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COMPLETE SPECIFICATION

Process for the Catalytic Reforming of Hydrocarbon Mixtures of the Gasoline Type

We, N. V. 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 a process for the catalytic reforming of hydrocarbon mixtures of the gasoline type with a relatively low naphthene content using platinum-containing catalysts.

It is known that a considerable increase in the octane number of gasolines can be obtained by catalytic reforming, by which is meant here a catalytic treatment of gasoline hydrocarbons in the presence of hydrogen at elevated temperature and pressure, usually without any consumption of hydrogen. Platinum-containing catalysts are very suitable for this purpose, and a particularly attractive catalytic reforming process in which such catalysts are used is the so-called "Platforming" process, which is being applied to an increasing extent. ("Platforming" is a Registered Trade Mark). In this process the gasoline to be reformed is vapourized and contacted at elevated temperature and under pressure in the presence of hydrogen, with the platinum-containing catalyst, such as one which comprises 0.3% by weight of platinum on an alumina carrier which may or may not contain halogen.

If the hydrocarbon mixtures used as starting material have only a relatively low naphthene content (less than 30% by weight), such as many gasolines obtained from Middle East crude oils, and the reforming is carried out under such conditions that mainly dehydrogenation and isomerization of the naphthenes and isomerization of the paraffin hydrocarbons occur, the resultant reformate generally has too low an octane number. This drawback may be overcome by reforming under such conditions that, in addition to the above-mentioned conversions, hydrocracking of the paraffin hydrocarbons present also occurs to a sufficient extent, the larger molecules being broken up into smaller molecules with saturation of the unsaturated hydrocarbons thereby formed. Since in hydrocracking reactions hydrogen is consumed which must itself be supplied by the dehydrogenation reactions, and, since moreover, the partial pressure of the hydrogen in the reacting vapour mixture must be maintained at a high value in order to prevent a decline in activity of the catalyst, it is very important for the application of the reforming process on a technical scale, that the dehydrogenation reactions and the hydrocracking reactions which occur be kept in balance.

It is already known that in the dehydrogenation of lower aliphatic or cyclo-aliphatic hydrocarbons by means of metal oxide catalysts the activity of these catalysts can be increased or maintained by supplying to the reaction mixture a proportion of water vapour which preferably does not exceed 3% by volume and usually varies between 0.03 and 0.2% by volume.

It is also known that in the catalytic reforming of paraffin and naphthene-containing liquid hydrocarbon mixtures with the use of platinum-containing catalysts, the presence of water affects the degree to which hydrocracking occurs, in the sense that the addition of water has a suppressive effect on the hydrocracking reactions. In the patent literature the use of relatively high concentrations of water (e.g. 0.5 to 1.5 mol % or even considerably more, calculated on the feed) is mentioned. At these relatively high concentrations less hydrocracking occurs as more water is added to the reacting mixture.

It has now been found that in the catalytic reforming of hydrocarbons of the gasoline type containing less than 30% by weight of naphthenes, with the use of catalysts containing platinum on a carrier with acid properties, and at least 8-fold molar proportion of hydrogen, and operating under reaction conditions in

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which a considerable degree of hydrocracking occurs, it is particularly advantageous to ensure that the water vapour content of the reaction mixture is kept at a small value not exceeding 0.03% by volume.

Accordingly, the present invention provides a process for catalytically reforming hydrocarbon mixtures of the gasoline type with a naphthene content of less than 30% by weight, which comprises contacting the hydrocarbon mixture to be reformed, together with at least an 8-fold molar proportion of hydrogen, at a temperature of at least about 470° C. and a pressure of at least about 10 atmospheres, with a catalyst containing platinum on a carrier with acid properties, the degree of hydrocracking being such that at least 15% by volume of the reformed product boils below the lower cutting point of the hydrocarbon mixture to be reformed and there being maintained in the reacting mixture a small proportion of water vapour not exceeding 0.03% by volume.

