CHEMISCHE WERKE HÜLS AG
- RSP PATENTS -

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Process for the preparation of highly pure isobutene by dehydration of tertiary butanol

The invention relates to a process for the preparation of highly pure isobutene by dehydration of tertiary butanol (TBA) in the presence of a strongly acidic synthetic resin cation exchanger as the catalyst.

The dehydration of TBA proceeds reversibly and endothermically. With regard to the chemical equilibrium, the conversion to isobutene and water increases in principle with rising temperature.

On an industrial scale, the dehydration of TBA is therefore carried out predominantly at high temperatures of about 180 to 450°C in the presence of weakly acidic catalysts such as silica gel, thorium oxide, titanium-IV oxide or especially aluminium oxide. (German Offenlegungsschrift 2,716,132 = US Patent Specification 4,036,905, German Auslegeschrift 2,058,478 = US Patent Specification 3,665,048, US Patent Specification 2,377,026). Although a high TBA conversion is achieved by the use of high temperatures, the considerable isobutene losses due to oligomerisation of the isobutene are unsatisfactory. Moreover, in addition to the oligomerisation of the isobutene, an isomerisation of the isobutene formed to n-butenes undesirably takes place (German Auslegeschrift 2,058,478), and this leads to a further product loss and above all, with particular disadvantage, makes the separation and isolation of pure isobutene more difficult.

If the dehydration of TBA is carried out at temperatures lower than 180°C, more active, strongly acidic catalysts are necessary. Because of the disadvantages involved with these, such as corrosion, effluent problems, expensive reprocessing and the like, the homogeneous acidic catalysts such as, for example, mineral acids, organic sulphonic acids and heteropoly acids lose

importance for the dehydration reaction. By contrast, cation exchanger resins gain importance as catalysts.

Owing to the less favourable equilibrium relationships, only partial TBA conversions are still possible at lower temperatures. Higher degrees of conversion therefore require that the reaction products are separated off continuously.

This is effected by setting relatively low reaction pressures below 2 bar, so that the isobutene as the lowest-boiling component continuously distils off from the reaction mixture, together with a fraction of TBA and water in accordance with the partial pressure (US Patent Specification 3,256,250). Since the rate of formation, which is anyway low, sharply decreases with increasing water content in the reaction mixture, these procedures are suitable only for TBA rich reaction mixtures. For TBA solutions, which are richer in water, as a feed mixture, process steps have been described which propose the use of inert entrainers for the water of reaction (US Patent Specification 3,510,538 and US Patent Specification 4,155,945). However, in the case of the addition of, for example, benzene or xylene as an entrainer, increased oligomerisation of isobutene takes place, particularly above 100°C, according to the teaching of US Patent Specification 3,510,538. Moreover, the addition of a third substance assisting the reaction makes working-up more difficult, since this auxiliary must be discharged and recovered again.

To overcome these disadvantages, it has been suggested to feed the aqueous TBA solution to the rectifying section of the column, from which, preferably at 85°C and under a pressure of a maximum of 1.9 bar, a TBA-rich, water-containing vapour stream is driven through the catalyst bed located as a loose packing above the rectifying section (German Auslegeschrift 2,454,998 = US Patent Specification 4,012,456). The isobutene, together with

the proportionate TBA and water, is taken off as a gas from the reaction section. This process is satisfactorily selective, but requires a cation exchanger resin in a special form which is not commercially available.

In addition to often complicated reaction control, all these processes have a serious fundamental disadvantage:

Isobutene is obtained as a gas, together with a fraction of TBA and water in accordance with the partial pressure, under a pressure at which it can no longer be condensed by means of coolants conventional in industry.

