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COMPLETE SPECIFICATION

A Process for the Isomerisation of Waxy Hydrocarbons

We, NAAMLOOZE VENNOOTSCHAP DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ, of 30, Carel van Bylandtlaan, The Hague, The Netherlands, a Company organised under the Laws of 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 a process for the isomerisation of waxy hydrocarbons in the liquid phase.

Throughout this Specification and the claims hereinafter appearing the term "waxy hydrocarbons" means normally solid hydrocarbons obtainable from natural or synthetic high-boiling hydrocarbon mixtures.

It has already been proposed to subject paraffin wax to an isomerising treatment in order to convert the normal or branched alkanes present therein into branched or more highly branched alkanes. According to British Patent Specification No. 634,602, this isomerisation takes place by treating the starting material in the liquid phase at an elevated temperature, for example at 80°C. to 100°C., in the presence of a catalyst consisting of a hydrocarbon-metal-halide-complex, for example a toluene-aluminium chloride-complex. In order to avoid pronounced decomposition of the starting material and the formation of products having a lower molecular weight, a large quantity of a cracking inhibitor, for example decahydro-naphthalene, should also be present. Under the reaction conditions employed isomerisation takes place only slowly.

According to the Applicants' previous British Patent No. 713,910, the isomerisation of normally solid paraffin wax can be effected more successfully by passing the base material, in vapour form together with hydrogen at a temperature between 300°C. and 550°C. and under reduced, atmospheric or increased pressure, into contact with a catalyst containing not more than 1% by weight of platinum applied to a carrier. In this process, which is carried out in the vapour phase, the desired isomerisation proceeds rapidly and selectively, thus ensuring a high degree of conversion even when the period of contact is short. However, a disadvantage of the process is that large quantities of hydrogen, for example 50 moles of hydrogen per mole of paraffin wax, or even more, are required to bring the starting material into the vapour state and to maintain the activity of the catalyst. Furthermore, the process is less suitable for treating very high-boiling base materials which can only with difficulty be passed into the vapour state without cracking reactions occurring.

If the treatment is carried out in the liquid phase by passing a liquid stream of the starting material, for example in an upward direction, through the catalyst bed, considerably less favourable results are generally obtained, especially in terms of the yield of isomerised product, under those conditions of temperature and pressure which are otherwise the same as those prevailing in the vapour phase process. Moreover the activity of the catalyst rapidly decreases. This is also true when the process is carried out in the presence of suitable quantities of hydrogen to protect the catalyst against contamination.

It has been found that catalytic isomerisation of a hydrocarbon mixture containing at least 20% by weight of waxy hydrocarbons may be carried out with particular advantage by treating the hydrocarbon mixture in the liquid phase at an elevated temperature and in the presence of hydrogen using the so-called "trickle technique". According to this technique, the hydrocarbon mixture to be treated flows in liquid form in a thin layer over a catalyst arranged as a fixed bed.

Accordingly the present invention pro-

[*Price* 3/-]

Price 4s 6d

vides a process for the catalytic isomerisation of a hydrocarbon mixture containing at least 20% by weight of waxy hydrocarbons, which comprises passing a thin layer of the said hydrocarbon mixture in the liquid phase at an elevated temperature and in the presence of hydrogen, over a fixed bed of a solid catalyst which has dehydrogenating properties and an acid character.

In the process according to this invention not only waxy hydrocarbons, such as paraffin wax, produced from paraffin-containing mineral oils may be used as such as starting materials, but natural or synthetic hydrocarbon fractions having a content of at least 20% by weight, and preferably 50% by weight or more, of waxy hydrocarbons may also be used. This content is found from the oil content of the hydrocarbon material determined according to the A.S.T.M. method D 721-51 T.

Suitable catalysts comprise all those catalysts which are solid at the reaction temperatures employed, which have dehydrogenating properties and an acid character, and which promote the isomerisation to be attained without simultaneously causing pronounced decomposition of the starting hydrocarbons to products of lower molecular weight. In addition to platinum on a carrier of an acid nature, such as alumina, other catalysts having dehydrogenating properties and an acid character are also suitable. Particularly suitable are the metals of the sixth group, left-hand column, and on the eighth group of the Periodic System, or compounds, especially the oxides and sulphides of these metals, applied to acid carriers, for example natural or artificial alumina, silica-magnesium oxide or alumina-silica gels, and bauxite.

