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PROCESS FOR THE SEPARATION OF C₅ HYDROCARBONS PRESENT IN
STREAMS PREVALENTLY CONTAINING C₄ PRODUCTS USED FOR THE
PRODUCTION OF HIGH-OCTANE HYDROCARBON COMPOUNDS BY THE SE-
10 LECTIVE DIMERIZATION OF ISOBUTENE

The present invention relates to a process for the
separation of C₅ hydrocarbons present in the C₄ charges
used for the production of high-octane hydrocarbon com-
pounds by the selective dimerization reaction of isobutene
15 and to a lesser extent of possible linear olefins, in the
presence of linear and branched alcohols and alkyl ethers,
which favour the production of higher selectivities on the
part of the catalyst. The mixture obtained can then be hy-
drogenated with conventional methods to obtain a product
20 with further enhanced octane characteristics.

For mainly environmental reasons, the composition of
gasolines is being reformulated and the general tendency is
towards the production of fuels which burn better and have
lower evaporative emissions. The main measures for achiev-
25 ing this objective are listed below (D. Sanfilippo, F. An-

cillotti, M. Marchionna, Chim. & Ind., 76, (1994), 32):

- reduction in the content of aromatic compounds and elimination of benzene;
- reduction in the volatility of gasolines to minimize evaporative losses;
- reduction in the content of light olefins, photochemically extremely reactive;
- reduction in the sulfur content and final boiling point of the gasolines.

10 All these measures consequently create the necessity of projecting new production processes of purely hydrocarbon compounds capable of positively contributing to the above demands.

Among these, alkylated products are extremely important as they have a high octane number, a low volatility and are practically free of olefins and aromatic compounds. The alkylation process in liquid phase is a reaction between isoparaffinic hydrocarbons, such as isobutane, and olefins, for example propylene, butenes, pentenes and relative mixtures thereof, in the presence of an acid catalyst for the production of C₇-C₉ hydrocarbons with a high octane number to be used in gasolines (A. Corma, A. Martinez, Catal. Rev.-Sci. Eng., 35, (1993), 483).

The main problem of alkylation processes is due to the fact that, with growing environmental regulations, both of

the traditional processes (with hydrofluoric and sulfuric acid) are encountering considerable difficulties, which create uncertainties for the future; the process with hydrofluoric acid due to the toxicity of this acid, especially in populated areas, and that using sulfuric acid, as a result of the large production of acid sludge as well as the considerably corrosive nature of the catalyst.

Alternative processes with solid acid catalysts are being developed but their commercial applicability has yet to be demonstrated.

A hydrocarbon product of this type, on the other hand, is becoming increasingly more requested due to its octane characteristics (both the Research Octane Number (RON) and the Motor Octane Number (MON) are high) and those relating to the boiling point (limited volatility but low end-point) which position it in the group of compositions of great interest for obtaining gasolines which are more compatible with current environmental requirements.

An alternative refinery process for obtaining products with characteristics similar to those of alkylated products can be offered by the hydrogenation of so-called "polymer" gasoline.

Oligomerization processes (often inaccurately called polymerization in the refining industry) were widely used in the '30s' and '40s' for converting low-boiling C_3 - C_4

olefins into gasolines. The process leads to the production of a gasoline with a high octane number (RON about 97) but with a high sensitivity (difference between RON and MON) due to the purely olefinic nature of the product (J.H.Gary, 5 G.E. Handwerk, "Petroleum Refining : Technology and Economics", 3rd Ed., M. Dekker, New York, (1994), 250).

Typical olefins which are oligomerized are mainly propylene, which gives dimers or slightly higher oligomers depending on the process used, and isobutene which mainly 10 gives dimers but is always accompanied by a considerable quantity of higher oligomers.

With particular attention to the oligomerization of isobutene, it is known that this reaction can be carried out either batchwise, semi-batchwise or in continuous, either 15 in gas or liquid phase, generally at temperatures ranging from 50 to 300°C and at atmospheric pressure or such pressures as to maintain the reagents in liquid phase, if necessary.

