PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Processes for the Isomerisation of Waxy Hydrocarbons.

We, NAAMLOOZE VENNOOTSCHAP DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ, a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to processes for the isomerisation of waxy hydrocarbons, and in particular to the use of catalysts pretreated in a specific way by a conditioning treatment, by means of which catalysts this isomerisation can be effected in an improved manner.

Throughout this specification, the term "waxy hydrocarbons" is intended to include normally solid wax-like products usually obtained from high-boiling natural or synthetic hydrocarbon mixtures, and usually containing normally liquid hydrocarbons.

In the process of this invention the starting material need not only be waxy hydrocarbons as such, for example paraffin wax derived from paraffin-containing mineral oils; thus natural or synthetic hydrocarbon fractions may also be used, which fractions contain at least 20% by weight, and preferably 50% by weight or more, of waxy hydrocarbons. This hydrocarbon content is found from the oil content of the hydrocarbon material, determined by the A.S.T.M. method D 721-51 T.

It is known that the normal or branched alkanes present in paraffin wax may be converted into branched or more highly branched alkanes by subjecting them to a catalytic isomerising treatment.

The present Applicant's prior Patent Specification No. 713,910 discloses that this isomerisation can be carried out rapidly and selectively by contacting the paraffin wax in vapour form, together with hydrogen, at a temperature between 300°C and 550°C, and preferably between 350° C and 450° C, with a catalyst containing not more than 1% by weight of platinum applied on a carrier, for example alumina. The present Applicant's prior Patent Specification No. 579/54, discloses that the desired isomerisation can also be effected by means of such a catalyst by treating the paraffin wax in the liquid phase under conditions which are otherwise the same. Furthermore, the present Applicant's prior Patent Specification No. 9,081/54 discloses that cheaper catalysts containing no platinum, viz. those consisting of one or more metals or compounds of metals, especially oxides or sulphides, of group 6A and/or group 8 of the Periodic Table (with the exception of the platinum metals), supported on a carrier with an acid nature which may be caused or increased by introducing a halogen, preferably fluorine, may be used for isomerising mixtures of hydrocarbons containing at least 20% by weight of waxy hydrocarbons.

Lower melting products which may be used as components in high-grade lubricants and diesel oils can be obtained from higher melting, paraffinous starting materials, practically the same molecular weight being retained, by means of these processes, which processes are carried out at increased pressure, for example at pressures from 10 to 40 atmospheres. The isomerisation is effected without the occurrence of cracking reactions to any considerable extent.

It has now been found that in the catalytic isomerisation of hydrocarbon mixtures containing at least 20% by weight of waxy hydrocarbons, an increase in the conversion of the starting material into the desired isomerisation products can be obtained by previously applying a conditioning treatment to the catalyst, which treatment consists in heating the catalyst in the presence of hydrogen under pressure to a high temperature of at least 250°C.

Accordingly, the present invention provides for the catalytic isomerisation of a

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hydrocarbon mixture containing at least 20% by weight of waxy hydrocarbons which comprises subjecting a solid catalyst which is capable of effecting isomerisation of such a hydrocarbon mixture to a conditioning treatment which consists in heating said catalyst to a temperature of at least 250°C in the presence of hydrogen under increased pressure, and then contacting the said hydrocarbon mixture in the presence of hydrogen at a temperature within the range from 300°C to 550°C and under increased pressure with the said catalyst.

The duration of this conditioning treatment, which may vary fairly considerably according to the nature of the catalyst and the heating temperature, is usually several hours, for example 5 to 10 hours.

In isomerisation processes, heating of the catalyst to the required reaction temperature is sometimes carried out in a hydrogen atmosphere; but such a method of heating up the catalyst, in which the latter is rapidly raised to the reaction temperature, is not, however, to be compared with the conditioning treatment employed in the present invention, for which a fairly lengthy heating with hydrogen under pressure is required.

The said conditioning treatment employed in the present invention may be effected by gradually heating the catalyst from room temperature to the required high temperature of at least 250°C while passing hydrogen through under pressure. If desired, this high temperature may be maintained for some time and conveniently corresponds approximately to the temperature which is used subsequently during the isomerisation.

The conditioning treatment of the catalyst should be carried out at an increased hydrogen pressure, for example 5 atmospheres or higher, pressures of between approximately 25 and 100 atmospheres being generally preferred. The hydrogen need not be pure, and gases may also be used which are rich in hydrogen. The gas which is employed may contain components which under the pretreatment conditions are inert, such as gaseous methane hydrocarbons or nitrogen, in addition to hydrogen.

