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I-20121 Milano(IT)(54) **Oxygenated, high-octane-number composition for fuel, and method for its preparation.**

(57) The invention relates to an oxygenated, high-octane-number composition for fuel, constituted by methanol, methyl-tert-butyl ether (MTBE) and tert-butyl alcohol (TBA).

The invention relates also to a method for the preparation of the above-said composition, consisting in submitting a C₄-charge, free from butadiene, and containing isobutene at a concentration of from 10 to 55% by weight to one or more hydration treatment(s), in the presence of an acidic catalyst of Amberlyst 15 type, in separating TBA from the other inert components, which do not react in the hydration reaction, and from residual isobutene, in introducing said other isobutene-containing, inert components into an isobutene etherifying section, wherein isobutene reacts with methanol and forms MBTE, in separating, by fractionation, MTBE with methanol and possible traces of TBA from the other components, and in finally mixing TBA with the MTBE-methanol mixture. The feed to the hydration reactor (water and olefins) is rendered homogeneous by means of the partial recycle of TBA or of TBA-containing mixtures.

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"OXYGENATED, HIGH-OCTANE-NUMBER COMPOSITION FOR FUEL, AND METHOD FOR ITS PREPARATION"

The present invention relates to an oxygenated, high-octane-number composition for fuel, and to a method for its preparation.

It is known that methanol has interesting high-octane-rating characteristics, such that the addition thereof to the gasolines is one of the suggested means to cope with the lead-alkyls reductions. Such a use shows however a severe drawback in that methanol, when admixed with hydrocarbons, if the resulting mixtures absorb even very minor amounts of water (500-700 ppm), undergoes phase separations.

Because of its hydrophilic character, when two phases separate from each other, methanol tends to concentrate in the aqueous phase, thus depriving gasoline of its antiknock-value improving contribution. It is clear that such a behaviour jeopardizes the use of methanol in the field of fuels.

An indirect way of adding methanol, with no problems, to a gasoline, consists in reacting it with isobutene, or with other branched C_5 - C_7 olefins, yielding high antiknock-rating ethers which, once that they have been admixed with gasolines, do not show any longer phenomena of instability in the presence of water. Such a procedure allows however small methanol amounts, practically only the stoichiometric amount, to be added, which means 57 parts by weight per each 100 parts of reacted isobutene, such parts decreasing then to 46, if on the contrary a C_5 olefin, such as the isoamylenes, is used.

It is known that the presence of higher alcohols endows methanol/gasoline mixtures with improved water stability, such that a preferred form of use of methanol in gasolines is precisely that carried out in the presence of a higher alcohol -e.g., a mixture containing equal parts by weight of methanol and tert-butyl alcohol (TBA). Inasmuch as TBA can be obtained by isobutene hydration, it is logical to observe how by that way introducing 132 parts of methanol per each 100 parts of reacted isobutene becomes possible, which is more than the double of the amount which one succeeds in introducing by the etherifying of a same amount of olefins.

However, the hydration reaction shows, relatively to the etherifying reaction, a more unfavourable thermodynamics, so that, whilst it is possible to accomplish, in the etherifying step, high ($\geq 99\%$) isobutene conversions, reaching in the hydration step a conversion of 80% is practically impossible, unless extremely complex process schemes are used.

Obviously, such a fact lowers the yields and, by not completely removing isobutene from the used olefinic fraction, it endangers the subsequent use thereof as the starting material for the recovery of butene-1.

Another disadvantageous characteristic of the hydration is the mutual immiscibility of the reactants - (H_2O -olefins) with each other, which makes it necessary to use a third component, acting as a solvent.

As regards this latter disadvantage, it should be observed that the third component causes serious technical problems as for its separation and recycle, so that the production of TBA is presently carried out on a commercial scale via the reduction of tert-butyl hydro peroxide in propylene oxide syntheses.

