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(54) Lubricating oils

(57) This invention relates to a process for the production of lubricating oils having a viscosity index of at least 120 and a pour point of -45°C or less, said process comprising oligomerizing a feedstock comprising one or more C5 - C18 1-olefins in the presence of an oligomerization catalyst comprising an ionic liquid to form a lubricating oil.

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Description

This invention relates to a process for the production of lubricating oils from a mixed feedstock comprising 1-olefins having 5 to 18 carbon atoms.

It is well known to oligomerize 1-olefins to hydrocarbons of higher molecular weight and then to hydrogenate or isomerise the oligomer so formed to produce lubricating oils (See eg) US-A-3763244. In most ofthese cases, the 1-olefins are derived initially from ethylene (by the so called "ethylene chain growth and displacement" method) which is a relatively expensive source for such 1-olefins. Moreover, lubricating oils have been produced by oligomerization of relatively pure 1-olefins (see US-A-3780128 and EP-A-0 468 109). This last document also discloses that once the oligomers have been produced, the oligomers of various 1-olefins can be blended either before or after the hydrogenation or isomerization steps in order to produce the lubricating oils of the desired properties such as viscosity index and pour point. For instance, a feedstock containing substantially pure olefin such as eg 1-decene gives rise to a lubricant having a relatively high viscosity index but these products comprise exclusively of units which are multiples of 10 as would be expected of oligomers of decene and predominate in discrete units having 30, 40, 50, 60 and 70 carbon atoms. Such a blend, whilst suitable for some purposes, is not an ideal synthetic lubricant since it is desirable for the molecular weight distribution of the components in a synthetic lubricant blend to simulate those of a mineral oil in their dispersity index, ie a standard deviation curve so that there is continuity and gradual blending of the components in the mixture of products. The molecular weight distribution of the products from discrete multiples of 10 described above do not resemble a standard deviation curve and would therefore lack the consistency of properties due to absence of a continuity and gradual blending of closely related oligomers. That is, the blend lacks consistency of properties due to the absence of a continuity and gradual blending of closely related/matched oligomers. Furthermore, the use of a relatively pure single olefin is relatively expensive. It is also known to oligomerize the olefinic products from a Fischer Tropsch synthesis followed by hydrogenation or isomerization of the oligomer to form lubricating oils (see eg Monoolefins, Chemistry & Technology, by F Asinger, pp 900 and 1089 (1968) and published by Pergamon Press). However, these publications relating to use of the Fischer Tropsch products as the source material for the oligomerization step do not indicate the product mix required to achieve the desired oligomer or the catalyst suitable for the oligomerization step. In our prior published EP-A-0583072 we have claimed and described a process for the catalytically oligomerising an olefinic feedstock comprising a mixture of C5 to C18 olefins but having at least 6% w/w of 1-hexene and at least 2.6% w/w of 1-decene to lubricating oils.

It is therefore the object of the present invention to look at feedstock which would firstly meet the criteria of forming a product with the right blend of components but would also be producible from a relatively inexpensive and commercially available raw material. One such feedstock is the mixture of olefins from a Fischer Tropsch synthesis which is readily available. However, the choice of the feedstock alone is insufficient to achieve this objective since it is also necessary to identify a catalyst system and the oligomerisation conditions which would give rise to the right blend of oligomers.

It has now been found, for instance, that a mixture of 1-olefins which is commercially available eg from conventional Fischer Tropsch processes is a very desirable feed for the oligomerization step and the oligomers thus formed can be converted to lubricating oils by using specific catalysts.

Accordingly, the present invention is a process for the production of lubricating oils having a viscosity index of at least 120 and a pour point of -45°C or less, said process comprising oligomerizing a feedstock comprising one or more C5 - C18 1-olefins in the presence of an oligomerization catalyst comprising an ionic liquid to form a lubricating oil.