The hydrogen pressure which is employed during the conditioning treatment of the catalyst may be equal to or different from the pressure under which the subsequent isomerisation of the waxy hydrocarbons is carried out, but is preferably lower than this pressure.

It has been found that during isomerisation with the conditioned catalyst it is often advantageous to reduce the pressure, for example from 40-50 atmospheres to 25-35 atmospheres, after the lapse of a relatively short operation period, for example a period of 50 to 150 hours, because this reduction in pressure is often attended by a considerable further increase in the conversion. The conversion is thus noticeably higher than the conversion which is obtained on immediately beginning the isomerisation at the lower pressure, conditions remaining otherwise unchanged. This advantage is obtained particularly when the catalyst is subjected to the conditioning treatment at a lower pressure than that at which the subsequent isomerisation is begun.

The isomerisation may be carried out either in the vapour phase or in the liquid phase. Operating in the liquid phase is especially suitable for hydrocarbon starting materials which have such a high molecular weight that they cannot, or only with extreme difficulty, be brought in to the vapour form without cracking reactions taking place, for example paraffin waxes with an average molecular weight of over 350 and boiling above 300°C. The so-called "trickle technique," wherein the material to be isomerised flows in a thin layer over a fixed catalyst may be advantageously used for liquid phase isomerisations.

The most favourable conditions for isomerisation vary somewhat according to the hydrocarbon starting material to be isomerised and the catalyst which is used. Isomerisation generally proceeds most favourably, especially when working in the liquid phase, with a temperature of from 400°C to 440°C, a pressure between 20 atmospheres and 40 atmospheres, a contact time of from 0.5 to 10 minutes and a throughput rate of from 1 to 5 kilograms of starting material per litre of catalyst per hour, the mol. ratio of hydrogen to starting material varying from 10:1 to 60:1.

The process of this invention has been found to be particularly useful when isomerisation catalysts are used which contain not more than 1% by weight of platinum supported on a carrier having an acid character, such as alumina which may contain a small percentage of chlorine or fluorine, as the effect of conditioning is usually greatest with these catalysts. The present process is not, however, limited to these catalysts and can also be successfully employed when other catalysts with an isomerising effect and having dehydrogenating properties as well as an acid nature are used, for example those described in the aforementioned Patent Specification No. 9,081/54, particularly molybdenum-alumina-fluorine catalysts containing less than 5% by weight of fluorine uniformly distributed over the active surface of the carrier.

By means of the process of this invention considerably higher yields of isomerised product can be obtained than by operating with a non-conditioned catalyst under otherwise the same reaction conditions. Thus when isomerising paraffin waxes boiling above 300°C (the average molecular weight of which was above 350), using platinum catalysts, yields of oil boiling above 300°C were obtained which, according to the conditions under which the catalyst was pretreated by the said conditioning treatment, were approximately 10% to 20% higher than the yields which were obtained using the unpretreated catalysts. Cracking reactions leading to the formation of products of lower molecular weight occur only to a slight degree; the conversion efficiency (i.e. the percentage by weight of isomerised product having the same molecular weight as the starting material, as compared with the total converted starting material), which may amount to 85% to 90% or even more, is at least as high as when an unpretreated catalyst is used; while the properties such as viscosity, viscosity index and pour point of the oils obtained in both cases show only insignificent differences.

The present invention is further illustrated by the following Examples:

EXAMPLE I

A solid paraffin wax melting at 54°C, boiling above 300°C, and with an average number of 27 carbon atoms per molecule, was passed at a throughput rate of 2 kilograms per litre of catalyst per hour, together with 10 mol of hydrogen per mol of paraffin wax, at 420°C and under a pressure of 35 atmospheres in a downward direction over a granular, commercialised so-called platforming catalyst. The molten paraffin wax was allowed to flow over the catalyst particles in a thin layer. The catalyst was preheated over a period of 8 hours from room temperature to 420°C, hydrogen being passed through at atmospheric pressure in a quantity of 1,000 N-litres per litre of catalyst per hour.

The hydrocarbons boiling below 300°C, comprising approximately 6% by weight of the starting paraffin wax, were removed by distillation from the product which was obtained, after which the product boiling above 300°C was dewaxed at −5°C. The oil thus obtained in a yield of 46.6% by weight, based on the paraffin wax starting material, had a pour point of 8°C, a viscosity index of 157, a viscosity of 11.6 centistokes at 100°F and 3.2 centistokes at 210°F.

The conversion efficiency of paraffin wax into oil was 88%.