By adjusting the water content at a value not exceeding the stated limit of 0.03% by volume, the extent of the hydrocracking reactions occurring in the catalytic reforming can be excellently controlled. In view of the low naphthene content of the starting material, these reactions should proceed to a considerable extent in order to obtain a final product with a sufficiently high octane number. The effect of the said very small proportions of water in the reacting mixture is found to be such that the hydrocracking is promoted as the proportions are increased and vice-versa, the degree of hydrocracking is reduced by decreasing the water content. This is therefore contrary to what is known to occur when operating with considerably higher water vapour contents than 0.03% by volume, in which case an increase of the water vapour content is accompanied by a suppression of the hydrocracking.

If, in the process according to the invention an increase in the water content already present is necessary, this may be accomplished by adding water or by adding substances which form water under the reaction conditions, e.g. alcohols, such as isopropyl alcohol and the butanols.

When operating according to the invention it is therefore possible, by adjusting the water content of the reacting mixture, to regulate with precision the hydrocracking reactions occurring in catalytic reforming, i.e. to promote or repress them as desired, depending on the requirements of the final product. In this way the flexibility of the reforming process is considerably increased. If, for example, in reforming a certain starting material it is desired to obtain the greatest possible octane yield (viz. the sum of the yield of reformate and the octane number thereof), this can be attained by maintaining the water content in the reacting mixture at a maximum value of approximately 0.01% by volume; the hydrocracking then remains fairly limited and as a result the percentage of components of the reformate boiling up to 100° C is relatively low, e.g. from 15 to 20% by volume. If, on the other hand, it is desired to prepare a product with a higher volatility, the octane number remaining the same, for which purpose the hydrocracking reactions should be promoted, this can be attained by operating with a considerably higher water vapour content, e.g. 0.02% by volume or more, but not exceeding 0.03% by volume. Moreover, this type of operation has the advantage that the temperature chosen may be lower, e.g. 8 to 10°C lower, the other reaction conditions remaining the same. If desired, the octane number of the reformate can be increased by a similar increase in the water content and by operating at the same reaction temperature.

A maximum limit of 0.03% by volume is set to the water vapour content at which the reacting mixture is adjusted according to the invention, since it has been found that when the water content is increased above this limit only a small increase in the octane number is obtainable, and this does not outweigh the reduction in yield of reformate. This limit is set, moreover, since at higher water vapour contents, depending on the reaction conditions used, the extent of the hydrocracking reactions may become so great that the life of the platinum catalyst is considerably reduced, which, of course, is undesirable. On the other hand, with a maximum water content of a 0.03% by volume the original activity and selectivity of the platinum catalyst is almost completely retained in use, so that it can be used uninterruptedly for long operating periods, e.g. 2,000 hours or even more.

By adjusting the water content to the correct value, according to the present invention, it is possible to carry out the reforming process in such a way that in every single case the best compromise is effected between process selectivity (which depends on the yield of liquid product and hydrogen for a given octane level) and life of the catalyst on the one hand, and properties of the product obtained on the other hand.

In view of the relatively low naphthene content of the hydrocarbon material used as starting material in the process according to the invention, fairly sharply defined reaction conditions, such as temperatures of, for example, approximately 480°C to 500°C or even more, and relatively low liquid-space velocities should be used for obtaining reformates with a sufficiently high octane number. In this case it is important that the hydrogen in the reforming treatment should be present in a large molar proportion at least an eight-fold, for example, a 10-fold molar proportion with respect to the hydrocarbon material, since with the use of smaller proportions of hydrogen the

catalyst used loses its activity fairly rapidly.

The hydrogen in the presence of which the reforming treatment is carried out need not be pure, and can therefore be supplied in the form of a hydrogen-rich gas. In practice, a part of the hydrogen-rich gas which is formed in the reforming process, is used for the purpose, this gas being recycled in the process.

The starting material to be reformed normally has a low water content which is usually not more than approximately 0.01% by volume. In regulating the water content of the mixture of hydrogen and hydrocarbon to be reformed, account should, of course, be taken of this low water content of the feed and also of the proportion and the water content of the cycle gas. It is clear that the water content of the feed is an independent variable; the water content of the cycle gas on the other hand may depend directly on that of the feed, although this need not always be the case, since the water content of the gas to be recycled may also be entirely or partly derived from a treatment applied to that gas for removing any hydrogen sulphide present, for example, by means of an aqueous solution of amines or amino alcohols, such as mono-, di- or triethanol amine, or other suitable basic substances.