It has been now surprisingly found a high-octane-rating composition for fuels having, as its components, methanol, TBA and MTBE, wherein the components are comprised within the following percent ranges:

methanol: 30-45%, preferably 43.1% by weight;

TBA : 30-45%, preferably 43.1% by weight;

MTBE : 5-20%, preferably 13.8% by weight;

and a method for preparing it has been surprisingly found, by which the drawbacks of the prior art are overcome.

The high-octane-number composition for fuel according to the invention is such that it contains, in its preferred form, even 240 parts by weight of oxygen-containing high-octane-number components per each 100 parts of reacted isobutene, as compared to the 155 parts which can be obtained by means of the complete conversion of isobutene into MTBE.

The high-octane-number composition in accordance with the instant invention shows considerable advantages of stability as compared to methanol alone, and also relatively to methanol-TBA mixtures, as it shall be set forth in particular in Example 2.

The composition according to the invention is added to the gasolines in amounts comprised within the range of from 3 to 30% by weight.

The method according to the present invention comprises submitting a butadiene-free C_4 charge, containing a percentage of isobutene of from 10 to 55%, to one or more sequential hydration treatment(s) with water, in the presence of an acidic cationic resin, in particular based on sulphonated styrene-divinylbenzene of Amberlyst 15 type, thus partly converting isobutene into TBA, separating TBA from the

mixture of the other components, containing the residual isobutene, submitting the residual isobutene in said mixture to an etherifying treatment with an excess of methanol relatively to the stoichiometric amount, to the purpose of converting it into MTBE in the presence of an acidic cationic resin, in particular based on a sulphonated styrene-divinylbenzene of Amberlyst 15 type, and is characterized in that the reaction mixture (isobutene and water) is homogenised by means of a solvent selected from either pure or substantially pure TBA, and mixtures of TBA and water (water is at a concentration comprised within the range of from 0.1 to 18%), isobutene being converted into TBA at a temperature comprised within the range of from 40 to 90°C, by a percentage of from 75 to 80%, and the MTBE-containing mixture is submitted to fractionation, a mixture being separated of MTBE and methanol with possible minor traces of TBA, which is admixed with pure TBA up to the above-said concentrations.

The methanol excess is of from 8 to 15 times as the stoichiometric amount, as referred to the residual isobutene after the hydration.

The method of the present invention can be carried out in particular as illustrated in the following Example 1, which is not to be understood as being limitative of the invention. In it, the reaction of TBA formation is carried out as a process of two steps in series, and the solvent is constituted by a mixture of TBA and water, which is obtained as an intermediate fraction from the TBA separation step.

It is clear that changes can be supplied to the process pattern, without going out of the scope of the invention.

Example 1

To 100 parts by weight of an olefinic charge containing 50% by weight of isobutene (stream 1, see herewith attached figure), added are 145.82 parts by weight of stream 6, which is a recycle stream, and is formed by 129.78 parts of TBA and 16.04 parts of water. The resulting mixture is delivered, at an LHSV = 2, to reactor 10, containing an ion-exchange resin in the acidic form (Amberlyst 15), operating at the temperature of 60°C.

The ratios between water, hydrocarbons and TBA are so selected, that the mixture is in single phase. In reactor 10, TBA is formed, from isobutene and water. The reaction product (stream 2) has the following composition:

Inert butenes 50
Isobutene 20.70
TBA 168.48
H₂O 6.64

The isobutene conversion in 10 is of 58.6%.

To the stream 2, 13.03 parts of demineralized water, or anyway of water free from cations or organic bases, are added; the resulting mixture (stream 3), which is perfectly homogeneous, is passed at a space velocity = 1.6 over reactor 11 containing an ion-exchange resin in the acidic form (Amberlyst 15), and operating at 60°C. The resulting product (stream 4) has the following compositions:

Inert butenes 50
Isobutene 10.64
TBA 181.76
H₂O 16.44

The total conversion of isobutene is of 78.7%, with a nearly absolute selectivity to TBA.

The stream 4 is sent to the fractionation column 12.