The isomerisation was repeated under the same reaction conditions, using the same catalyst, except that the catalyst was first subjected to a conditioning treatment in which it was heated at a pressure of 35 atmospheres with hydrogen to a temperature of 420°C, but in other respects as indicated above. The oil thus obtained in a yield of 55% by weight had a pour point of 8°C, a viscosity index of 156, a viscosity of 11.5 centistokes at 100°F and of 3.0 centistokes at 210°F.

The conversion efficiency of the paraffin wax into oil was 90%.

EXAMPLE II

The starting material was the same paraffin wax as was employed in Example I, the same catalyst being used. The catalyst was heated over a period of 8 hours to 420°C while passing through 1,000 N-litres of hydrogen per litre of catalyst per hour at a pressure of 35 atmospheres. The isomerisation occurred under the same conditions as in Example I, except that the pressure was first held at 50 atmospheres and was then reduced to 35 atmospheres after approximately 70 hours. The product which was obtained was also worked up in the same way as in Example I. During the starting-up period at 50 atmospheres the yield of oil obtained gradually increased to a value of 47.2% by weight, calculated on the paraffin wax starting material. After the pressure was reduced to 35 atmospheres, there was a considerable increase in the yield, viz. to 66% by weight. The conversion efficiency of paraffin wax into oil was then 90%, while the oil obtained had a pour point of 8°C, a viscosity index of 151 and a viscosity of 11.9 centistokes at 100° F and of 3.2 centistokes at 210°F.

When the same platinum catalyst was heated up to 420°C while passing through 1,300 N-litres of hydrogen per litre of catalyst per hour at a pressure of 50 atmospheres and the catalyst thus treated was used for isomerising the same paraffin wax, operating under a pressure of 50 atmospheres a yield of dewaxed oil boiling above 300°C was obtained, which yield increased from 48% to 51% over a period of approximately 130 hours.

When isomerisation was then continued at a pressure reduced to 35 atmospheres, the conditions remaining otherwise unchanged, an increase in yield to 61% was obtained. The conversion efficiency of paraffin wax into oil was then 90%. The oil obtained had a pour point of 5°C, a viscosity index of 148 and a viscosity of 11.5 centistokes at 100°F and of 3.1 centistokes at 210°F.

What we claim is:—

1. A process for the catalytic isomerisation of a hydrocarbon mixture containing at least 20% by weight of waxy hydrocarbons which comprises subjecting a solid catalyst which is capable of effecting isomerisation of such a hydrocarbon mixture to a conditioning treatment which consists in heating said catalyst to a temperature of at least 250°C in the presence of hydrogen under increased pressure, and then contacting the said hydrocarbon mixture in the presence of hydrogen at a temperature within the range from 300°C to 550°C and under increased pressure with the said catalyst.

2. A process as claimed in claim 1, wherein, in the said conditioning treatment the catalyst is gradually heated to a temperature which approximates to that temperature at which the isomerisation is subsequently carried out.

3. A process as claimed in claim 1 or 2, wherein the said conditioning treatment is carried out under pressure which is lower than that under which the isomerisation is carried out.

4. A process as claimed in any one of the preceding claims, wherein the said conditioning treatment is carried out under a pressure between about 25 and 100 atmospheres.

5. A process as claimed in any one of the preceding claims, wherein the duration of the said conditioning treatment is between 5 and 10 hours.

6. A process as claimed in any one of the preceding claims, wherein the pressure under which the isomerisation is carried out is reduced after isomerisation has been carried out for a relatively short period of time.

7. A process as claimed in claim 6, wherein the said period of time is between 50 and 150 hours.

8. A process as claimed in claim 6 or 7, wherein the said pressure is reduced from a pressure between 40 and 50 atmospheres to a pressure between 25 and 35 atmospheres.

9. A process as claimed in any one of the preceding claims, wherein the catalyst is a platinum catalyst supported on a carrier.

10. A process as claimed in claim 9, wherein the said carrier has an acid character.

11. A process as claimed in claim 10, wherein the said carrier is alumina containing a small percentage of chlorine or fluorine.

12. A process as claimed in claim 9, 10 or 11, wherein the said platinum catalyst contains not more than 1% by weight of platinum.

13. A process as claimed in any one of the preceding claims, wherein the said hydrocarbon mixture contains at least 50% by weight of waxy hydrocarbons.

14. A process as claimed in claim 13, wherein the said hydrocarbon mixture is a paraffin wax.

15. Processes for the catalytic isomerisation of hydrocarbon mixtures wherein the catalyst is subjected to a conditioning treatment in the presence of hydrogen under increased pressure substantially as hereinbefore described with particular reference to the Examples.

16. Isomerised hydrocarbon products whenever prepared by a process as claimed in any one of the preceding claims.

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