To obtain pure isobutene by rectification, expensive compression and condensation stages are therefore necessary. In order to avoid this disadvantage, the dehydration of TBA in the process of German Offenlegungsschrift 2,913,796 = British Patent Specification 2,022,129 is carried out in the presence of acidic cation exchanger resins under a pressure of at least 5 bar. Correspondingly, such a high temperature is selected that the isobutene formed can be taken off as a gas together with the proportionate TBA and water from the reaction zone. Depending on the reaction pressure, temperatures of about 180°C or higher are required for this purpose, that is to say temperatures which are above the application limit of commercially available cation exchanger resins and therefore lead to the expectation of only a limited catalyst life under these conditions. Furthermore, the higher temperatures have the consequence of an isobutene selectivity which is lower than the abovementioned processes. All these processes, which represent the state of the art for the dehydration of TBA in the presence of acidic synthetic resin exchangers, share the common feature that the reaction components are present in a mixed phase, consisting of a gaseous phase and a liquid phase, and the catalyst is present as a third, solid phase. As a result, the mass transfer to the catalytically active centre of the catalyst is inhibited, and this has

the result that the rate of formation of isobutene, relative to the reactor volume, that is to say the space-time yield for isobutene, is unsatisfactory.

Large quantities of catalyst are therefore required for implementing the process on an industrial scale. This raises problems with respect to the equipment to be used and the supply of heat for the strongly endothermic cracking reaction since, because of the low temperature stability of the synthetic resin exchangers used, heat can be supplied only from a heat source of comparatively low temperature, so that a large heat transmission area is necessary.

To improve the mass transfer conditions for the cracking reaction, a moving catalyst bed is used in the processes of the state of the art. The synthetic resin skeleton of the commercially available cation exchangers, when used in polar agents such as TBA and water, undergoes extensive swelling and deformation, which seriously impair the mechanical stability of the catalyst.

Attrition and fracture of the catalyst particles can therefore not be prevented in a moving catalyst bed.

The present invention is intended to avoid the above disadvantages of the processes of the state of the art.

This leads to the object of discovering a process for the large-scale production of highly pure isobutene by dehydration of TBA, which enables the dehydration to be accomplished by a more productive and more economical process in accordance with a simple procedure.

According to the invention, this object is achieved in accordance with the features shown in the patent claims.

Both technical TBA, contaminated with isobutene oligomers, for example diisobutene, and pure TBA are suitable as the feed material. TBA/water mixtures such as, for example, the TBA/water azeotropes, which are obtained in working-up by distillation, are preferably employed.

Surprisingly, highly pure isobutene is obtained

by the process of the invention in a very high space-time yield at an isobutene selectivity of virtually 100 mol%, if the cracking or re-cracking of TBA to isobutene and water is carried out in a homogeneous liquid phase on a strongly acidic, organic ion exchanger arranged in a fixed bed, and the homogeneous liquid reaction product is fed to a distillation section separate from the reaction space, where the separation of the isobutene and the water from uncoverted TBA takes place which is recycled as an aqueous TBA solution into the dehydration stage. This was unexpected, since it is described in the already-mentioned German Offenlegungsschrift 2,913,976, page 20, columns 27 to 31, that the dehydration is difficult to accomplish under an unduly high pressure, that is to say in the presence of a homogeneous liquid phase. It was therefore surprising that, by the process according to the invention in a homogeneous liquid phase, isobutene is obtained at these temperatures in hitherto unattained space-time yield (STY) and selectivity.

A further advantage of the process according to the invention is the separation of reaction space and isobutene working-up, so that this selection of the optimum conditions for the reaction stage and for the distillation stage is free and flexible, which is a great advantage particularly with respect to the product quality and also in view of the catalyst stability.

The reaction temperature in the process according to the invention is 80 to 150°C. At elevated temperatures of, for example, 110°C, an adiabatic procedure is of advantage. The preferred temperature is 100 to 130°C, since, in this range, the space-time yield of isobutene and the catalyst life are at the optimum under economic aspects.

The reaction pressure is 5 to 25 bar, such a high pressure being selected that the isobutene formed in the reactor remains fully and homogeneously dissolved in the reaction mixture, without a gas phase being formed. In

general, it is advantageous if the reaction pressure is higher than the column pressure in the working-up section, because flash evaporation can then be utilised advantageously for assisting the isolation of isobutene.

The TBA content in the feed mixture upstream of the reactor is 40 to 90% per weight, preferably 55 to 85% by weight. The feed mixture introduced into the reactor is composed of the freshly fed tertiary butanol, preferably as the TBA/water azeotrope, and the recycled TBA/water mixture. This mixture is fed continuously to the reactor.