Typical catalysts for the industrial oligomerization 20 process of isobutene are represented by phosphoric acid, generally supported on a solid (for example kieselguhr), or cation-exchange acid resins. The latter allow blander conditions to be used compared with supported phosphoric acid both in terms of temperature and pressure (50-100°C and 25 0.2-3 MPa with respect to 200-220°C and 3-10 MPa).

Other catalysts are also claimed in literature, both liquid acids such as H_2SO_4 and derivatives of sulfonic acids, and solids such as silico-aluminas, mixed oxides, zeolites, fluorinated or chlorinated aluminas, etc.; none of these catalysts however has so far enabled an industrial process to be set up, as in the case of supported phosphoric acid (F. Asinger, "Mono-olefins: Chemistry and Technology", Pergamon Press, Oxford, pages 435-456) and that of cation resins (G. Scharfe, Hydrocarbon Proc., April 1973, 171).

From the product point of view, the main problem of this process lies in the fact that excessive percentages of heavy oligomers such as trimers (selectivity of 20-40%) and tetramers (selectivity of 1-5%) of isobutene, are produced in the oligomerization phase. Tetramers are completely outside the gasoline fraction as they are too high-boiling and therefore represent a net loss in yield to gasoline; as far as trimers are concerned, their concentration should be greatly reduced as they have a boiling point (170-180°C) at the limit of future specifications on the final point of reformulated gasolines.

The problem of reducing the formation of oligomers higher than dimers to percentages lower than 15% is, on the other hand, a problem typical of the oligomerization of isobutene, as also indicated in literature (C.T.O'Connor,

M. Kojima, K.W. Shcumann, Appl.Catal., 16, (1985),193). This level of heavy compounds is slightly higher than that of an alkylated product and is still tolerated in the gasoline pool.

5 From what is specified above, there is evidently great interest in obtaining a new dimerization process of isobutene which allows the synthesis of a higher-quality product, through reaching greater selectivities.

10 By carrying out the selective dimerization reaction of isobutene in the presence of moderate quantities of linear and branched alcohols and alkyl ethers, the production of a fraction of oligomers is selectively obtained, which is particular rich in dimers (>85%) and practically free of tetramers and higher oligomers (<0.5%).

15 The reaction product is then preferably hydrogenated to give a completely saturated end-product with a high octane number and low sensitivity.

20 The hydrogenation can be carried out with conventional methods as described, for example, in F. Asinger, "Mono-olefins: Chemistry and Technology", Pergamon Press, Oxford, page 455.

25 For illustrative purposes, Table 1 indicates the octane number and relative boiling points of some of the products obtained, by means of the process, object of the present invention.

TABLE 1

Product	RON	MON	b.p. (°C)
Diisobutenes	100	89	100-105
Iso-octane	100	100	99
Tri-isobutenes	100	89	175-185
Hydrogenated tri-isobutenes	101	102	170-180

The process, object of the present invention, for the separation of C₅ hydrocarbons present, in a quantity ranging from 0.2 to 20% by weight, in streams prevalently containing C₄ products used for the production of high-octane hydrocarbons, by the selective dimerization reaction of isobutene, is characterized in that the reaction is carried out in the presence of linear and branched alcohols and ethers in a quantity which is such as to have a molar ratio alcohols + ethers/isobutene in the feeding higher than 0.01 and preferably lower than 0.7.

It should also be pointed out that in the case of hydrocarbon streams also comprising C₄ and C₅ olefins, it has been observed that at least a part of the latter can be converted by reaction with isobutene into the hydrocarbon product without altering the octane value. It is therefore preferable to effect an enriching treatment, by means of pre-isomerization, of the internal linear olefins, in order to favour the overall octane number of the mixture.

The process claimed herein can be applied to cuts mainly containing isobutane, isobutene, n-butane, n-butenes and saturated and olefinic C₅ hydrocarbons.

Although a wide variety of sources are available for the supply of these streams, the most common are those deriving from Dehydrogenation processes of iso-paraffins, from FCC units, Steam Cracking or processes for the production of pure isobutene such as the dehydration of tert-butyl alcohol (TBA) or the Cracking of MTBE and/or ETBE; these streams differ from each other in the content of isobutene and linear butenes, as shown in Table 2.

