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Lubricating oils.

This invention relates to a process for producing lubricating oils from waste or virgin polymers, especially olefin polymers such as polyethylene. The polymer is first thermally cracked in a fluidised bed and under inert conditions to form a waxy product and the latter, optionally after a hydrotreatment step, is catalytically isomerized and fractionated to recover the lubricating oil. This oil can be used in automotive applications or can be subjected to further hydrofinishing.

The present invention relates to a process for producing lubricating oils from waste or virgin polymers, especially olefins polymers such as polyethylene.

It is well known to crack waste or virgin polyolefins to form gaseous products including ethylene and/or propylene by thermal cracking of such polyolefins. It is also known, for instance from US-A-3845157 to produce synthetic hydrocarbon lubricants by catalytic cracking of ethylene/olefin copolymers using a silica-alumina catalyst in a first stage. The catalyst used in this first stage not only facilitates the cracking step but also isomerises the product. In a second stage, the product resulting from the cracking is hydrogenated to form the synthetic lubricant. However, such a process which uses a catalyst in the first stage is unlikely to be successful with waste polymers because the impurities such as basic nitrogen compounds in the waste polymer are likely to poison and deactivate the catalyst.

Another prior art process, namely US-A-3676521, claims a particular ethylene/propylene copolymer oil containing 29-71 mol% of ethylene. A titanium-aluminium catalyst is used for the polymerization and the molecular weight of the resulting oil is adjusted by thermal cracking. This reference states that a high proportion of propylene in the polymerization step ensures that the product will have sufficient methyl groups on the carbon backbone which means that the process does not require an isomerization step. However, such a process cannot be employed with a waste polymer feed because such a feed inevitably has a varied composition and cannot be relied upon to have sufficient methyl groups in the carbon backbone for use in the thermal cracking step.

It has now been found that by applying a suitable cracking process to the polymer followed by a hydro-treatment step it would be possible to convert the waste or virgin polymers to a product suitable for use as a lubricating oil.

Accordingly, the present invention is a process for converting polymers to lubricating oils, said process comprising:

- a) thermally cracking the polymer in a fluidised bed of a material substantially inert under the reaction conditions at elevated temperature so as to produce a waxy product,
- b) optionally hydrotreating the waxy product when said product from step a) is contaminated with heteroatomic and/or polynuclear aromatic hydrocarbons so as to remove substantially all of the heteroatomic compounds and polynuclear aromatic compounds therefrom and then recovering the waxy product by distillation,
- c) isomerising the waxy product from step (a), or from step (b) when used, in the presence of a hydrogenation catalyst comprising a Group VI and/or a Group VIII metal supported on a refractory metal oxide to form an isomerizate, and
- d) fractionating the isomerizate from step (c) to recover a lubricating oil fraction having a boiling point of at least 370°C.

As stated above, the polymer used is preferably a polyolefin and can be polyethylene such as eg linear low density or high density polyethylene, polypropylene, EPDM, scrap rubber and the like. These can be waste polyolefins or virgin polyolefins which are of scrap value and recovered from processes using polyolefins during fabrication or other processing methods.

The fluidised bed used for thermally cracking the polymer is inert under the reaction conditions ie to the hydrocarbon reactants and the products produced therefrom. The fluidised bed is suitably formed from a solid particulate material selected from quartz sand, silica, ceramics, carbon black, aluminosilicates and the like. The fluidised bed material is catalytically inert towards the polymer and suitably comprises particles of a size capable of being fluidised, for example 100 to 2000µm.

The thermal cracking process is suitably carried out substantially in the absence of a catalyst at a temperature from 300 to 690°C, preferably from 300 to 550°C and is suitably carried out using a fluidising gas which is also inert under the reaction conditions, eg nitrogen.

By the expression "waxy product" is meant here and throughout the specification that the product has a molecular weight which is significantly lower than the starting olefin eg below 3500 but is at least 100, preferably greater than 300 as determined by GPC methods.

The waxy product formed in step (a) may be contaminated with heteroatomic compounds or polynuclear aromatic compounds depending upon the nature of the starting polymer. Moreover, the heteroatomic compounds may be open chain or heterocyclic compounds. Where such compounds are present in the waxy product from step (a) it would be necessary to subject this waxy product to a hydrotreating step. The hydrotreating step suitably comprises reacting the product from the first step (a) with hydrogen and a conventional hydrotreating catalyst such as cobalt/molybdenum, nickel/molybdenum or a combination of cobalt/nickel/molybdenum supported on eg alumina. The hydrotreating reaction is suitably carried out under standard, commercially accepted conditions eg temperature of 280-400°C, a liquid hourly space velocity (LHSV) in the range of 0.1 to 5 h⁻¹, pressure from 30-200 bar and hydrogen gas rates from 100 to 5000 NLL⁻¹. The process is preferably

carried out using a nickel/molybdenum catalyst supported on alumina in the presence of hydrogen.