The space velocity particularly advantageous in an individual case depends on the water content of the reaction mixture and, to a high degree, on the reaction temperature and on the activity of the catalyst used, and this must be determined individually for each catalyst.

The space velocity (LHSV) in litres of charge per litre of swollen catalyst per hour is in general 50 to 100 l/l h, at a reaction temperature of 80 to 100°C, 100 to 300 l/l h at 100 to 130°C and up to 600 l/l h at 130 to 150°C.

However, less favourable space velocities can also be selected. Comparative Example 1 shows the lower space-time yield and the markedly poorer selectivity in the case of the two-phase liquid reaction mixture. Comparative Example 2 demonstrates the increasingly poorer isobutene selectivity in the case of a TBA concentration above 90% by weight in the reaction mixture. Comparative Examples 3 and 4 in particular show the lower space-time yield and the poorer selectivity in the case of a gaseous/liquid reaction mixture, from which isobutene is taken off in the form of a gas.

Suitable organic ion exchangers are sulphonated organic resins (for example those prepared according to US Patent Specification 2,480,940), in particular the sulphonated polystyrene resins (US Patent Specification 2,922,822) which are crosslinked with divinylbenzene and which can be of a gel-like nature or, in order to

enlarge the surface area, can have a sponge structure with macropores (German Patent Specification 1,224,294 = British Patent Specification 957,000) or, to increase the hydrolytic stability of their catalytically active sulphonic acid groups, can have a halogenated synthetic resin skeleton (US Patent Specification 3,256,250). The commercially available organic ion exchangers are preferably used in the hydrogen form. However, commercial, macroporous cation exchangers, which have been modified by partial ion exchange or by thermal desulphonation, can also have satisfactory activity coupled at the same time with a higher hydrolytic stability of the sulphonic acid group.

The isolation of pure isobutene and the removal of the water take place in a working-up section separate from the reaction space. According to a preferred embodiment of the process according to the invention (Fig. 1), the homogeneous and liquid reaction mixture leaving the reactor via line 5 is passed to a pressure column (K1) for the isolation of pure isobutene.

The top pressure of the column K1 is in general 3 to 10 bar, preferably 5 to 7 bar, since a particularly economical distillation is possible in this range when the distillate is condensed with cooling water. The isobutene is distilled off over the top (line 6), together with the traces of water corresponding to the isobutene water azeotrope. The water settles out as a separate phase in the receiver and can be separated off without problems. The TBA/water mixture obtained as the bottom product contains in general less than 0.5% by weight of isobutene and the major part is recycled via line 2 to a point upstream of the reactor. The bottom temperature can, independently of the reactor inlet temperature, be selected such that, on the one hand, the distillation can be carried out under economical conditions and, on the other hand, the temperatures to be maintained to safeguard the stability of the catalyst are not exceeded.

Of course, lower and higher pressures can also be applied in this distillation stage, even though this is less advantageous for economic reasons.

In order to separate off the water formed in a quantity equivalent to the isobutene and the water introduced, as appropriate, with the fresh TBA, a part stream of the bottom product is fed via the line 7 to the column K2', in which isobutene dimers which are contained in the feed mixture or may be formed in traces during the reaction are distilled off over the top (line 8) as a ternary mixture with TBA and water. The bottom product is fed via line 9 to the column K2, in which a TBA/water mixture of azeotropic composition is taken off as the top product and recycled via line 3 to a point upstream of the reactor. In the bottom of the column K2, the excess water is removed from the system via line 10. The columns K2' and K2 are operated under normal pressure or an elevated pressure.

The ternary mixture from the top of K2' is advantageously separated by means of water, and the TBA-containing aqueous phase is recycled into the column. If the reaction mixture does not contain any isobutene dimers, the column K2' is unnecessary.

When the TBA/water azeotrope (about 88% by weight of TBA under normal pressure) is used as the fresh feed mixture (line 1), the ratio of the circulating streams from the bottom of column K1 and from the top of column K2 is preferably 2 to 130 : 1, in particular 5 to 30 : 1.