From column 12 three streams are collected:

-a overhead stream (stream 5), 61.04 parts, constituted by 50 parts of linear butenes, 10.64 parts of isobutene and 0.40 parts of H₂O. Water decants nearly totally as a separated phase, so that the stream 5 contains, after the phase separation, only 0.06 parts thereof.

-a side stream (stream 6), which constitutes the recycle stream, to be admixed with stream 1.

-a bottom stream, constituted by 51.98 parts of practically anhydrous TBA.

To the stream 5, after water being separated, 59.48 parts of methanol (16) are added, and the resulting mixture is passed over reactor 13 at an LHSV = 5, and at a temperature of 45°C.

The reaction product (stream 8) has the following composition:

Inert butenes 50
Isobutene 0.08
Methanol 53.46
5 MTBE 16.57
TBA 0.01
H₂O 0.05

The total isobutene conversion is thus higher than 99.8%.

The stream 8 is sent to the fractionation column 14, wherein a bottom fraction is obtained, which is
10 constituted by 16.57 parts of MTBE, 51.90 parts of methanol and 0.01 parts of TBA.

The remaining stream, constituted by C₄ hydrocarbons and azeotropic methanol is recovered overhead in 14.

The stream 7 and stream 9 can be either used separately, or they can be combined together, 120.46 parts being obtained of a mixture of high-octane-number oxygenated compounds, which has the following
15 composition:

Methanol 43.08%
TBA 43.16%
MTBE 13.76%

20 Example 2

A gasoline containing 25% of aromatic hydrocarbons is admixed with methanol, with methanol and TBA
25 and with such reaction product as obtained in Example 1. The ratios are so adjusted, that methanol is always 5% of the mixture.

On the mixture, the highest water content is determined, which can be tolerated without clouding appearing at the temperature of 20°C. The results are reported in the following Table:

30		Mixture_1	Mixture_2	Mixture_3
	Gasoline	95	90	88.4
	MeOH	5	5	5
35	TBA		5	5
	MTBE			1.6
40	Tolerated water, ppm	650	3200	3700

It can be observed that the stability of mixture 3 is higher not only than that of only methanol-containing mixture, but also than the stability of the mixture containing methanol and TBA.

45 **Claims**

1. Oxygenated high-octane-number composition for fuels, comprising a mixture of methanol, tert.butyl alcohol (TBA) and methyl-tert-butyl ether (MTBE), characterized in that methanol, TBA and MTBE are
50 comprised within the following percent ranges:

methanol: from 30 to 45% by weight;

TBA : from 30 to 45% by weight;

MTBE : from 5 to 20% by weight.

2. High-octane-number composition according to claim 1, characterized in that it is constituted by
55 43.1% by weight by methanol, by 43.1% by weight by TBA, and by 13.8% by weight by MTBE.

3. Method for the preparation of a high-octane-number composition for fuels according to claims 1 or 2, comprising submitting a butadiene-free C₄ charge, containing isobutene at a percentage, by weight, of from 10 to 55%, to one or more hydration treatment(s) in series with water, in the presence of an acidic cationic

resin, in particular based on sulphonated styrene-divinylbenzene of Amberlyst 15 type, isobutene being thus partly converted into TBA, separating TBA from the mixture of the other components, containing the residual isobutene, submitting the residual isobutene in said mixture to an etherifying treatment with an excess of methanol, as referred to the stoichiometric amount, to the purpose of converting it into MTBE in the presence of an acidic cationic resin, in particular based on sulphonated styrene-divinylbenzene of Amberlyst 15 type, characterized in that the reaction mixture (isobutene and water) is homogenised by a means of a solvent selected from either pure or substantially pure TBA, and mixtures of TBA with water, isobutene being converted into TBA at a temperature comprised within the range of from 40 to 90°C by a percentage comprised between 75 to 80%, and the MTBE-containing mixture is submitted to fractionation, a mixture being separated of MTBE and methanol, with possible minor traces of TBA, which is admixed with pure TBA up to the concentrations according to claims 1 or 2.

4. Method according to claim 3, characterized in that the mixture of TBA and water, used as the solvent, is obtained as an intermediate fraction in TBA separation step.

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