The regulation of the water vapour content of the reacting mixture to the value required to obtain the desired result in reforming may, according to circumstances, be carried out by withdrawing water or supplying small quantities of water or a substance which forms water under the reforming conditions; this regulation may be carried out in any suitable way.

The process according to the invention is preferably carried out by adjusting the hydrogen-rich gas obtained in the reforming operation, before recycling it back to the process, to such a water vapour content, that the water vapour content of the mixture of cycle gas and hydrocarbon material supplied to the reforming zone has the required value which does not exceed 0.03% by volume.

If the material to be reformed has a normal water content of approximately 0.01% by weight, the water content of the cycle gas must be adjusted to a maximum value of 200 mg per N—M³, depending on the demands made of the reformate to be prepared and the ratio of hydrogen to hydrocarbon material to be reformed at which the reforming treatment takes place.

Since the product gas rich in hydrogen generally has a water content of more than 200 mg per N—M³, it is usually necessary to reduce this water content before the gas is recycled. To this end the gas may be treated with one or more drying agents, the nature of which is adapted to achieve the degree of reduction in water content which is aimed at.

In practice a reduction of the water vapour content to approximately 200 mg per N—M³ may be simply obtained by passing the gas through a drying apparatus operating, for example with glycol or a glycol derivative, such as diethylene glycol.

Any further reduction required in the water content of the cycle gas may be effected by causing the drying with glycol or a glycol derivative or a similar liquid drying agent, to be followed by a further treatment with a solid substance which has a high water-binding power, e.g. bauxite, activated alumina or silica gel. It has been found that in this way the water content can be readily reduced to 25 to 50 mg per N—M³ of gas.

If the material to be reformed and the product gas rich in hydrogen should have such a low water content that, when recycling this gas, the water content of the mixture led to the reforming zone is below the desired value, this content may be increased to the correct value by supplying the necessary small quantity of water or water-yielding substance, such as isopropyl alcohol and sec. or tert. butanol, to the cycle gas or to the feed or to the mixture of both.

The process according to the present invention can be used for reforming any liquid hydrocarbon material of the gasoline type which has only a relatively low naphthene content, viz. less than 30% by weight, e.g. 20 to 25% by weight or even less, such as straight-run naphthas or naphtha-fractions obtained from Middle East crude oils.

In the present process, the platinum-containing catalysts used are preferably those usually used in catalytic reforming processes. These catalysts may consist of a small proportion, e.g. 0.1 to 1% by weight, of platinum on a carrier such as alumina, silica-alumina or silica-magnesia. Inasmuch as they comprise an alumina-containing carrier, they may be activated with small proportions, not exceeding 1% by weight, of one or more halogens, in particular chlorine and fluorine.

The temperatures to be used in reforming, which may vary somewhat according to the starting material and the catalyst, are at least approximately 470°C. and preferably between 480°C and 510°C. The pressures usually lie between 10 and 100 atm. and preferably between 20 and 50 atm., while relatively low space velocities are used, usually below approximately 5 and preferably between 2 and 2.5 litres of starting material per litre of catalyst per hour.

Operating under pressures of less than 30 atm. may be an advantage, since in this way products with somewhat higher octane numbers may be obtained, the yield remaining the same or only slightly lower, than when the reforming treatment is carried out with pressures of over 30 atm. In this case it is advisable to use a molar ratio of hydrogen to hydrocarbon of more than 10:1, e.g. 12:1, in order to avoid the risk of a decline in catalyst

activity, and moreover, it is desirable to adjust the water content of the reacting mixture to a value of less than 0.02% by volume, since the octane yield is found to fall too sharply with these lower pressures and a water content of from 0.02 to 0.03% by weight, while the catalyst life is also reduced.

The process according to the invention will be further illustrated by the following examples.