The TBA/water mixture is preferably passed downwards to the fixed catalyst bed of the reactor R.

A further embodiment, according to the invention, of the process, which is particularly economical, is reproduced in Fig. 2 for clarification.

The homogeneous liquid reaction product is fed via line 3 to the pressure column K1, in which the pure isobutene is distilled off as the water azeotrope over the top. The entrained water separates out as a separate

phase in the receiver. In the stripping section of the column, the TBA azeotrope is distilled off from the water running down, so that the water freed from isobutene and TBA is taken off at the bottom of the column K1 via line 5. A TBA/water mixture enriched in TBA is branched off as a side stream via line 4 from an intermediate tray above the stripping section, is mixed as a circulating stream with the fresh educt stream (line 1) and then passed via line 2 through the reactor, preferably downwards. If the reaction mixture contains isobutene oligomers, these can be removed by means of a side take-off in the rectifying section of the column K1 via line 7.

This special preferred embodiment of the process is particularly economical, for the reason that condensation of the TBA/water azeotrope, when separating off the water, in a particular condenser, as in the case of using the column K2, is unnecessary and, instead, the heat of condensation is utilised for separation in the reaction circulation which consumes energy.

By means of the process described above, highly pure isobutene can be obtained in a simple manner from TBA with a selectivity for isobutene of more than 99.9 mole %. The degree of conversion of TBA is virtually 100%. Since the reaction is carried out under mild conditions on a fixed catalyst bed, even commercially available, organic cation exchangers reach industrially satisfactory catalyst lives. The reaction can be carried out with continuous or discontinuous fresh TBA feed into the reaction circulation. The continuous procedure is preferred. The purity of the isobutene obtained is greater than 99.9%. As a rule, values of up to 99.99% can be reached. The remainder is water. The highly pure isobutene obtained according to the invention is preferably used for the production of polyisobutene, butyl rubber and for alkylations.

The examples which follow serve to illustrate the process, but are not intended to restrict it in any way.

Example 1

The catalyst used is a commercial, strongly acidic ion exchanger resin (macroporous, sulphonated polystyrene resin crosslinked with divinylbenzene). Other characteristic data of the resin are: BET surface area about $40 m^2/g$ of dry resin, divinylebenzyne content about 18%, particle size distribution 0.5 to 1.3 mm, hydrogen ion capacity about 3.8 milliequivalents H^+/g of dry resin.

According to Fig. 1, 711 kg/h of fresh educt containing 623 kg/h of TBA, 85 kg/h of water and 2.85 kg/h of C_8-olefines are passed via line (1) into the reactor R which is charged with 78 l of the catione exchanger resin described above, 10,455 kg/h of circulating mixture which is recycled from the bottom of column K1 and contains 6,480 kg/h of TBA, 3,938 kg/h of water and 36.9 kg/h of C_8 olefines are passed in via line (2) and 565 kg/h of circulating mixture from the top of column K2, which contains 497 kg/h of TBA and 68 kg/h of water, are passed in via line (3), that is to say a total of 11,731 kg/h of feed mixture containing 64.7% by weight of TBA via line (4).

The cracking reaction is carried out under 10 bar and at a mean temperature of 120°C.

The reaction mixture is fed via line 5 to the column K1 and, before entry, flashed to the column pressure of 6 bar ($\hat{=}$ top pressure). 470 kg/h of pure isobutene are taken off in the column K1 over the top (line 6). The distillate contains water corresponding to the azeotrope; this water settles out as a separate phase in the receiver and is removed from the system. The bottom product of column K1 has the composition 6,980 kg/h of TBA, 4,242 kg/h of water and 39.75 kg/h of C_8 olefines. The major part is recycled via line (2). A part stream of 806 kg/h is fed via line (7), after flashing to the column oressure of 1.2 bar ($\hat{=}$ top pressure), to the column K2'. 2.85 kg/h of C_8-olefines together with 2.2 kg/h of TBA and 0.65 kg/h of water are taken off as a ternary mixture over the top

line (8) of column K2'. The bottom product is fed via line (9) to column K2, in which the azeotropic TBA/water mixture is taken off over the top (top pressure 1.02 bar) and recycled via line (3). The ratio of the circulating streams from columns K1 and K2 is 18.5 : 1. In the bottom of column K2, 235 kg/h of water are obtained which are removed from the system via line (10). The isobutene selectivity is virtually 100%. When the C_8/TBA/water mixture from the top of column K2' is separated by means of water and the aqueous phase containing TBA is recycled, the degree of conversion of TBA is likewise virtually 100%. The isobutene purity is 99.99%.

