain an amount of sulfur in the range of from 10 to 5000 p.p.m.w. (0.5% w.) and more preferably of from 100 to 2000 p.p.m.w. If residual lubricating oil base materials containing more than 1% w. of sulfur are taken as starting materials, such as the crude oils originating from the Middle East, the liquid product of the first zone will, after removal of hydrogen sulfide, as a rule contain sufficient sulfur in the form of organically-bound sulfur and/or hydrogen sulfide to keep the catalyst of the second zone in the sulfided state. However, if the sulfur content of the said liquid product of the first zone is too low, then quantities of sulfided compounds, such as mercaptans, carbon disulfide and the like, should be introduced such that the sulfur content lies in the range defined above. In order not to affect the catalyst selectivity adversely, preferably not more than 2500 and more preferably less than 1500 p.p.m.w. of sulfur in the form of sulfur compounds is added to the liquid product of the first zone.

Feed to the process of the invention consists of a residual lubricating oil which is entirely or substantially free from asphalt or asphaltic material. Such an oil can be obtained by deasphalting an asphalt-containing residue with light hydrocarbons such as propane, propylene, butane, pentane or mixtures thereof. In addition, mixtures of such hydrocarbons with light alcohols such as methanol and isopropanol can be applied for the deasphalting. The residue is preferably a short residue obtained by vacuum distillation of a crude oil, a topped crude oil or a long residue. If desired, the feed may also be a long residue or the residual oil can be a mixture of a deasphalted short residue with one or more lubricating oil distillates; but these possibilities do not as a rule offer additional advantages in the process of the invention. The residual oil may also be a bright stock, that is a deasphalted residual oil subjected to a treatment with a solvent which is selective towards aromatics.

The deasphalting of residual oils, such as a short residue, and the conditions to be applied in such a process are known in the art. The viscosities of the deasphalted residual oils may vary within very wide limits (15–300 cs. at 210° F.) and depend on the solvent used for the deasphalting. Depending on the origin of the crude oil a short residue deasphalted with pentane can have a viscosity at 210° F. of 260° cs., whereas the same residual oil has a viscosity at 210° F. of 160 cs. if a mixture of pentane and alcohol has been employed as a solvent for the deasphalting. The deasphalted residue obtained with the aid of the lightest hydrocarbons, that is hydrocarbons lighter than pentane, usually has a viscosity at 210° F. of from 24 to 95 cs. and a viscosity index of from 60 to 95 and the use of such a residue is preferred. Special preference is given to the use of a propane-deasphalted short residue (viscosity at 210° F. of from 27 to 55 cs.). The sulfur content of the said residual oils can vary from a value as low as 0.05% to a value as high as 8% w.

The conditions in the first and second zones of the process according to the invention are preferably chosen such that after the first zone the viscosity index of the lubricating oil fraction of the total liquid product has been increased to 95 to 120. If the severity of the conversion in the first zone is chosen to be higher, then a relatively smaller improvement of the viscosity index occurs in the

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second zone but the yields of desired lubricating base oil of high viscosity and viscosity index decrease strongly.

The process for the preparation of a lubricating base oil according to the invention is preferably carried out at a pressure in the first and in the second zone which is higher than 2100 p.s.i.g. and more preferably at a pressure in the range of from 2500 to 4300 p.s.i.g. Application of pressures above 2100 p.s.i.g. in both the first and the second zones is advantageous in that the yield of desired lubricating base oil is increased. Particular preference is given to pressures between 2600 and 3200 p.s.i.g. Although not strictly necessary, the pressure in the second zone is equal to that in the first zone, but there are no overriding objections against a lower or a higher pressure in the second zone.

When the liquid product leaves the first zone, it is preferably first brought to a lower pressure by means of one or more high-pressure and low-pressure separators and then again brought to the pressure desired for the second zone. Such a procedure is very suitable to eliminate the excess hydrogen sulfide present and to increase the selectivity of the sulfided catalyst in the second zone. By an appropriate choice of the pressure reduction it can be ensured that sufficient hydrogen sulfide remains dissolved in the liquid product to keep the catalyst of the second zone in the sulfided state.