EXAMPLE I

A heavy straight-run naphtha-fraction boiling between 110°C and 190°C, containing 60% by weight of paraffins, 24% by weight of naphthenes and 16% by weight of aromatics, and having an F—2 octane number of approximately 30, and the water content of which was approximately 0.01%, by weight, was passed over a commercial platinum-containing catalyst at a space velocity of 2.3 litres per litre of catalyst per hour, together with a sufficient quantity of 85% by volume of hydrogen-containing cycle gas for the molar ratio of hydrogen to hydrocarbon material to be 10:1, at an inlet temperature of the catalyst bed of 495°C, and at a pressure of 40 atm.

In order to demonstrate the effect of minimal quantities of water vapour, the water content of the reaction mixture to be passed over the catalyst was varied. This was effected by drying the cycle gas almost completely and adding isopropyl alcohol to the hydrocarbon feed in such amounts that the water content of the reaction mixture is adjusted to the desired value. At water vapour contents of the reaction mixtures varying from below 0.017 to 0.05% by volume the following results were obtained, the numbers shown for the octane yield being the sum of the yield of reformate (C_5^+) and the octane number thereof.

Water content of reaction mixture % by volume	<0.011	0.017	0.028	0.05
Reformate (C_5^+) yield, by weight	88.6	85.8	84.3	83.1
F—2 octane number	73.9	76.4	77.6	77.9
Octane yield	162.5	162.2	161.9	161.0
Tops boiling up to 100° C., % by volume of reformate	16	21	25	27
Aromatic yield, % by weight of feed	40.7	41.0	40.9	40.7
Gas produced (85% by volume of H_2), litre/kg of naphtha	104	95	88	78

These results show that when the reaction conditions remain the same the water content has practically no effect on the formation of aromatics, but according as the water content is higher the degree of hydrocracking increases, particularly in the range in which the water content of the reaction mixture is up to 0.03% by volume, as a result of which the yield of reformate falls and the octane number rises.

EXAMPLE II

The starting material and the conditions were the same as in Example I, except that now the inlet temperature of the catalyst bed was varied in order to maintain the F—2 octane number of the reformate constant at from 77.5 to 78.0.

The results obtained with a varying water content were as follows:

Inlet temperature, °C.	503	498	495	492
Water content of reaction mixture, % by volume	<0.011	0.017	0.028	0.05
Reformate (C_5^+) yield, % by weight	85.8	84.7	84.3	83.8
Tops boiling to 100° C., % by volume of reformate	20	23	25	27
Yield of aromatics, % by weight of feed	43.5	42.0	40.9	39.5
Gas produced (85% by volume of H_2), litre/kg of naphtha	120	100	88	76

These results clearly show the effect of the water content of the operating temperature required to maintain a particular octane level, and on the properties of the product obtained.

EXAMPLE III

The same heavy naphtha-fraction as in Example I was passed over a commercial platinum-containing catalyst at a space velocity of 2.3 litres per litre of catalyst per hour, together with a sufficient quantity of cycle gas rich in hydrogen for the molar ratio of hydrogen to hydrocarbon material to amount to 12:1 at an inlet temperature of the catalyst bed of 495°C, and at a pressure of 27.2 atm. Before being recycled the cycle gas was adjusted to a water content of less than 50 mg per N—M³ by drying with activated alumina.

The yield of reformate (C_5^+) thus obtained was 87.1% by weight and the F—2 octane number 78.7, the content of components of the reformate boiling up to 100°C was 16% by volume.

When the space velocity was reduced to 2.0, the reaction conditions being otherwise the same, the reformate obtained in a yield of 86.1% by weight then showed an F—2 octane number of 80.6 and a content of components boiling up to 100°C of 18% by volume. After continuously operating for 670 hours, during which time the inlet temperature of the catalyst bed was increased to 501°C, the yield of the reformate was still 85.3% by weight and the octane number 81.2.

On repeating the experiment described in the previous paragraph, the water content of the cycle gas being, however, 200 mg per N—M³ and the temperature 485°C, a yield of reformate of 83.7% by weight was obtained at an octane number of 79.6, the content of components boiling up to 100°C being 25% by volume. In this case, therefore, the octane yield fell from 166.7 to 163.3.