The hydrotreatment process is designed to remove substantially all of the heteroatomic compounds and the polynuclear compounds from the product of step (a). By the expression "remove substantially all of the heteroatomic compounds and the polynuclear compounds" is meant here and throughout the specification that

the waxy product contains no more than 5 ppm of nitrogen and no more than 20 ppm of sulphur. It is however, preferable that the waxy product contains no more than 2 ppm of nitrogen and no more than 5 ppm sulphur. The polynuclear aromatic content of the waxy product is suitably less than 5%w/w, preferably less than 2%w/w. The desired waxy product is recovered from the hydrotreatment step by distillation.

The waxy product from step (a), or, where the hydrotreatment step (b) is used, from step (b) is then subjected to an isomerization step (c). The isomerization is carried out in the presence of an isomerization catalyst comprising a hydrogenating metal component from Group VI and/or a Group VIII metal supported on a refractory metal oxide which should preferably be doped with halide ions.

By the expression "Group" as used herein is meant here and throughout the specification the Groups in the Periodic Table given in the text-book, Advanced Inorganic Chemistry by Cotton, F A and Wilkinson, G, 4th Edition (1980) published by Wiley (New York). The metal component of the catalyst used is suitably selected from the Group VIII metals, and is preferably platinum. The refractory metal oxide support used is suitably a transition metal oxide such as γ -alumina or η -alumina which is suitably doped with a halide ion, preferably a fluoride ion. Thus, fluorided alumina is a preferred support in the Case where step (c) is used.

The isomerization catalyst may have to be suitably sized to meet handling considerations. For example, the catalyst may be ground up using eg a pestle and mortar and then screened to obtain the desired size. Such sizing will ensure that the catalyst has acceptable flow characteristics for the reaction depending upon the type of reactor used.

The isomerization catalyst is suitably activated prior to use, eg by heating at elevated temperature in the presence of hydrogen. The activation is suitably carried out at a temperature from 350 to 520°C, preferably from 400 to 510°C.

The isomerization step is carried out in the presence of hydrogen used at pressures of 30 to 200 bar, preferably from 60 to 100 bar. Hydrogen gas rates of 150 to 2000 NLL⁻¹, and an LHSV in the range of 0.1 to 10 h⁻¹, preferably 0.5 to 2 h⁻¹ can be used in this step.

The isomerization treatment is suitably carried out at a temperature in the range from 270 to 400°C, preferably from 300 to 360°C.

It is, however, known to carry out the hydrotreatment and the isomerization, ie steps (b) and (c) above, in a single step using a catalyst system which performs both functions. Such a technique is described for instance in the published FR-A-2124138. Catalysts and methods disclosed in this publication are incorporated herein by reference for this type of combined step. Specifically, such catalysts which perform both functions can eg be oxides or sulphides of nickel and tungsten supported on silica-alumina. In this Case, it is not necessary to dope the catalyst support with halide ions. The isomerized product (termed herein as "isomerizate") is then fractionated to recover the desired lubricating oil. The oil so formed generally has a high viscosity index eg in excess of 130. The lubricating oil so produced can be used in eg automotive applications, and can be subjected to further hydrofinishing processes using conventional catalysts such as cobalt/molybdenum or nickel/molybdenum on alumina supports. Such conventional techniques enable removal of undesirable impurities from the lubricating oil product thereby further improving product quality.

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

EXAMPLE 1:

A hydrocarbon wax (prepared by cracking high density polyethylene at 500-550°C in a sand bed fluidised using nitrogen gas) was distilled to give a fraction with a boiling range of about 190°C to 712°C. This was isomerized over a platinum on fluorided alumina catalyst made by first fluoriding a platinum loaded 1/16 inch η -alumina extrudate (0.32 %w/w platinum) using an aqueous ammonium fluoride solution (insipient wetness) after which the fluorided metal loaded extrudate was dried under vacuum on a rotary evaporator at 80°C for 50 minutes. The metal loaded fluorided extrudate was calcined in flowing air (1000 ml/min) as follows: hold at 120°C for 2h; heat from 120 to 515°C at 10°C/min and from 515 to 550°C at 1°C/min; hold at 515°C for 25 min; cool to room temperature at natural cooling rate. It was then crushed and sieved (0.5-1.4mm) to produce a catalyst with a fluoride content of 5.9%w/w.

The catalyst thus sized was activated by heating at 510°C in flowing hydrogen at 12 bar in the following manner: room temperature to 510°C at 2.5°C/min; hold for 2h. This catalyst was initially used to process a commercially available hydrocarbon wax (Huels, Vestowax SP 1044) prior to switching over to the polyolefin derived waxy product after 686 h on stream. The data presented in the Table below were obtained using the polyolefin

derived waxy product as feed.