Table 2

	Steam Cracking	FCC	Dehydrogenation	Pure isobutene
Isobutene	30-50	10-25	45-55	> 90
n-butenes	35-60	25-50	1-2	< 10
Saturated C ₄	4-10	30-60	45-55	< 1

Should streams from Steam Cracking contain diolefins in addition to the desired mono-olefins, they must be eliminated by means of typical removal treatment (for example solvent extraction or selective hydrogenation).

Saturated and olefinic C₅ hydrocarbons can be present in these streams, in various amounts (0.2 - 20% by weight), depending on the efficiency of the C₄-C₅ separation step.

The C₅ olefins possibly present can be involved in dimerization reactions.

The stream sent to the reaction steps can contain branched alcohols or a blend of alcohols and alkyl ethers,
5 in addition to the hydrocarbon components.

The alcohols used are linear, preferably containing a number of carbon atoms ranging from 1 to 6, preferably from 4 to 7 carbon atoms; preferred linear alcohols are methanol and/or ethanol, whereas preferred branched alcohols are
10 tert-butyl alcohol (TBA) and/or tert-amyl alcohol (TAA).

The alkyl ether used can be selected from those containing a number of carbon atoms ranging from 5 to 10: MTBE (methyl tert-butyl ether), ETBE (ethyl tert-butyl ether), MSBE (methyl sec-butyl ether), ESBE (ethyl sec-butyl
15 ether), TAME (methyl tert-amyl ether), TAEE (ethyl tert-amyl ether) or mixtures thereof are preferred.

Isobutene, together with the hydrocarbon stream in which it is contained, is sent with the mixture of alcohols and alkyl ethers, in stoichiometric defect, into contact
20 with the acid catalyst where the dimerization takes place. The linear primary alcohol, in addition to interacting with the catalyst, also helps to limit the possible cracking of the alkyl ether and can possibly react with the dimers and linear C₄ olefins, whereas the branched alcohol (tertiary)
25 does not react with the olefins due to its steric hin-

drance.

In order to obtain the dimerization product with the desired selectivity to dimers, it is essential to maintain a constant level of oxygenated products in the reaction environment but above all the contemporaneous presence of the three oxygenated compounds (linear alcohol, branched alcohol and alkyl ether) which, due to a synergic effect are capable of forming the catalytic species with the correct activity and stability. The optimal level of the sum of alcohols and alkyl ethers which should be present in the reaction environment to obtain selectivities to dimers close to 85% by weight, depends on the composition of the hydrocarbon charge. The higher the olefin content in the charge, the lower the amount of oxygenated products to be used.

A wide variety of acid catalysts can be used for this process, but those preferred are styrene-divinyl benzene polymeric resins having sulphonic groups as catalytic centres.

A large range of operative conditions can be used to produce high-octane hydrocarbons from isobutene in the desired selectivities. It is possible to operate in vapour or liquid-vapour phase, but operating conditions in liquid phase are preferred.

The pressure is preferably higher than the atmospheric value, in order to maintain the reagents in liquid phase,

generally below 5 MPa, more preferably between 0.2 - 2.5 MPa. The reaction temperature preferably ranges from 30 to 120°C.

The feeding space velocities of the oxygenated-
5 hydrocarbon stream are preferably lower than 30 h⁻¹, more preferably ranging from 1 and 15 h⁻¹.

Isobutene is mainly converted in the reaction zone, however part of the C₄-C₅ olefins present can also be converted to useful product; in principle, there are no limits
10 to the concentration of iso-olefin in the hydrocarbon fraction, even if concentrations ranging from 2 to 60% are preferred; in case of streams having a high isobutene concentration (dehydration or cracking) it is therefore convenient to dilute the charge with C₄-C₇ hydrocarbons. There
15 are no limits, on the contrary, for the ratio between isobutene and linear olefins.

The process, object of the present invention, can be effected batchwise or in continuous, bearing in mind however that the latter is much more advantageous in industrial practice. The reactor configuration selected is generally a double reaction step comprising one or more fixed
20 bed reactors which can be optionally selected from a tubular and adiabatic reactor.