If desired, the acid nature of the catalyst employed can also be produced or intensified by the introduction of halogen, preferably fluorine, for example by applying a hydrogen fluoride treatment. Examples of such catalysts include platinum on alumina-silica + fluorine (if desired), a platinum-molybdenum oxide or alumina + fluorine, nickel sulphide-tungsten sulphide on alumina + fluorine, and molybdenum oxide on boron oxide-alumina.

In the process according to this invention, the hydrogen, which may if desired be supplied in the form of a hydrogen-containing gas, is conveniently recycled. Although the hydrogen may be passed in counterflow with the hydrocarbon mixture to be isomerised which descends over the catalyst, it is preferred to pass the hydrogen together with the liquid hydrocarbon mixture starting material in parallel flow from the top of the catalyst bed downwards. The feed rate of the hydrocarbon mixture should be adjusted in such a manner that it flows in a thin layer over the catalyst.

The temperatures employed generally lie between 300°C. and 550°C., and preferably between 350°C. and 450°C., while the pressure may vary from 5 to 200 atmospheres and preferably lies between 10 and 40 atmospheres. The most favourable conditions for isomerisation vary somewhat according to the hydrocarbon mixture and the catalysts used. However, isomerisation generally proceeds most successfully when the following reaction conditions are applied:—

Temperature	400°C. to 440°C.
Pressure	25 to 40 atmospheres
Contact time	0.5 to 10 minutes
Throughput rate	1 to 5 kilograms per litre of catalyst per hour
Molar ratio of hydrogen to hydrocarbon mixture	10:1 to 50:1

Compared with the liquid phase treatment without using the trickle technique, considerably higher yields of isomerised product are obtained by means of the process according to the present invention, while cracking reactions leading to the formation of products of lower molecular weight occur only to a slight extent. The yield of the conversion, namely the percentage by weight of isomerised product with respect to the total quantity of the hydrocarbon mixture converted, is therefore considerably higher. Thus, isomerising hydrocarbon mixtures comprising paraffin waxes of high molecular weight (average molecular weight exceeding 350 and boiling above 300°C.) under the optimum conditions indicated above, gave yields of more than 40% by weight, calculated on hydrocarbon mixture starting material, of product boiling above 300°C. per passage over the catalyst, while the quantity of product formed boiling below 300°C. was only slight, remaining below 10% by weight. Thus the conversion yield is high, namely 85% to 90%.

A further advantage of the process according to this invention is that the activity of the catalyst, even after prolonged use, is not at all, or is only very slowly, impaired. This is due to the fact that the catalyst particles are all surrounded by a hydrogen atmosphere which easily diffuses through the thin film of the hydrocarbon mixture to be isomerised which envelops these particles, with the result that the hydrogen may exercise its protective effect on the catalyst surface.

The quantity of hydrogen used in the process of this invention may be considerable smaller than that required for the isomerisation in the vapour phase. For instance, when 10 moles of hydrogen are present per mole of hydrocarbon mixture, results may be obtained which are as favourable as those for which in the vapour phase process 60 moles of hydrogen per mole of hydrocarbon mixture are required, the reaction conditions being otherwise the same. Compared with the operation in the vapour phase, the process of this invention has the added advantage that it can be applied highly successfully to paraffinous materials which have such a high boiling point that they cannot, or can only with great difficulty, be passed over in the vapour phase without cracking reactions taking place, and which are therefore not, or are practically not, suitable for isomerisation in the vapour phase.

If resin-forming constituents and/or nitrogen and/or sulphur compounds which might adversely affect the life of the catalyst are present in the hydrocarbon mixtures, it may be advisable to subject the hydrocarbon mixtures to a pretreatment by which these harmful components may be entirely, or be for the greater part, removed. Such a pretreatment, the selection of which depends on the nature of the components to be removed, may, for instance, consist of a treatment with concentrated sulphuric acid or similar chemical refining agents, an extraction treatment with lower alkanes, such as propane, or a refining hydrogenation treatment.