EXAMPLE 2:

A hydrocarbon wax was prepared by cracking linear low density polyethylene (LLDPE) at 500-550°C in a sand bed fluidised using nitrogen gas. This was distilled to give a fraction with a boiling range of about 190°-750°C and was isomerized over a platinum on alumina catalyst prepared and activated as in Example 1 above. The catalyst was again initially used to process Vestowax SP 1044 (ex Chemische Werke Huels) prior to switching over to the LLDPE derived waxy product after 144 hours on stream. The data presented in Table below were obtained using the LLDPE derived waxy product as feed.

Parameters	Example 1	Example 2
Catalyst Temperature (°C)	341	347
Pressure (Bar)	70	70
LHSV (h ⁻¹)	0.825	1.125
H ₂ :Hydrocarbon (NLL ⁻¹)	1800	1330
Dewaxed Oil* Yield >370°C (% wt on feed)	35.6	32.7
Fuels Yield <370°C (%wt on feed)	14.2	18
Product Quality		
a) KV 40 (Cst)	26.3	36.59
b) KV 100 (Cst)	5.77	7.25
c) Viscosity Index	171	167

*Dewaxing Temperature (-18°C).

Claims

1. A process for converting polymers to lubricating oils, said process comprising:
 - a) thermally cracking the polymer in a fluidised bed of a material substantially inert under the reaction conditions at elevated temperature so as to produce a waxy product,
 - b) optionally hydrotreating the waxy product when said product from step a) is contaminated with heteroatomic and/or polynuclear aromatic hydrocarbons so as to remove substantially all of the heteroatomic compounds and polynuclear aromatic compounds therefrom and then recovering the waxy product by distillation,
 - c) isomerising the waxy product from step (a), or from step (b) when used, in the presence of a hydrogenation catalyst comprising a Group VI and/or a Group VIII metal supported on a refractory metal oxide to form an isomerizate, and
 - d) fractionating the isomerizate from step (c) to recover a lubricating oil fraction having a boiling point of at least 370°C.
2. A process according to Claim 1 wherein the polymer used is a polyolefin.
3. A process according to Claim 1 or 2 wherein the polymer used is a polyethylene which may be of the linear low density or high density polyethylene type, polypropylene, EPDM, scrap rubber and the like.
4. A process according to any one of the preceding Claims wherein the fluidised bed used for thermally crack-

ing the polymer is inert under the reaction conditions ie to the hydrocarbon reactants and the products produced therefrom.

5. A process according to any one of the preceding Claims wherein the fluidised bed is formed from a solid particulate material selected from quartz sand, silica, ceramics, carbon black, aluminosilicates and the like.
6. A process according to any one of the preceding Claims wherein the thermal cracking process is carried out substantially in the absence of a catalyst at a temperature from 300 to 690°C using a fluidising gas which is also inert under the reaction conditions.
7. A process according to any one of the preceding Claims wherein the waxy product formed in step (a) is subjected to a hydrotreating step by reacting the product from the first step (a) with hydrogen in the presence of a hydrotreating catalyst.
8. A process according to any one of the preceding Claims wherein the hydrotreating reaction, when used, is carried out at a temperature of 280-400°C, a liquid hourly space velocity (LHSV) in the range of 0.1 to 5 h⁻¹, a pressure from 30-200 bar and hydrogen gas rates from 100 to 5000 NLL⁻¹.
9. A process according to Claim 8 or 9 wherein said hydrotreating reaction is carried out using a nickel/molybdenum catalyst supported on alumina in the presence of hydrogen.
10. A process according to any one of the preceding Claims wherein the waxy product from step (a), or, where the hydrotreatment step (b) is used, from step (b) is then subjected an isomerization step (c) carried out in the presence of a isomerization catalyst comprising a hydrogenating metal component from Group VI and/or a Group VIII metal supported on a refractory metal oxide which is doped with halide ions.
11. A process according to any one of the preceding Claims wherein the metal component of the catalyst used in step (c) is platinum and the refractory metal oxide support used is a transition metal oxide doped with a fluoride ion.
12. A process according to any one of the preceding Claims wherein the isomerization catalyst is activated prior to use by heating at elevated temperature from 350-520°C in the presence of hydrogen.
13. A process according to any one of the preceding Claims wherein the isomerization step (c) is carried out in the presence of hydrogen used at pressures of 30 to 200 bar, hydrogen gas rates of 150 to 2000 NLL⁻¹, and an LHSV in the range of 0.1 to 10 h⁻¹.
14. A process according to any one of the preceding Claims wherein the isomerization step (c) is carried out at a temperature in the range from 270 to 400°C.
15. A process according to any one of the preceding Claims wherein the hydrotreatment and isomerization steps (b) and (c) above are carried out in a single step using a catalyst system which performs both functions.
16. A process according to Claim 15 wherein the catalyst which performs both functions is an oxide or sulphide of nickel and tungsten supported on silica-alumina.
17. A process according to any one of the preceding Claims wherein the isomerized product from step (c) is fractionated to recover the desired lubricating oil.