The presence of C₅ hydrocarbons in the feed, however,
25 complicates the process schemes, as these compounds have

intermediate boiling temperatures between C₄ and oxygenated products, and they also form azeotropic mixtures with the branched alcohols as shown in Table 3, which indicates the boiling points of the most representative low-boiling components present in the streams

Table 3

Compound	Boiling point, °C
C ₄ /Methanol azeotropic product	-5
C ₄ products	-12/1
Isopentane/TBA azeotropic product	25
Isopentane	28
1-pentene	30
2-methyl-1-butene	31
n-pentane	36
2-methyl-2-butene	39
Cyclopentane	49
MTBE	55
Methanol	65
Dimers/TBA azeotropic product	78
TBA	82
Dimers	100 - 105

The C₅ products cannot therefore be removed from the plant together with the C₄ products, as they would introduce oxygenated products (branched alcohols and ethers) into the stream, which are difficult to remove by means of

the traditional techniques used for removing methanol (water washing) and which are poisonous for the subsequent treatment processes of the streams (polymerization, alkylation and metathesis). The C₅ products, on the other hand, cannot be maintained in the oxygenated stream as they would rapidly accumulate. With respect to the schemes shown in literature (US 6,011,191), it is therefore necessary to introduce a C₅/branched alcohol azeotropic separation step, which can be inserted in different positions of the plant in relation to the C₅ content in the charge and also the relative concentration of the C₅ products present.

The separation of the C₅/branched alcohol azeotropic product can be effected using traditional fractionation columns in which the azeotropic mixture can be recovered at the head, bottom or as side cut.

The process, object of the present invention, can be carried out, in particular, by means of the following essential steps:

- a) feeding a stream containing isobutene and C₅ hydrocarbons, together with one or more streams containing oxygenated products (linear and branched alcohols, ethers and water), to one or more reaction steps (consisting of one or more reactors);
- b) separating the C₄/linear alcohol azeotropic product and possibly the C₄ products from the C₅ hydrocarbons, from

the remaining oxygenated products and from the hydrocarbon product, in one or more distillation columns;

c) recovering the linear alcohol from the azeotropic mixture with the C₄ products by means of conventional processes such as washing with water or absorption on inorganic solids;

d) separating the C₅ products (as an azeotropic compound with the branched alcohol) from the remaining oxygenated products and from the reaction product, in one or more distillation columns, in order to obtain three streams with the desired purity;

e) recycling the stream containing the remaining oxygenated products and that containing the linear alcohol recovered, to the two reaction steps;

f) feeding linear alcohol and water (which forms the branched alcohol in the reactors by reaction with the tertiary olefin) to the reaction steps to compensate the losses of linear alcohol, which can react with the dimers and linear C₄ olefins, and branched alcohol which, on the contrary, leaves the plant together with the C₅ products;

g) recycling part of the C₄ products, with or without linear alcohol, to the reaction steps in order to maximize the isobutene conversion.

For the process comprising the essential steps indi-

cated above, the C₅ products are present in the streams prevalently containing C₄ products in a quantity preferably ranging from 0.5 to 10% by weight.

The separation of the C₅/branched alcohol azeotropic product is preferably carried out starting from blends of:

- a) C₅ - oxygenated products (ethers and branched alcohols) - reaction product, wherein the C₅ hydrocarbons are recovered as an azeotropic compound with the branched alcohol as head effluent using a scheme based on a column, with recovery of the remaining oxygenated products as side cut, or two fractionation columns;
- b) C₅ - oxygenated products (ethers and branched alcohols) - dimers, wherein the C₅ hydrocarbons are recovered as an azeotropic compound with the branched alcohol as head effluent of a fractionation column;
- c) C₄-C₅ - oxygenated products (ethers and branched alcohols) - reaction product, effluent from a reaction step, wherein the C₅ hydrocarbons are recovered as an azeotropic compound with the branched alcohol as side cut of a fractionation column from whose head the C₄/linear alcohol azeotropic product and possibly the C₄ products are recovered, whereas a mixture containing the oxygenated products and the reaction product is recovered at the bottom;
- d) C₄-C₅ - oxygenated products (linear and branched alco-

holds) wherein the C₅ hydrocarbons are recovered as an azeotropic compound with the branched alcohol as bottom effluent of a fractionation column from whose head the C₄/linear alcohol azeotropic product and possibly the C₄ products are recovered.

Six process schemes are shown in figures 1-6, in order to clearly illustrate the present invention.