Example 2

The catalyst used is a commercially available, strongly acidic ion exchanger resin (macroporous, sulphonated polystyrene resin crosslinked with divinylbenzene) having the following characteristic data: BET surface area about 25 m^2/g of dry resin, divinylbenzene content about 8%, particle size distribution 0.5 to 1.2 mm, hydrogen ion capacity about 4.1 milliequivalents of H^+/g of dry resin.

In accordance with the flow diagram in Fig. 2, the TBA cracking is carried out as follows, at a mean temperature of 120°C and under a pressure of 20 bar.

4,161 kg/h of TBA, 1,040 kg/h of water and 3.4 kg/h of C_8-olefines are fed with the stream (2) into a reactor R charged with 42 l of the catalyst described above. The stream (2) contains 80% by weight of TBA and is composed of the fresh feed stream (line 1), which contains 675 kg/h of TBA, 92 kg/h of water and 2.8 kg/h of C_8-olefines, and the circulating stream which is recycled via line 4 from the pressure column K1 and contains 3,486 kg/h of TBA, 948 kg/h of water and 0.6 kg/h of C_8-olefines. The circulating stream recycled via line 4 contains 78.6% by weight of TBA. The reactor product is fed via line 3 to the column K1 and flashed to the column pressure of 7 bar ($\triangleq$ top pressure). In column K1, 510 kg/h of pure isobutene are distilled off over the top (line 6). The

distillate contains water corresponding to the azeotrope, and this is separated off as a separate phase in the receiver. 256 kg/h of water are obtained in the bottom and are removed from the system via line 5. 2.9 kg/h of C_8-olefines together with 2.5 kg/h of TBA and 0.7 kg/h of water are removed from the rectifying section of the column K1 via a side take-off. The C_8-olefines/TBA water mixture is separated by means of the water from the receiver of the top product and a part of the water removed from the bottom, and the TBA-containing aqueous phase is recycled. The circulating stream is branched off as a side stream from the stripping section of the column K1 via line 4 and recycled to a point upstream of the reactor. The isobutene selectivity is 99.98%, the degree of conversion of TBA is virtually 100% and the isobutene purity is 99.99%.

Examples 3 to 8

In a series of further examples, TBA is dehydrated by the procedure according to Example 1 (compare Figure 1). The commercial macroporous, strongly acidic ion exchanger resin (sulphonated polystyrene resin crosslinked with divinylbenzene) used as the catalyst has the following characteristic data: BET surface area about 35 m^2/g of dry resin, divinylbenzene content 10%, particle size distribution 0.5 to 1.2 mm, hydrogen ion capacity about 4.5 milliequivalents of H^+/g of dry resin. 100 ml of this resin swollen in TBA/water azeotrope (about 12% by weight of water) are charged into the lower quarter of a 100 cm long tube reactor (internal diameter 2.29 cm) with a heating jacket. The remainder of the volume is charged with V4A stainless steel packing and serves as a preheating zone. A displaceable thermocouple is arranged centrally in the reactor. Inspection windows for checking the homogeneity of the liquid mixture are fitted upstream and downstream of the reactor. The volume of the column bottoms of columns K1, K2' and K2 is kept constant by means of an automatic level control. Fresh TBA/water

mixture of azeotropic composition and free of isobutene oligomer is fed in via line 1. The conditions used and the results thus obtained are summarised in Table 1 which follows. The space velocity (LHSV) is given in litres of charge per litre of swollen catalyst per hour, and the isobutene space-time yield (STY) is given in kg of isobutene per litre of swollen catalyst per hour. The analysis of the flow streams was carried out by gas chromatography. With the exception of Example 5, column K2' is unnecessary. The isobutene obtained has a degree of purity of 99.99%.