The 1-olefin feedstock comprises one or more olefins having 5-18 carbon atoms, preferably from 6-12 carbon atoms. A particularly preferred example of such a feedstock is the olefin stream formed by the Fischer Tropsch synthesis. Such an olefin feedstock is preferably a mixture of olefins

Normally in a Fischer Tropsch synthesis (hereafter "FTS"), a mixture of carbon monoxide and hydrogen is passed over or through a heated catalyst bed to form a wide variety of hydrocarbons. When the hydrogen content of the reactant mixture is high, the reaction products predominantly contain paraffinic hydrocarbons. However, if the proportion of hydrogen in the reaction mixture is low, the reaction products predominantly contain olefinic hydrocarbons.

It is, however, important that even in the case where the reaction products of the FTS are predominantly olefins, the reaction conditions of the FTS have to be controlled to obtain the desired mixture of 1-olefins. For instance, Gasol derived by FTS and described in "Mono-olefins Chemistry & Technology", by F Asinger, page 1089 (1968), published by Pergamon Press, contains about 50% but-2-ene and is said to give poor lubricating materials on polymerization with aluminium chloride. Thus, any unspecified product mix of an unspecified FTS is unlikely to be suitable as feedstock for the process of the present invention. If the products of an FTS are used as feedstock, the FTS can be operated in such a manner that the olefin products of the synthesis contain predominantly a mixture of C7-C10 1-olefins. One such FTS product contains at least 2.6% w/w of 1-decene, preferably at least 7% w/w, and at least 6% w/w of 1-hexene, preferably at least 13% w/w. Such a product mix can be obtained by the conventional FTS processes in which the conditions of operation should be so controlled that the product has a Schulz-Flory alpha value from 0.6 - 0.9, preferably

from 0.7 - 0.8. The Schulz-Flory alpha value is a well recognised concept and is defined eg by P J Flory in "J Am Chem Soc", 58, 1877 (1950); and by G V Schulz in "Z Phys Chem", B43, 25 (1935). This value can be defined by the following equation:

$$\log[Wn/n] = n\log\alpha + [(1-\alpha)^2/\alpha]$$

where Wn is the weight fraction, n is the carbon number and α the probability of chain growth.

In this context the choice of the oligomerization catalyst used is very important. Whilst any of the conventional cationic polymerization catalysts can be used for oligomerization in general, it is essential that an ionic liquid catalyst is used if a lubricating oil of higher viscosity than that achievable by conventional catalysts is desired.

Ionic liquids are primarily mixtures of salts which melt below room temperature. Such salt mixtures include (a) aluminium or gallium compound in combination with one or more of (b) imidazolium halides, pyridinium halides or phosphonium halides and the latter may be further substituted by alkyl groups. Thus, the ionic liquid catalyst used may comprise (a) an aluminium or gallium compound which is suitably a tri-halide, such as aluminium trichloride or gallium trichloride, or, an alkyl aluminium/gallium dihalide such as an alkyl aluminium/gallium dichloride or a dialkyl aluminium/gallium halide and is preferably ethyl aluminium/gallium dichloride. The component (b) in the ionic liquid is suitably a hydrocarbyl substituted imidazolium halide, a hydrocarbyl substituted pyridinium halide, an alkylene substituted pyridinium dihalide and/or a hydrocarbyl substituted phosphonium halide. Specific examples of component (b) include 1-methyl-3-ethyl imidazolium chloride, 1-ethyl-3-butyl imidazolium chloride, 1-methyl-3-butyl imidazolium chloride or bromide, 1-methyl-3-propyl imidazolium chloride, ethyl pyridinium chloride or bromide, ethylene pyridinium dichloride or dibromide, butyl pyridinium chloride, benzyl pyridinium bromide and the like. Methods of preparation of these and other higher alkyl substituted imidazolium halides are described in our prior published EP-A-0 558 187 and WO 95/21871. Furthermore, ionic liquids which are ternary melts and comprise in addition ammonium salts such as those described in our prior published WO 95/21872 can also be used. The ionic liquids described in these prior publications are incorporated herein by reference.