Figure 1 shows a process scheme wherein C₅ hydrocarbons are not present in the charge and the oxygenated products are methanol (linear alcohol), TBA (branched alcohol) and MTBE (alkyl ether).

The stream (1) containing isobutene, together with the reintegration feeding of methanol and water (2) and the recycled streams of oxygenated products (MTBE and TBA) (15) and methanol (18), is sent to a first reaction step R1, which can consist of one or more reactors, in which the C₄ iso-olefin is selectively converted to dimers.

The effluent (4) from the first reaction step, is sent to a first separation column C1 in which a stream (5) essentially containing C₄ hydrocarbons and methanol is removed from the head, whereas a stream (6) essentially containing the reaction product and remaining oxygenated compounds, is collected at the bottom.

The head stream (5) is then fed, together with the recycled streams of oxygenated products (16) and methanol

(17), to a second reaction step R2, which can consist of one or more reactors, wherein the isobutene present is selectively converted to dimers.

The effluent (8) from the second reaction step is separated in a column C2 from whose bottom a stream (10) essentially containing MTBE, TBA, the dimerization product and part of the C₄ products, is removed and sent to the column C1 for the recovery of the product and oxygenated products. The head stream (9), consisting of C₄ products and the C₄/methanol azeotropic mixture is, on the other hand, sent to an MR unit for the recovery of the alcohol which can consist, for example, of an absorption system on molecular sieves or a water washing column. In both cases, the alcohol recovered (14) can be sent back to the two reaction steps (streams 17 and 18) whereas the hydrocarbon stream (13) can be used in subsequent operations.

The bottom stream (6) of the column C1 is sent to a further separation column C3 wherein a stream (11) essentially containing MTBE, TBA and dimers is removed at the head and is recycled to the two reaction steps (streams 15 and 16), whereas the reaction product (12) essentially consisting of dimers, trimers and small quantities of oligomers and ethers of dimers, is recovered at the bottom.

When C₅ hydrocarbons are present in the charge, on the contrary, according to the present invention, different

plant configurations can be used, schematised in the following figures 2-6, to recover the C₅/TBA azeotropic product, depending on the quantity of C₅ products present and the required purity of the streams.

5 Figure 2 therefore shows a possible process scheme which differs from the previous scheme in that the stream containing oxygenated products to be recycled (11) (ethers and TBA) is removed from the column C3 as side cut, whereas the C₅/TBA azeotropic product (19) is recovered from the head
10 of the column and can optionally be joined with the reaction product.

 The process scheme becomes more complex when a more efficient separation of the mixture of C₅ products/oxygenated products/reaction product is to be effected, as a new fractionation column C4 must be inserted,
15 as shown in figure 3. In this new scheme, the head stream of the column C3 (11) is sent to a new column C4 where the C₅/TBA azeotropic mixture (20) is separated at the head and the stream of oxygenated products (19) is separated at the
20 bottom and recycled to the two reaction steps.

 Alternatively, the C₅ hydrocarbons can be recovered using the two fractionation columns of the C₄ products wherein the C₅/TBA azeotropic mixture can be thus recovered as side cut (19) both in the column C1 (figure 4) and in
25 the column C2 (figure 5). A further option however consists

in effecting the separation of the C_4 - C_5 products in a last new column C5, as shown in figure 6, in which the C_5 /TBA azeotropic product is recovered as bottom stream (19).

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CLAIMS

- 1) A process for the separation of C₅ hydrocarbons present, in a quantity ranging from 0.2 to 20% by weight, in hydrocarbon streams prevalently containing C₄ products used for the production of high-octane hydrocarbon compounds, by the selective dimerization of isobutene, characterized in that the dimerization reaction is carried out in the presence of linear and branched alcohols and alkyl ethers in such a quantity as to have a molar ratio alcohols + alkyl ethers/isobutene in the feeding higher than 0.01.
- 2) The process according to claim 1, wherein the molar ratio alcohols + alkyl ethers/isobutene is lower than 0.7.
- 3) The process according to claim 1, wherein the reaction is carried out at a temperature ranging from 30 to 120°C, at a pressure lower than 5 MPa and at feeding space velocities lower than 30 h⁻¹.
- 4) The process according to claim 1, wherein the feeding space velocities range from 1 to 15 h⁻¹.
- 5) The process according to claim 1, wherein the linear alcohol has a number of carbon atoms ranging from 1 to 6.
- 6) The process according to claim 5, wherein the linear alcohol is selected from methanol and/or ethanol.
- 7) The process according to claim 1, wherein the branched alcohol has a number of carbon atoms ranging from 4 to

7.