What we claim is:—

1. A process for catalytically reforming hydrocarbon mixtures of the gasoline type with a naphthene content of less than 30% by weight, which comprises contacting the hydrocarbon mixture to be reformed, together with at least an 8-fold molar proportion of hydrogen, at a temperature of at least about 470°C and a pressure of at least about 10 atmospheres with a catalyst containing platinum on a carrier with acid properties, the degree of hydrocracking being such that at least 15% by volume of the reformed product boils below the lower cutting point of the hydrocarbon mixture to be reformed and there being maintained in the reacting mixture a small proportion of water vapour not exceeding 0.03% by volume.

2. A process as claimed in claim 1, wherein the proportion of water vapour in the reacting mixture is controlled by adjusting the water vapour content of the hydrogen-rich gas which is formed in the reforming process to such a value that when this gas is recycled in the process the water vapour content in the reacting mixture will have the desired value, and recycling the said gas in the process.

3. A process as claimed in claim 2, wherein the hydrogen-rich gas to be recycled is adjusted to a water vapour content of less than 200 mg per N—M³.

4. A process as claimed in claim 2 or 3, wherein the water content of the hydrogen-rich gas to be recycled is adjusted by treating the said gas with one or more drying agents.

5. A process as claimed in claim 4, wherein the hydrogen-rich gas to be recycled is first treated with a liquid drying agent and afterwards with a solid drying agent.

6. A process as claimed in claim 5, wherein the hydrogen-rich gas to be recycled is first treated with glycol or a glycol derivative and afterwards with bauxite.

7. A process as claimed in any one of the preceding claims, wherein the reforming treatment is carried out at a temperature between 480 and 510°C and at a pressure between 20 and 50 atm.

8. A process as claimed in any one of the preceding claims, wherein the reforming treatment is carried out at a pressure of less than 30 atm. and at a molar ratio of hydrogen to hydrocarbon of more than 10:1, the water content of the reacting mixture being maintained at less than 0.02% by volume.

9. A process as claimed in any one of the preceding claims, wherein the catalyst contains not more than 1% by weight of platinum supported on an alumina carrier, and is activated with halogen.

10. A process for catalytically reforming hydrocarbon mixtures of the gasoline type with a naphthene content of less than 30% by weight as claimed in claim 1, substantially as hereinbefore described with particular reference to the Examples.

11. Hydrocarbon mixtures whenever produced by a process as claimed in any one of the preceding claims.

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1. A process for catalytically reforming hydrocarbon mixtures of the gasoline type with a naphthene content of less than 30% by weight, which comprises contacting the hydrocarbon mixture to be reformed, together with at least an 8-fold molar proportion of hydrogen, at a temperature of at least about 470°C and a pressure of at least about 10 atmospheres with a catalyst containing platinum on a carrier with acid properties, the degree of hydrocracking being such that at least 15% by volume of the reformed product boils below the lower cutting point of the hydrocarbon mixture to be reformed and there being maintained in the reacting mixture a small proportion of water vapour not exceeding 0.03% by volume.

2. A process as claimed in claim 1, wherein the proportion of water vapour in the reacting mixture is controlled by adjusting the water vapour content of the hydrogen-rich gas which is formed in the reforming process to such a value that when this gas is recycled in the process the water vapour content in the reacting mixture will have the desired value, and recycling the said gas in the process.

3. A process as claimed in claim 2, wherein the hydrogen-rich gas to be recycled is adjusted to a water vapour content of less than 200 mg per N—M^3.

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7. A process as claimed in any one of the preceding claims, wherein the reforming treatment is carried out at a temperature between 480 and 510°C and at a pressure between 20 and 50 atm.

8. A process as claimed in any one of the preceding claims, wherein the reforming treatment is carried out at a pressure of less than 30 atm. and at a molar ratio of hydrogen to hydrocarbon of more than 10:1, the water content of the reacting mixture being maintained at less than 0.02% by volume.

9. A process as claimed in any one of the preceding claims, wherein the catalyst contains not more than 1% by weight of platinum supported on an alumina carrier, and is activated with halogen.

10. A process for catalytically reforming hydrocarbon mixtures of the gasoline type with a naphthene content of less than 30% by weight as claimed in claim 1, substantially as hereinbefore described with particular reference to the Examples.

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