Table 1

Example No.	Temperature °C	kg/h of fresh azeotrope	LHSV l/l h	Ratio of the mass flows 1 : 2 : 3			% by weight of TBA in stream 4	% by weight of H_2O	Isobutene STY kg/l h	Isobutene selectivity mol %
3	110	0.39	54	1	9.3	1	70	30	2.6	100
4	110	0.69	140	1	15.5	1.1	70	30	4.6	100
5	120	0.44	45	1	6.5	0.9	70	30	2.9	99.9
6	120	1.02	139	1	8.2	1.3	70	30	6.8	100
7	120	0.48	80	1	12.6	0.6	60	40	3.2	100
8	120	1.0	206	1	16.0	0.6	60	40	6.5	100

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Example 9

The catalyst used is the commercial cation exchanger resin from Example 1. An 80 cm long steel tube reactor of 2.29 cm internal diameter, which has a jacket serving as a thermostat and two zones which can be heated to different temperature levels, is packed with 20 ml of exchanger resin swollen in TBA/water azeotrope. The resin is located in the lower third of the reactor. The remaining reactor volume is charged with 4VA stainless steel packing and serves as a preheater zone. A displaceable thermocouple is arranged centrally in the reactor. An inspection window fitted upstream and downstream of the reactor enables the homogeneity of the liquid mixture to be checked. In a series of tests, the TBA cracking is carried out by an almost isothermal procedure (maximum 2°C temperature difference in the catalyst bed) according to the procedure of Example 2, but under a pressure of 11 bar, the temperature and the TBA concentration in mass stream 2 being varied. The fresh TBA is fed in via line 1 as pure TBA (99%) free of isobutene oligomer. The TBA concentration in the side stream take-off from the stripping section of the column (line 4) is about 58% by weight with 60% by weight of TBA in stream 2, about 68% by weight with 70% by weight of TBA, about 78% by weight with 80% by weight of TBA and about 85% by weight with 90% by weight of TBA. The flow streams are analysed by gas chromatography. The conditions used and the results thus obtained are summarised in Table 2. The definition of Examples 3 to 8 applies to the space velocity (LHSV) and space-time yield (STY).

Example 10

A macroporous ion exchanger resin having the characterisic data given in Example 1 is deactivated with 1 mmol/g of dry resin of Na ions in such a way that a residual hydrogen ion capacity of 2.8 milliequivalents of H^+/g of dry resin remains. 30 ml of resin swollen in TBA/water azeotrope are charged into the reactor described in Example 9. The dehydration of the TBA is carried out in accordance with

the procedure indicated in Example 9. The conditions and the results obtained are indicated in Table 3.

Table 2

Temperature °C	LHSV l/l h	Isobutene STY (kg/l h) at % by weight of TBA in stream 2				Isobutene selectivity (mol %) at % by weight of TBA in stream 2			
		90	80	70	60	90	80	70	60
90	120		2.0	1.4	1.0		100	100	100
100	120		4.1	3.0	2.2		100	100	100
116	120		7.3	6.0	4.8		100	100	100
120	120		15.1	12.0	9.8		99.9	100	100
130	300		22.6	19.2	15.3		99.9	99.9	100
140	300	40.5				99.8			

The purity of the isobutene is 99.99%.

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Table 3

Temperature °C	LHSV l/l h	Isobutene STY (kg/1 h) at % by weight of TBA in stream 2		
		90	70	60
100	100		2.5	1.9
110	120		5.2	4.1
120	130		10.5	9.2
140	300	28.3		

In all cases, the isobutene selectivity is 100 mol % and the isobutene purity is 99.99%.

Comparative Example 1

This example shows the activity and selectivity of the catalyst resin with a two-phase, liquid reaction mixture. The catalyst and test procedure correspond to the data in Examples 3 to 8. At a mean reaction temperature of 130°C, a reaction pressure of 15 bar and a space velocity of 120 l/l h, 0.16 kg/h of fresh azeotrope are passed via line 1, together with the circulation streams from lines 2 and 3, downwards through the reactor. The ratio of the mass flows from lines 1, 2 and 3 is 1 : 64.5 : 0.12. The TBA/water mixture at the reactor inlet contains 25% by weight of TBA and 75% by weight of water. The reactor product is two-phase and liquid. The isobutene space-time yield is 1.1 kg/1 h, and the isobutene selectivity is 97.8 mol %.

