

Process for the cleavage of alkyl tert-alkyl ethers into isoolefins and alkanols over acid catalysts

5 The present invention relates to a process for the cleavage of alkyl tert-alkyl ethers by reactive distillation in the presence of acid catalysts to give the corresponding olefins and alkanols.

10 The cleavage of ethers, in particular alkyl tert-alkyl ethers into alkanols and olefins, is known and can be used for the preparation of pure olefins. Thus, for example, isobutene is produced in technical-grade purity by dehydrogenation of C₄ mixtures. These C₄ mixtures comprise, apart from traces of C₃ and C₅ compounds, isobutene, 1-butene and 2-butene. Separation of this mixture by simple distillation to isolate pure isobutene is uneconomical because of the very small boiling point difference or
15 separation factor for 1-butene and isobutene.

Pure isobutene is therefore usually obtained by cleavage of methyl tert-butyl ether (MTBE) back into isobutene and methanol.

20 The acid-catalyzed cleavage of ethers such as MTBE to obtain pure olefins such as isobutene is a process known per se. A distinction is made here between two different process variants. Firstly, the cleavage can be carried out in the liquid phase over acid ion exchange resins as described, for example, in DE 3 509 292 A1 or DE 3 610 704 A1 or over acidic
25 aluminum oxides as disclosed, for example, in DD 240 739 A1. In the latter case, the reaction conditions (167°C and 1 bar or 297°C and 10 bar) are chosen so that the MTBE cleavage occurs in the gas/liquid region or in the pure gas phase.

30 Secondly, the cleavage reaction can be carried out in the gas/liquid phase in a type of combined reaction distillation column over acid catalysts, as disclosed in EP 0 302 336 A1 or DE 4 322 712. EP 0 302 336 A1 describes the elimination of methanol from MTBE over an acid ion exchange resin which is positioned in the bottom of the column. The
35 cleavage of the ether here takes place in the bottom of the column, i.e. the catalyst is continually surrounded by a mixture of ether, olefin and alcohol. This is a disadvantage for the preparation of isobutene, since, firstly, it does not ensure that the isobutene which oligomerizes readily under acid conditions is taken off quickly and, secondly, the acid centers of the

catalyst are occupied by methanol. A different route is taken in DE 4 322 712. In that document, the tertiary ether is fed into a reaction distillation column above the reaction zone, and the rectification section of the column serves to purify the isobutene while in the stripping section of the column, methanol is separated from the MTBE/methanol azeotrope. The azeotrope goes back into the reaction zone. As acid catalyst, use is made of a sulfated titanium dioxide extrudate.

In both procedures, catalyst poisons present in the feed, for example metal ions, can deactivate the Brönsted acid catalyst. In addition, the introduction of an MTBE/methanol mixture in this arrangement would decrease the reaction rate of the MTBE cleavage and thus reduce the conversion. Methanol inhibits the actual cleavage reaction due to it occupying the acid centers of the catalyst.

In the case of cleavage processes which are carried out in the pure liquid phase, it has to be noted that high MTBE conversions cannot be achieved in principle. This is because the cleavage reaction is a typical equilibrium reaction. Thus, for example, a liquid phase at reaction equilibrium at 100°C and the corresponding total pressure has the following composition:

mole fraction of isobutene	= ~ 14 mol%
mole fraction of MTBE	= ~ 70 mol%
mole fraction of methanol	= ~ 16 mol%

A further problem in this process is the isobutene dissolved in the homogeneous liquid phase, which can undergo subsequent reactions. The most important reactions of this type are acid-catalyzed dimerization and oligomerization. For this reason, undesired C₈ and C₁₂ components are also found in addition to the desired target product isobutene. The undesired C₈ molecules are 2,4,4,-trimethyl-1-pentene and 2,4,4,-trimethyl-2-pentene. Furthermore, owing to the sometimes high reaction temperature, a further subsequent reaction in which two methanol molecules react to eliminate water and form dimethyl ether occurs. Since this reaction causes a considerable methanol loss, fresh methanol has to be fed in, especially if the cleavage is integrated in a circuit with an MTBE synthesis.

In the process variant in which the cleavage reaction is carried out in the pure gas phase, the problems of dimerization or oligomerization of the isobutene formed to undesirable downstream products likewise occur. Dilution of the gaseous starting material stream with inert gas can reduce these reactions, but not eliminate them entirely. Dilution of the starting material stream at the same time reduces the efficiency of the production plant.

The reactions carried out in the gas phase or at high temperatures in the processes described have the disadvantage that high-boiling cracking products are formed during the cleavage process and deposit on the catalyst, thus deactivating it. Deactivated catalysts and/or high temperatures favor the formation of by-products and reduce the selectivity of the reaction. Particularly the isobutenes obtained by ether cleavage tend to undergo undesirable thermal polymerization. Carrying out the reaction at lower temperatures frequently results in a low conversion.