The temperatures which are used in the second zone preferably lie in the range of from 715 to 885° F. Very suitable temperatures are those between 750 and 830° F. Depending on the activity of the catalyst applied in the second zone the temperature may be lower or higher than or equal to the temperature employed in the first zone. However, the best results as regards yield, viscosity and viscosity index have been obtained in those cases where the temperature in the second zone was at least equal to and preferably 10 to 50° F. higher than the temperature in the first zone. Suitable temperatures for the first zone lie in the range of from 760 to 830° F.

The space velocity applied can vary from 0.5 to 5 liters of feed per liter catalyst per hour for both zones. In order to make the operation more severe, in general relatively low space velocities will be applied, from 0.7 to 1.5. The hydrogen gas supply, however, may vary within wide limits and is as a rule between 250 and 5000 Nl. hydrogen per kilogram feedstock. The process according to the invention can be carried out in such a way that the total quantity of hydrogen required for the first and second zones is directly added to the feed to the first zone or in such a way that in each zone hydrogen is added separately. Which method is chosen depends on whether or not hydrogen sulfide and/or ammonia is removed immediately by pressure reduction. Thus, if the pressure is reduced between the first and the second zones, as a rule hydrogen will have to be supplied, whereas in the case where no intermediate pressure reduction is applied hydrogen can be added in the second zone.

The catalysts applied in the first and second zones should have a substantially non-acidic catalyst carrier in order to avoid excessive cracking under the reaction conditions employed. Acidity of the catalyst carrier promotes those hydrocarbon conversions which are based on the formation of carbonium ions, that is dealkylation and hydrocracking. Suitable non-acid catalyst carriers which can be used in the process of the invention are the heat-resistant and chemically inert inorganic oxides such as alumina, boria, silica, magnesia, zirconia and the like. In addition, mixtures of some of these oxides can be applied, such as alumina-magnesia or magnesia-zirconia, but mixtures of oxides which contain silica are entirely unsuitable. The most preferred catalyst carrier is alumina, in particular alumina containing less than 1% w. silica. The alumina may contain small quantities of alkali and alkaline earth metals such as potassium, sodium, magnesium and calcium to ensure the non-acidic character of the carrier. Eligible quantities are from 0.05 to 1.5% w. cal-

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culated as oxide. From the foregoing it follows that commercial aluminas containing silica in quantities of more than 5% w., or halogens such as chlorine or fluorine, are unsuitable as catalyst carrier for the process according to the invention.

The metals of the Groups VI-B, VII-B and VIII to which preference is given are molybdenum, tungsten, rhodium and the metals from the Iron Group of Group VIII, namely cobalt, nickel and iron. These metals can be present on the catalyst carrier as oxides or sulfides; for the process of the invention the catalysts are applied in the sulfided state and, if necessary, these catalysts should therefore be sulfided beforehand. Preference is given to the use of sulfided catalysts which contain at least one metal from Group VI-B and at least one metal from Group VIII (Iron Group). Suitable combinations are cobalt-molybdenum, nickel-molybdenum, nickel-cobalt-molybdenum, tungsten-nickel or tungsten-nickel-rhodium. These metals can be present on the carrier in quantities of from 3 to 35% w. for the metals from Group VI-B and of from 0.5 to 10% w. for the metals from Group VIII (Iron Group).

The liquid product of the first zone will contain products boiling below the lubricating oil range. Although these products can be removed from the said liquid product by distillation, this is by no means necessary and the process according to the invention offers the advantage that, preferably after intermediate pressure reduction as discussed hereinbefore, the liquid product from the first zone can as a whole be introduced into the second zone.

The product of the second zone will also contain lower-boiling products, such as gasoline, kerosene and gas oil. These lower-boiling non-lubricating oil products must be separated from the lubricating-oil fraction, which takes place by means of distillation. As a rule the fraction boiling above 700° F. is recovered as lubricating oil fraction. The lubricating base oil obtained from this fraction after dewaxing has a minimum viscosity index of 120; as a rule this fraction has a viscosity index in the range of from 125 to 140. Further fractionation of this fraction >700° F. may yield several lubricating oil fractions with different viscosities and viscosity indices. The lubricating base oils of the invention are usually obtained as a fraction boiling above 900° F. with a viscosity index of at least 120 and a viscosity at 210° F. higher than 9.6 cs. (after dewaxing). The initial boiling point of this base oil, however, may vary from 860 to 960° F.