The relative ratios of the two components (a) and (b) in the ionic liquid should be such that they are capable of remaining in the liquid state under the reaction conditions. Typically, the relative mole ratio of aluminium/gallium compound to the component (b) in the ionic liquid is suitably in the range from 1 : 2 to 3 : 1, preferably from 1.5 : 1 to 2 : 1. Within this range, the amount of component (a) is preferably greater than 50 mole % of the total ionic liquid.

It is also important to control the ratio of the catalytic components to the 1-olefin in the feed. For instance, if the 1-olefin feed in the mixture comprises a blend of C6-C10 1-olefins, the mole ratios of olefin to the aluminium and/or gallium halide in the ionic liquid may suitably vary in the range from 1 : 1 to 300 : 1 preferably from 10 : 1 to 200 : 1.

The precise concentration of the two catalytic components chosen would depend upon the specific property desired in the final lubricating oil such as eg the viscosity.

The oligomerization is suitably carried out at ambient temperature, eg temperatures at or below 30°C, preferably around -20 to +20°C. The reaction pressures can be ambient or elevated.

The oligomerization is suitably carried out in the presence of a solvent inert under the reaction conditions, preferably a paraffinic hydrocarbon eg n-hexane.

It is preferable to add the ionic liquid catalyst to the 1-olefin feedstock and is preferably added dropwise with continuous stirring. After the addition of the catalyst, the reaction mixture is allowed to stand for a duration to effect oligomerisation and the reaction mixture can thereafter be neutralised eg by bubbling ammonia therethrough, then diluted by addition of water. This step of neutralisation and dilution with water may be avoided since the ionic liquid forms a separate phase from the reaction mixture when allowed to stand and can be separated by simple decantation. This is a further advantage over the process using conventional catalysts such as tertiary butyl chloride and alkyl aluminium halides which are soluble in the reaction mixture. The organic products can then be rendered free of the inert solvent by eg rotary evaporation. The above steps can be, if desired, carried out in continuous operation.

The resultant residue is an oligomer. This oligomer is a lubricating oil with important and desirable properties but may contain a small proportion of olefinic groups.

The oligomerisation products of the present invention are excellent lubricants and can be used as such or for blending with other additives in a lubricating oil. The products of the present process can have pour points of up to -60°C and viscosity index values above 155, eg 198. These viscosity index values are superior to those achievable by using conventional catalysts.

The present invention is further illustrated with reference to the following Examples:

EXAMPLES:

The ionic liquid used was prepared by adding aliquots of aluminium chloride solid with stirring to 1-ethyl-3-methyl

imidazolium chloride solid in a mole ratio of
2 : 1 respectively with cooling to 8°C. The mixture was then heated to 60°C with stirring. The resultant ionic liquid was cooled and stored in a glove box.

The 1-olefin feedstocks used for these Examples were either single olefins or mixtures eg Raffinate II was mixed with 1-decene in various ratios as shown in the Tables below.

The catalysts were tested in a glass autoclave cooled to -5°C. A heptane diluent was used to reduce reaction exotherms, typically 350 g of heptane were used. In the Examples, 450g of the olefinic feedstock was used (typically comprising 225 g each of Raffinate II and 1-decene). The feedstock was added to the heptane with stirring (at 1000 rpm). Molecular sieves (about 10 g) were added to dry the reaction mixture prior to the addition of the catalyst.

When using the ionic liquid catalyst according to the invention, 5 ml of this catalyst was added to the reaction mixture with stirring.

When using a tertiary butyl chloride/ethyl aluminium dichloride catalyst (comparative test, not according to the invention), 13 g of tertiary butyl chloride was added rapidly to the reaction mixture followed by dropwise addition of 15 ml ofa 1 molar hexane solution of ethyl aluminium dichloride with stirring.