By means of the process according to this invention, lower melting products may be obtained from higher melting paraffinous hydrocarbon mixtures while almost the same molecular weight is retained. These lower melting products may be used as components in high grade lubricants and Diesel oils.

The present invention is further illustrated by the following Example:—

A solid paraffin wax, melting at 54.3°C. and boiling above 300°C., having an oil content of 4.7% (determined according to A.S.T.M. method D 721-51 T) and an average number of carbon atoms per molecule of 27, was passed at a throughput rate of 2 kilograms per litre of catalyst per hour together with 10 moles of hydrogen per mole of paraffin wax, at 420°C. and under a pressure of 35 atmospheres over a granular commercial so-called platforming catalyst from the top downwards in such a manner that the molten paraffin wax flowed in a thin layer over the particles of the fixed catalyst bed. The contact time was approximately 0.5 minute.

The small quantity of hydrocarbons boiling below 300°C., namely 6% by weight calculated on the starting paraffin wax, were removed from the product by distillation. The resulting product was then dewaxed at −5°C. in a liquid medium of 5 parts by weight of methyl ethyl ketone to 1 part by weight of product. The oil thus obtained in a yield of 50.5% by weight, calculated on the starting paraffin wax, had a pour-point of 8°C., a viscosity index of 155, a viscosity at 100°F. of 11.7 centistokes and at 210°F. of 3.2 centistokes. Thus the conversion yield of paraffin wax in oil was 88.4%. After a continuous operation of 135 hours, the activity of the catalyst was not impaired at all.

For purposes of comparison it is noted that in a test in which a stream of molten paraffin wax together with hydrogen was passed, under conditions which were otherwise the same as those employed previously, from the bottom to the top of the bed with the same catalyst, more than 10% by weight of the paraffin wax was converted into hydrocarbons boiling below 300°C., while the yield of product boiling above 300°C. was, after dewaxing, not more than 30.5% by weight calculated on paraffin wax. This occurred notwithstanding the fact that the contact time was considerably longer than that employed previously, namely approximately 6 minutes. After an operating period of 132 hours, the activity of the catalyst was so reduced that the oil yield dropped to 25.9%.

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 passing a thin layer of the said hydocarbon mixture in the liquid phase at an elevated temperature and in the presence of hydrogen, over a fixed bed of a solid catalyst which has dehydrogenating properties and an acid character.

2. A process as claimed in Claim 1, wherein the hydrocarbon mixture flows through the catalyst from the top of the catalyst downwards.

3. A process as claimed in Claims 1 or 2, wherein the hydrogen is passed in parallel flow with the hydrocarbon mixture.

4. A process as claimed in any one of the preceding claims, wherein the process is carried out at a temperature between approximately 300°C. and 550°C., and under a pressure between approximately 5 atmospheres and 200 atmospheres.

5. A process as claimed in Claim 4, wherein the process is carried out at a temperature between 350°C. and 450°C., and under a pressure between 10 atmospheres and 40 atmospheres.

6. A process as claimed in Claim 5, wherein the process is carried out at a temperature between 400°C. and 440°C. and under a pressure between 25 atmospheres and 40 atmospheres with a throughput rate of 1 to 5 kilograms per litre of catalyst per hour, a contact time of 0.5 to 10 minutes and with a molar ratio of hydrogen to the hydrocarbon mixture of from 10:1 to 50:1.

7. A process as claimed in any one of the preceding claims, wherein the hydrocarbon

mixture comprises a paraffin wax.

8. A process as claimed in any one of the preceding claims, wherein the hydrocarbon mixture comprises a high boiling paraffinous material which cannot, or can only with difficulty, be passed over in the vapour phase without cracking taking place.

9. A process as claimed in any one of the preceding claims, wherein the catalyst employed is a platforming catalyst.

10. A process for the isomerisation of hydrocarbon mixtures containing at least 20% by weight of waxy hydrocarbons substantially as hereinbefore described with particular reference to the Example.

11. Isomerisation products whenever prepared by a process as claimed in any one the preceding claims.

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