Dewaxing of the wax-containing lubricating oil fractions takes place with the aid of methods known in the art and with the solvents normally used in these methods. As the dewaxing takes place at lower temperatures, the loss in yield of filter oil increases, which for oils boiling above 900° F. may be as high as 30%. At the same time the viscosity index decreases by about 2 to 3 points. According to the process of the invention, lubricating oil fractions or lubricating base oils can be obtained which have a high viscosity at 210° F. and at the same time a high viscosity index. The viscosities vary from 9.6 to 14.0 cs. (at 210° F.) at a viscosity index of from 120 to 135. Very suitable lubricating base oils are those which have a viscosity of at least 9.6 cs. and a viscosity index of at least 128. However, the liquid product of the second reaction zone is preferably recovered as a lubricating oil fraction with a viscosity index of at least 132 and a viscosity at 210° F. of at least 9.6 cs., that is a 10W/30 lubricating base oil.

Special preference is given to the use of a nickel-containing catalyst in the first reaction zone. In the second zone the same catalyst can be applied as in the first zone, which facilitates operation of the process. However, this is by no means necessary.

The lubricating base oils with a viscosity at 210° F. of at least 9.6 cs. and a viscosity index of at least 128, in particular the 10W/30 lubricating base oils that are obtained according to the process of the invention, consti-

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tute a novel product. These oils, in particular the 10W/30 oils, can be used as multigrade lubricating oils as such or after addition of small quantities of the usual thickeners and/or VI-improvers. Quantities of from 1 to 10% w. of such compounds are as a rule sufficient. Without too high additive cost such oils can be formulated to 5W/30, 5W/40 or 10W/40 multigrade oils. As will be clear to those skilled in the art, the lubricating base oils obtained according to the invention can also, if desired, be mixed with other lubricating base oils, such as distillate oils.

The process according to the invention can be carried out by any method known in the art. For example, both in the first and in the second reaction zones a fluidized catalyst bed or a fixed bed can be applied and the lubricating oil base material to be treated can be passed through the bed together with hydrogen in an upward or downward direction. Recycle of hydrogen to the first or second zones may, or may not, be applied. The hydrogen treatment according to the process of the invention preferably takes place under so-called trickle conditions in both zones. Under these conditions the lubricating oil base material, part of which may be in the vapor and part in the liquid phase, passes in the presence of hydrogen or a hydrogen-containing gas in a downward direction over a fixed catalyst bed; the liquid lubricating oil base material flows as a thin film over the catalyst particles.

Instead of pure hydrogen a hydrogen-containing gas mixture can be used, for example, a mixture of hydrogen and methane. The hydrogen-containing gas mixture preferably contains more than 50% v. hydrogen. If an excess of hydrogen is applied, it is advantageous to recycle the used hydrogen to the previous reaction zone, for example, after removal of undesired compounds such as ammonia and excess of hydrogen sulfide.

The process according to the invention will be further elucidated with the aid of the following examples. In these examples the catalysts applied have first been sulfided at a temperature of 600° F. and a pressure of about 14 p.s.i.g., with the aid of a H_2/H_2S mixture containing 10% v. hydrogen sulfide. Dewaxing of the various lubricating oil fractions has in all cases been effected at -4° F. using a methyl ethyl ketone/toluene mixture (50/50), unless specified otherwise. The viscosity index has been determined according to ASTM-D-567.

EXAMPLE I

A deasphalted residual oil obtained by propane treatment of a short residue of a crude oil originating from the Middle East was treated with hydrogen in a two-zone process in the presence of a commercial desulfurization catalyst. The liquid product of the first zone was substantially freed from hydrogen sulfide by passing it successively through a high-pressure and a low-pressure separator. Before it was introduced into the second zone, the liquid product from the low-pressure separator of the first zone was again pressurized and heated together with fresh hydrogen. The total liquid product from the low-pressure separator of the second zone was separated by distillation into a product boiling mainly below 700° F. (fraction <700° F.) and a fraction boiling above 700° F. (fraction >700° F.), from which fraction the desired lubricating base oil with high viscosity and viscosity index can be obtained by distillation.