Following the reaction, the catalyst was neutralised by bubbling ammonia through the reaction mixture for 1-2 minutes, followed by addition of 100 ml of water. [This step was used for both the catalyst systems to compare like with like although when using an ionic liquid this step can be eliminated since ionic liquids form a separate phase from the reaction mixture and hence can be readily separated by decantation unlike the tertiary butyl chloride/ethyl aluminium dichloride catalyst which is soluble in the reaction mixture].

After washing, the solvent and light polymers were removed by rotary evaporation at 100°C under vacuum. The resultant products were analysed and the following results were obtained:

Table 1 -

Using Ionic Liquid Catalyst:							
Ex. No	1-Decene (g)	Raffinate II (g)	KV (40) cSt	KV(100) cSt	VI	Pour Point (°C)	Yield %
1	0	475	47.95	6.75	92	-51	76
2	113	338	35.15	6.39	135	<-50	74
3	225	225	45.2	8.21	159	<-53	90
4	338	113	17.22	4.57	198	<-49	nd
nd - not determined							

Table 2 -

Using Tertiary Butyl Chloride/Ethyl Aluminium Dichloride Catalyst:							
CT No	1-Decene (g)	Raffinate II (g)	KV (40) cSt	KV(100) cSt	VI	Pour Point (°C)	Yield %
1	0	450	22.5	4.1	65	<-52	82
2	113	338	33.5	5.92	121	-51	56
3	225	224	55.1	8.76	136	-57	84
4	338	113	58.9	9.69	149	<-51	90
5	450	0	62.1	11.04	172	-57	97
CT - Comparative Tests, Not according to the invention.							

The above data clearly show by using an olefinic feedstock comprising 1-decene with or without Raffinate II, ionic liquid catalysts produce a synthetic lubricant of a higher viscosity index than that achievable using a conventional tertiary butyl chloride/ethyl aluminium dichloride catalyst. Moreover, in the case of Raffinate II/1-decene mixed feed, the ionic liquid catalyst can produce a synthetic lubricant having a VI > 120 for as little as approximately 20% w/w of the 1-decene comonomer.

Example 5

A solution of mixed C_{6-10} olefins was prepared as follows:

204 g (2.429 moles) 1-hexene
158 g (1.411 moles) 1-octene
113 g (0.807 moles) 1-decene

The solution of 460 g mixed olefin (4.647 moles olefin) was added to 213 g heptane solvent with stirring (1000 rpm) and cooling to -5°C.

Ionic liquid preparation was as follows: 130.0 g of solid aluminium chloride were added slowly with stirring to 71.5 g of 1-ethyl-3-methyl-imidazolium chloride solid with cooling to 8°C. The mixture was then heated to 60°C for 1 h, then transfered to a glove box. The resultant ionic liquid consisted of 66 mol% AlCl3. 5ml of ionic liquid catalyst (7.0 g = 0.0509 moles) was added dropwise to the reaction mix. Thus, feed:catalyst ratio was 91.3. An exotherm of +7°C was observed upon catalyst addition. The reaction was allowed to proceed for 3h.

Following reaction, catalyst neutralisation was effected by bubbling with ammonia for 1-2 mins, followed by addition of 100 ml water as previously. After washing, solvent and light polymer were removed by rotary evaporation at 100°C under vacuum.

Table 3

Using Ionic Liquid Catalyst:					
Ex No.	KV(40) cSt	KV(100) cSt	VI	PP °C	Yield %
5	151.3	19.85	152	-45	88

The data clearly show that the ionic liquid catalyst can produce synlube having a viscosity index above 150 cSt and a pour point of -45°C from a mixed 1-olefin feed in which each of the olefins have more than five carbon atoms.

Claims

1. A process for the production of lubricating oils having a viscosity index of at least 120 and a pour point of -45°C or less, said process comprising oligomerizing a feedstock comprising one or more C5 - C18 1-olefins in the presence of an oligomerization catalyst comprising an ionic liquid to form a lubricating oil.