Comparative Example 2

According to the test procedure described in Example 9, a TBA/water mixture with 95% by weight of TBA and 5% by weight of water is passed through the reactor via line 2 (compare Figure 2) at 150°C, a space velocity of 120l/l h and a reaction pressure of 15 bar. The reaction product is homogeneous and liquid. The isobutene space-time yield is 21.6 kg/h, and the isobutene selectivity is 98.6 mol %.

Comparative Examples 3 and 4

The test procedure followed is as in Example 2, with the following modifications. 100 ml of cation exchanger resin from Example 1, swollen in TBA/water azeotrope, are as a loose packing in an 80 cm long glass reactor (internal diameter 4.5 cm) with a displaceable thermocouple in the middle and a heating jacket. The reaction pressure is selected such that the reaction mixture boils at the particular reaction temperature. The fresh TBA/water mixture of azeotropic composition and free of isobutene oligomer is admixed to the circulated TBA/water mixtures and passed upwards through the reactor. The turbulence caused as a result and by the evaporation of the isobutene formed maintains the catalyst in dispersion. The isobutene formed is taken off continuously in the gaseous form via a bubble cap tray column (10 trays) located on the top of the reactor. For separating off the catalyst, the liquid reaction phase is taken off from the reaction space (volume 1.2 l) via a filter candle at the upper reactor end and treated analogously to the procedure described in Example 2. The conditions used and the results obtained are shown in Table 4. The space velocity and the space-time yield are related in each case to the swollen catalyst volume. The mass streams were analysed by gas chromatography.

Table 4

Comparative Example No.	Temperature °C	Reaction pressure bar	LHSV l/l h	% by weight in the stream of isobutene upstream of the reactor TBA	H_2O	STY kg/l h	Selectivity mol %
1	80	1.05	90	80	20	0.32	99.7
2	90	1.4	110	80	20	0.75	99.5

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Patent Claims:

1. Process for the preparation of highly pure isobutene by dehydration of tertiary butanol in the presence of an acid catalyst, characterised in that

a) tertiary butanol in an aqueous solution which contains 40 to 90% by weight of tertiary butanol is continuously fed to a reactor and dehydrated in homogeneous and liquid phase on a fixed catalyst bed, consisting of a strongly acidic ion exchanger resin, at a temperature of 80 to 150°C and under a pressure of 5 to 25 bar,

b) the homogeneous liquid reaction mixture is then fractionated in a distillation section separate from the reaction space and the isobutene is separated from water and the unconverted tertiary butanol,

c) the tertiary butanol/water mixture containing the unconverted tertiary butanol is then, after enrichment of the tertiary butanol by distillation, recycled to the reactor at a circulating flow rate selected such that the mixture of the freshly fed tertiary butanol and the recycled tertiary butanol/water mixture at the reactor inlet contains 40 to 90% by weight of tertiary butanol, and the water produced at a rate equivalent to the isobutene formed and, if appropriate, fed to the reaction circulation with fresh tertiary butanol, is removed from the system.

2. Process according to Claim 1, characterised in that tertiary butanol is dehydrated at a temperature of 100 to 130°C.

3. Process according to Claim 1 and 2, characterised in that the total mixture of tertiary butanol and water at the reactor inlet contains 55 to 85% by weight of tertiary butanol.

4. Process according to Claim 1 to 3, characterised in that, in a distillation column, the isobutene is separated off form the tertiary butanol/water mixture over

the top, the tertiary butanol is azeotropically distilled off in the stripping section of the column from the water running down, the water freed from isobutene and tertiary butanol being obtained in the bottom of the column and being removed from the system, and a tertiary butanol water mixture enriched in tertiary butanol is branched off, at an intermediate tray above the stripping section, as a side stream which is directly fed back to the reactor as a recycle stream.