After dewaxing with the aid of methyl isobutyl ketone the deasphalted residual oil (DAO) had the following properties.

70 Dewaxed oil >700° F.:

Yield, percent w. on DAO	83.2
Viscosity at 210° F., cs.	43.3
VI	76
Sulfur content, percent w. S	2.5
Total nitrogen content, p.p.m.w. N	798

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The catalyst applied in both the first and the second zones had the following composition: 3.1 p.b.w. Ni, 11.7 p.b.w. Mo and 100 p.b.w. Al_2O_3 . The catalyst was sulfided beforehand in the way indicated. The liquid product from the low-pressure separator of the first zone had a sulfur content of 0.02% w. S, which was sufficient to keep the catalyst in the second zone in the sulfided state.

The pressure applied in both zones was 2850 p.s.i.g. and the temperature of the second zone was varied from 750 to 805° F. The liquid hourly space velocity in both zones was 1.0 and the hydrogen gas supply was 2000 NI. per liter feedstock.

Table 1 shows the yields of oil boiling above 700° F. and 900° F. obtained after distillation and dewaxing of the liquid product of the second zone. The dewaxed oil boiling above 700° F. is a base oil which can be separated into the various lubricating oil fractions by distillation. The oil boiling above 900° F. has been obtained from the preparation of multigrade lubricating oils because of its high viscosity at 210° F. and its high viscosity index.

TABLE 1

Ni/Mo/ Al_2O_3 catalyst			
First zone:			
Reaction temperature, ° F.....	770		
Dewaxed oil >700° F.:			
Yield, percent w. on DAO.....	50.0		
Viscosity at 210° F., cs.....	11.35		
VI.....	112		
Ni/Mo/ Al_2O_3 catalyst			
Second zone:			
Reaction temperature, ° F.....	750	790	805
Dewaxed oil >700° F.:			
Yield, percent w. on DAO.....	39.2	30.4	23.7
Viscosity at 210° F., cs.....	7.95	6.24	5.47
VI.....	125	131	137
Dewaxed oil >900° F.:			
Yield, percent w. on DAO.....	18.8	11.2	6.4
Viscosity at 210° F., cs.....	13.02	11.06	9.72
VI.....	121	127	131

After the hydrogen treatment in the first zone the viscosity index of the dewaxed oil boiling above 700° F. was increased to 112, thus converting this oil to an HVI base oil. After the treatment in the second zone the viscosity index was above 120, depending on the temperature applied in the second zone. The oil fraction boiling above 900° F. and obtained at a second-zone temperature of 805° F. marginally meets the 10W/30 multigrade lubricating oil specification without addition of viscosity and viscosity-index improvers.

EXAMPLE II

The experiments of Example I were repeated with the aid of an experimental catalyst containing a slight quantity of added alkali in the carrier. The catalyst had a composition of 2.35 p.b.w. Ni, 29.4 p.b.w. W, 0.4 p.b.w. Na and 100 p.b.w. Al_2O_3 and had been obtained as follows.

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198 p.b.w. Al_2O_3 were impregnated with 1.83 p.b.w. sodium carbonate which had been dissolved in 200 p.b.w. distilled water. After it had been allowed to stand for 15 minutes, the impregnated alumina was dried at 250° F. and calcined for 3 hours at 930° F. Subsequently 82.5 p.b.w. ammonium tungstate (70.6% w.) were dissolved in as little water as possible with the aid of monoethanolamine and 23.0 p.b.w. $\text{NiNO}_3 \cdot 6\text{H}_2\text{O}$ were dissolved also in as little water as possible. The two solutions were then combined and made up to 200 ml. The calcined alumina was next impregnated with the combined solution and after standing for 15 minutes dried at 250° F. After drying the impregnated alumina was again calcined at 930° F. for 3 hours. The catalyst thus obtained was applied in the second zone of the process according to the invention.