2. A process according to Claim 1 wherein the 1-olefin feedstock comprises one or more olefins having from 6-12 carbon atoms.

3. A process according to Claim 1 or 2 wherein the 1-olefin feedstock is an olefin stream formed by the Fischer Tropsch synthesis (hereafter "FTS") comprising passing a mixture of carbon monoxide and hydrogen over or through a heated catalyst bed operated in such a manner that the olefin products of the synthesis have a Schulz-Flory alpha value from 0.6 - 0.9 and contain predominantly a mixture of C7-C10 1-olefins.

4. A process according to any one of the preceding Claims wherein 1-olefin feedstock produced by FTS contains at least 2.6% w/w of 1-decene and at least 6% w/w of 1-hexene.

5. A process according to any one of the preceding Claims wherein the ionic liquid catalyst is primarily a mixture of salts which melt below room temperature and is selected from (a) an aluminium or a gallium compound in combination with one or more of (b) imidazolium halides, pyridinium halides or phosphonium halides which may be further substituted by alkyl groups.

6. A process according to Claim 5 wherein the aluminium or gallium compound in the ionic liquid catalyst is a trihalide or an alkyl aluminium/gallium dihalide or a dialkyl aluminium/gallium halide.

7. A process according to Claim 5 or 6 wherein the component (b) in the ionic liquid is selected from one or more of a hydrocarbyl substituted imidazolium halide, a hydrocarbyl substituted pyridinium halide, an alkylene substituted pyridinium dihalide and a hydrocarbyl substituted phosphonium halide.

8. A process according to Claim 7 wherein component (b) is selected from one or more of 1-methyl-3-ethyl imidazolium chloride, 1-ethyl-3-butyl imidazolium chloride, 1-methyl-3-butyl imidazolium chloride or bromide, 1-methyl-3-propyl imidazolium chloride, ethyl pyridinium chloride or bromide, ethylene pyridinium dichloride or dibromide, butyl py-

ridinium chloride and benzyl pyridinium bromide.

9. A process according to any one of the preceding Claims wherein the ionic liquid catalysts are ternary melts and comprise in addition ammonium salts.

10. A process according to any one of the preceding Claims 5-8 wherein the relative ratios of the two components (a) and (b) in the ionic liquid catalyst are such that they are capable of remaining in the liquid state under the reaction conditions.

11. A process according to Claim 10 wherein the relative mole ratios ofthe component (a) aluminium/gallium compound to the component (b) in the ionic liquid are suitably in the range from 1 : 2 to 3 : 1.

12. A process according to Claim 11 wherein the amount of component (a) is greater than 50 mole % of the total ionic liquid.

13. A process according to any one of the preceding Claims 5-12 wherein the mole ratios of the aluminium and/or gallium halide catalytic component to the 1-olefin in the feedstock comprising a blend of C6-C10 1-olefins are in the range from 1 : 1 to 300 : 1.

14. A process according to any one of the preceding Claims wherein the oligomerization is carried out at a temperature at or below 30°C.

15. A process according to any one of the precedings Claims wherein the oligomerization is carried out in the presence of a solvent inert under the reaction conditions.

16. A process according to any one of the preceding Claims wherein the ionic liquid catalyst is added dropwise to the 1-olefin feedstock with continuous stirring.

17. Lubricating oils having pour points of up to -60°C and viscosity index values above 155 whenever produced by a process according to any one of the preceding Claims.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 30 0875

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X Y A	US 4 827 064 A (MOBIL OIL CORP.) * claims 1,4-8,13,20,21 * * column 9, line 19; claim 23 *	17 1 1,2,14	C10G50/02
D,Y A	EP 0 558 187 A (BP CHEMICALS) * claims 1,6-10 * * page 3, line 12 - line 25 *	1 1,5-8, 10-12, 14,16	
D,A	EP 0 583 072 A (BP CHEMICALS) * claims 1-4,6,7 *	1-3,5,6, 14,15	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)
C10G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	5 June 1997	De Herdt, O

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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