8) The process according to claim 7, wherein the branched alcohol is selected from tert-butyl alcohol or tert-amyl alcohol.

5 9) The process according to claim 1, wherein the alkyl ether has a number of carbon atoms ranging from 5 to 10.

10) The process according to claim 9, wherein the alkyl ether is selected from MTBE, ETBE, MSBE, ESBE, TAME, TAAE or mixtures thereof.

10 11) The process according to claim 1, wherein other possible olefins present in the charge react to form high-octane products.

12) The process according to claim 1, wherein isobutene content in the charge is modified by dilution with C₄-
15 C₇ streams.

13) The process according to at least one of the previous claims comprising the following essential steps:

a) feeding the C₄-C₅ hydrocarbon cut containing isobutene, together with one or more streams containing oxygenated products (linear and branched alcohols, ethers
20 and water), to one or more reaction steps (consisting of one or more reactors);

b) separating the C₄/linear alcohol azeotropic product and possibly the C₄ products from the C₅ hydrocarbons,
25 from the remaining oxygenated products and from the hy-

drocarbon product, in one or more distillation columns;

c) recovering the linear alcohol from the azeotropic mixture with the C₄ products by means of conventional processes such as washing with water or absorption on inorganic solids;

d) separating the C₅ hydrocarbons, as an azeotropic compound with the branched alcohol, from the remaining oxygenated products and from the reaction product, in one or more fractionation columns, in order to obtain three streams with the desired purity;

e) recycling the streams containing the oxygenated products (branched alcohol and ether) and the linear alcohol recovered, to the two reaction steps;

f) feeding linear alcohol and water (which forms the branched alcohol in the reactors by reaction with the tertiary olefin) to the reaction steps to compensate the losses of linear alcohol, which can react with the dimers and linear C₄ olefins, and branched alcohol which, on the contrary, leaves the plant together with the C₅ products;

g) recycling part of the C₄ products, with or without linear alcohol, to the reaction steps in order to maximize the isobutene conversion.

14) The process according to claims 1 and 13, wherein the separation of the C₅/branched alcohol azeotropic prod-

uct can be carried out starting from blends of:

- a) C₅ - oxygenated products (ethers and branched alcohols) - reaction product, wherein the C₅ hydrocarbons are recovered as an azeotropic compound with the branched alcohol as head effluent using a scheme based on a column, with recovery of the remaining oxygenated products as side cut, or two fractionation columns;
- b) C₅ - oxygenated products (ethers and branched alcohols) - dimers, wherein the C₅ hydrocarbons are recovered as an azeotropic compound with the branched alcohol as head effluent of a fractionation column;
- c) C₄-C₅ - oxygenated products (ethers and branched alcohols) - reaction product, effluent from a reaction step, wherein the C₅ hydrocarbons are recovered as an azeotropic compound with the branched alcohol as side cut of a fractionation column from whose head the C₄/linear alcohol azeotropic product and possibly the C₄ products are recovered, whereas a mixture containing the oxygenated products and the reaction product is recovered at the bottom;
- d) C₄-C₅ - oxygenated products (linear and branched alcohols) wherein the C₅ hydrocarbons are recovered as an azeotropic compound with the branched alcohol as bottom effluent of a fractionation column from whose head the C₄/linear alcohol azeotropic product and possibly the

C₄ products are recovered.

15) The process according to claims 1, 13 and 14, wherein the C₅/branched alcohol azeotropic mixture is joined to the reaction product.

5 16) The process according to claims 1 and 13, wherein the dimerization reaction is carried out in one or more fixed bed, tubular and/or adiabatic reactors.

10 17) The process according to claim 13, wherein the C₅ hydrocarbons are present in streams prevalently containing C₄ products in a quantity ranging from 0.5 to 10% by weight.