After sulfiding the catalysts in the first and second zones the experiments were carried out under the same conditions as regards pressure, space velocity and hydrogen gas supply as in Example I. The liquid product from the low-pressure separator had a sulfur content of 0.02% w. S, which was sufficient to keep the catalyst in the second zone in the sulfided state.

The results are given in Table 2.

TABLE 2

Ni/Mo/ Al_2O_3 catalyst			
First zone:			
Reaction temperature, ° F.....	750		
Dewaxed oil >700° F.:			
Yield, percent w. on DAO.....	56.6		
Viscosity at 210° F., cs.....	15.11		
VI.....	97		
W/Ni/ Al_2O_3 catalyst			
Second zone:			
Reaction temperature, ° F.....	715	790	825
Dewaxed oil >700° F.:			
Yield, percent w. on DAO.....	57.5	41.4	17.6
Viscosity at 210° F., cs.....	13.33	8.15	4.82
VI.....	104	122	143
Dewaxed oil >900° F.:			
Yield, percent w. on DAO.....	19.2	2.2	
Viscosity at 210° F., cs.....	13.74	10.11	
VI.....	117	128	

The use of a lower temperature in the second zone than applied in the first zone slightly increases the viscosity index of the dewaxed oil. In addition, a 750° F. reaction temperature in the first zone and too large a temperature difference between the first and second zones reduced the yield of desired product in the second zone.

EXAMPLE III

The experiments of Example II were repeated at higher temperatures for the first zone and using the same catalysts in the first and second zones. The results obtained after dewaxing of the various product streams are presented below.

TABLE 3

Ni/Mo/ Al_2O_3 catalyst						
First zone:						
Reaction temperature, ° F.....	770			790		
Dewaxed oil >700° F.:						
Yield, percent w. on DAO...	50.5			38.9		
Viscosity at 210° F., cs.....	11.35			8.53		
VI.....	112			122		
W/Ni/ Al_2O_3 catalyst						
Second zone:						
Reaction temperature, ° F.....	715	770	815	715	750	805
Dewaxed oil >700° F.:						
Yield, percent w. on DAO...	49.1	37.7	22.7	38.1	35.0	18.0
Viscosity at 210° F., cs.....	10.48	8.59	5.39	8.11	7.22	5.07
VI.....	115	121	140	124	129	144
Dewaxed oil >900° F.:						
Yield, percent w. on DAO.....	17.9	5.5	16.9	14.		3.3
Viscosity at 210° F., cs.....	13.69	10.79	13.47	12.10		10.14
VI.....	117	128	120	124		132

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These data show that a second-zone temperature below about 750° F. contributes little toward increasing the viscosity index. The dewaxed oil boiling above 900° F. obtained at reaction temperatures of 790 and 805° F. in the first and second zones, respectively, meets the 10W/30 multigrade lubricating oil specification without further addition of viscosity and viscosity index improvers. Further, a first-zone temperature above 750° F. increases the yield of these desired oils.

EXAMPLE IV

The following example has been included to show that first-zone pressures below 1775 p.s.i.g. are undesirable.

The feed applied was the same as used in the previous examples. The first-zone catalyst was a commercial desulfurization catalyst and had the following composition: 3.9 p.b.w. Co, 9.8 p.b.w. Mo, and 100 p.b.w. Al₂O₃.

The second-zone catalyst was the same Ni/Mo/Al₂O₃ catalyst as that employed in Example I for both the first and the second zones. The pressure applied in the first zone was 710 p.s.i.g., while the liquid hourly space velocity was 2.0. The hydrogen gas supply was 500 NI. per liter feed. The conditions in the second zone were a pressure of 2850 p.s.i.g., a space velocity of 1.0 liter, and 2000 NI. hydrogen per 1 liter feed. The experiments were carried out after the catalysts in the first and second zones had been sulfided in the usual way.

The results obtained were as follows:

TABLE 4

Co/Mo/Al ₂ O ₃ catalyst				
First zone:				
Reaction temperature, ° F.....	715		750	
Pressure, p.s.i.g.....		710		
Dewaxed oil >700° F.:				
Yield, percent w. on DAO.....	80.5		77.2	
Viscosity at 210° F., cs.....	23.4		24.1	
VI.....	90		87	
Ni/Mo/Al ₂ O ₃ catalyst				
Second zone:				
Reaction temperature, ° F.....	790	840	770	835
Pressure, p.s.i.g.....		2,850		
Dewaxed oil >700° F.:				
Yield, percent w. on DAO.....	61.3	21.07	58.5	30.4
Viscosity at 210° F., cs.....	16.02	6.02	15.71	7.21
VI.....	95	124	97	122
Dewaxed oil >900° F.:				
Yield, percent w. on DAO.....	41.5		46.2	12.9
Viscosity at 210° F., cs.....	23.06		21.70	14.03
VI.....	95		100	112

A comparison of the results obtained in the first zone with the properties of the oil feed which was used as the starting material shows that only a marginal improvement of the viscosity index has been obtained and that the yield of dewaxed oil boiling above 700° F. has remained virtually equal. However, the viscosity at 210° F. has decreased, which indicates that only the highest-boiling molecular compounds have been converted to some extent. The main reaction that has taken place is desulfurization. To obtain viscosity indices above 115 the liquid product of the first zone must be passed over the catalyst in the second zone at a considerably higher temperature than that in the first zone. This results in a reduced yield of dewaxed oil boiling above 700° F., while a dewaxed oil boiling above 900° F. with a very low viscosity index is obtained.

EXAMPLE V

This example demonstrates influence of the removal of hydrogen sulfide between the two zones on the yield of lubricating base oil.

The deasphalted residual oil of Example I was treated with hydrogen in two zones at a pressure of 2850 p.s.i.g. In each zone fresh hydrogen was supplied. The catalyst applied in both zone was the experimental alkali-metal-containing W/Ni/Al₂O₃ catalyst described in Example II. The liquid hourly space velocity was 1.0 and the hydrogen supply 2000 NI. per liter of feed for each of

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the two zones. The temperature in the first zone was 815° F.

In one experiment the liquid product from the reactor of the first zone was introduced into the reactor of the second zone without intermediate removal of hydrogen sulfide; in another experiment this product was substantially freed from the hydrogen sulfide formed in the first zone by pressure reduction and subsequently it was repressured and introduced into the reactor of the second zone. The results are shown below.

TABLE 5

W/Ni/Al ₂ O ₃ catalyst			
First zone:			
Reaction temperature, ° F.....		815	
Dewaxed oil >700° F.:			
Yield, percent w. on DAO.....		61.0	
Viscosity at 210° F., cs.....		10.87	
VI.....		109	
W/Ni/Al ₂ O ₃ catalyst			
	Without H ₂ S removal	With H ₂ S removal	
Second zone:			
Reaction temperature, ° F.....	790	770	
Dewaxed oil >600° F.:			
Yield, percent w. on DAO.....	24.4	33.2	
Viscosity at 210° F., cs.....	6.50	7.65	
VI.....	128	124	
Dewaxed oil >900° F.:			
Yield percent w. on DAO.....	9.0	20.5	
Viscosity at 210° F., cs.....	11.67	12.9	
VI.....	120	1	

The table clearly shows the great influence of the intermediate hydrogen sulfide removal on the yield of desired lubricating oil product. Apart from the fact that the hydrogen sulfide removal leads to a higher yield, it also influences the required reaction temperature. Thus, for a product with about the same viscosity index a lower reaction temperature can be applied in the second zone.

It should be observed that the temperatures given in this example are not optimum for the production of lubricating oils with high viscosity indices and that the example given only illustrates the influence of the hydrogen sulfide removal.

EXAMPLE VI

The experiment of Example V with intermediate hydrogen sulfide removal was repeated at a pressure of 2100 p.s.i.g. for both zones. The results are summarized in the table below.

TABLE 6

W/Ni/Al ₂ O ₃ catalyst			
First zone:			
Reaction temperature, ° F.....		790	
Dewaxed oil >700° F.:			
Yield, percent w. on DAO.....		53.2	
Viscosity at 210° F., cs.....		12.59	
VI.....		104	
W/Ni/Al ₂ O ₃ catalyst			
Second zone:			
Reaction temperature, ° F.....	760	795	
Dewaxed oil >700° F.:			
Yield, percent w. on DAO.....	45.3	28.9	
Viscosity at 210° F., cs.....	8.70	6.37	
VI.....	118	130	
Dewaxed oil >900° F.:			
Yield, percent w. on DAO.....	20.4	9.7	
Viscosity at 210° F., cs.....	14.12	11.36	
VI.....	116	124	

At a pressure of 2100 p.s.i.g. and a second-zone temperature lower than the first-zone temperature, the dewaxed lubricating base oil boiling >900° F. produced does not meet the requirements set. When the second-zone temperature is higher than that in the first zone, the yield of desired oil is not optimum.

We claim as our invention:

1. A process for the production of high viscosity index lubricating oils which comprises hydrocracking a deasphalted residual lubricating oil in a first reaction zone at a pressure of at least 2100 p.s.i.g. and a temperature of 760 to 830° F., hydrocracking the liquid product from the first reaction zone in a second reaction zone at a

temperature of 715 to 885° F., the hydrocracking in each reaction zone being effected in the presence of hydrogen over a sulfided catalyst consisting essentially of a non-acidic support selected from the group consisting of alumina, boria, silica, magnesia and zirconia, and a hydrogenation component selected from the group consisting of Group VI-B, Group VII-B, Group VIII and mixtures thereof, and recovering from the second reaction zone liquid product a lubricating oil base which on dewaxing has a viscosity at 210° F. of 9.6 to 14.0 centistokes and a viscosity index of 125 to 135.

2. The process of claim 1 wherein hydrogen sulfide and ammonia are substantially removed from the first reaction zone liquid product before it is introduced into the second reaction zone.

3. The process of claim 2 wherein the first reaction zone liquid product contains 10-5000 p.p.m.w. sulfur.

4. The process of claim 3 wherein the pressure in both reaction zones is between 2500-4300 p.s.i.g.

5. The process of claim 2 wherein the pressure in both reaction zones is between 2600-3200 p.s.i.g., the liquid product from the first zone contains 100-2000 p.p.m.w. sulfur, the temperature in the second reaction zone is 10-50° F. higher than that in the first zone, the liquid hourly space velocity in both zones is between 0.5-5.0, the hydrogen/oil ratio in both zones is between 500-5000 NL per kilogram of feed, and the catalyst consists essentially of a hydrogenation metal component selected from the group consisting of 0.5-10% w. Iron Group, 3-35% w. Group VI-B and mixtures thereof and a non-acidic alumina support.

6. The process of claim 5 wherein the Iron Group metal is selected from the group consisting of nickel and cobalt, the Group VI-B metal is selected from the group consisting of molybdenum and tungsten.

7. The process of claim 5 wherein the feedstock to the first reaction zone is a residual substantially asphalt-free lubricating oil having a viscosity at 210° F. between 24-95 centistokes and a viscosity index between 60-95, the viscosity index after dewaxing the first reaction zone liquid product is between 95-120.

8. A process for the production of a lubricating base oil which on dewaxing has a viscosity at 210° F. of at least 9.6 centistokes and a viscosity index of at least 132 which comprises hydrocracking a deasphalted residual lubricating oil having a viscosity at 210° F. between 27-55 centistokes and a viscosity index between 60-95 in a first reaction zone at a temperature of 760-830° F. to obtain a liquid product which on dewaxing has a viscosity index between 95-120, substantially removing hydrogen sulfide and ammonia from said liquid product, hydrocracking same in a second reaction zone at a temperature of 10-50° F. higher than the first reaction zone, the hydrocracking in each reaction zone being effected at a pressure of 2600-3200 p.s.i.g. in the presence of hydrogen over a sulfided catalyst consisting essentially of a non-acidic alumina support containing less than 1% w. silica and from 0.05 to 1.5% w. alkali and alkaline earth metal oxides, and a hydrogenation metal component selected from the group consisting of 0.5-10% w. Iron Group, 3-35% w. VI-B and mixtures thereof.

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