It is therefore an object of the present invention to develop a process for the cleavage of alkyl tert-alkyl ethers which achieves a high ether conversion together with low downstream product formation and low catalyst deactivation.

It has surprisingly been found that the acid-catalyzed cleavage of alkyl tert-alkyl ethers into the corresponding olefins and alkanols can be carried out at high conversions and with low by-product formation when using an azeotrope of the ether and the corresponding alkanol.

The present invention accordingly provides a process for the cleavage of alkyl tert-alkyl ethers into the corresponding isoolefins and alkanols by acid-catalyzed reactive distillation, wherein the reactive distillation apparatus has, in an upward direction, a bottom zone, at least one distillation zone and a reaction zone and, if desired, a further distillation zone and the alkyl tert-alkyl ether is fed into the reaction zone via an azeotrope of the alkyl tert-alkyl ether and the corresponding alkanol.

The particular advantages of the process of the invention are that the endothermic equilibrium reaction:



occurring in the ether cleavage by reactive distillation is favorably influenced by removal of the olefin by distillation. Furthermore, the olefin concentration in the liquid phase is so low that the formation of undesired downstream products by dimerization:



or oligomerization is reduced compared to the pure liquid-phase process.

As catalyst in the process of the invention, it is possible to use an acid ion exchange resin or any other acid catalyst having an inorganic or organic basis. The acid catalyst can be located in conventional distillation/reaction packing made of woven metal mesh.

In the process of the invention, it is possible to cleave all alkyl tert-alkyl ethers which form a minimum azeotrope with the corresponding alkanol and can be cleaved in the presence of acid catalysts. The starting material for the process of the invention can therefore be a pure alkyl tert-alkyl ether or a mixture of the alkyl tert-alkyl ether with the corresponding alkanol and/or the isoolefin.

When using the pure ether, addition of the alkanol which is produced by the cleavage reaction is advisable. Although it is in principle possible to add other alkanols, the subsequent work-up of the alkanols is made more difficult. If separation is not necessary, i.e. the isoolefin is the actual target product, it can be useful for the purpose of forming the azeotrope to add an alkanol other than that produced in the cleavage.

The cleavage of the alkyl tert-alkyl ethers according to the invention leads to the corresponding olefins, i.e. generally to the branched olefins from the part of the ether molecule which bears the tertiary alkyl group. The tertiary alkyl part of these ethers from which the corresponding isoolefin subsequently results can contain from 3 to 10 carbon atoms.

The second cleavage product obtained is the corresponding alkanol. The alkyl part of the ether from which the corresponding alkanol subsequent results can be branched or unbranched and contain from 1 to 10 carbon atoms.

- In the process of the invention, n-alkyl tert-alkyl ethers can be cleaved into n-alkanols and isoolefins, sec-alkyl tert-alkyl ethers can be cleaved into secondary alkanols and isoolefins, and tert-alkyl tert-alkyl ethers can be
- 5 cleaved into tertiary alkanols and isoolefins.

Examples of such compounds are:

Alkyl tert-alkyl ether	Olefin	Alkanol
Methyl tert-butyl ether(MTBE)	Isobutene	Methanol
Ethyl tert-butyl ether (ETBE)	Isobutene	Ethanol
tert-Amyl methyl ether (TAME)	Isopentene	Methanol
tert-Amyl ethyl ether (TAEE)	Isopentene	Ethanol
tert-Butyl isopropyl ether (TBIPE)	Isobutene	Isopropanol
tert-Butyl sec-butyl ether (TBSBE)	Isobutene	2-Butanol
tert-Butyl tert-butyl ether (TBTBE)	Isobutene	Isobutanol

- 10 The alkyl tert-alkyl ether to be cleaved is fed into the reaction zone of the reaction distillation apparatus via an azeotrope of the ether and the corresponding alkanol.

- A series of process variants can be used, and these are shown by way of
- 15 example in Figures 1-6. In the figures, F: feed (introduction of the starting material), O: olefin outlet, A: alkanol outlet, R: reaction zone, D, D1, D2, D3: distillation zone, E: empty zone (can also be omitted), B: bottom zone. The bottom zone is heated externally or internally, and the olefin outlet is provided with a condenser (not shown).

- 20 The azeotrope can be obtained by feeding the ether (i.e. the starting material) into the reactive distillation apparatus below the reaction zone, preferably between the reaction zone and the bottom zone (e.g. Fig. 1 and Fig. 2). As starting material, it is possible to use ether/alkanol mixtures of any composition. An appropriate MTBE/methanol mixture is frequently
- 25 produced by MTBE production plants.

- After the ether/alkanol azeotrope has been cleaved in the reaction zone, the corresponding olefin is taken off from the top of the apparatus as olefin/alkanol azeotrope, while the major part of the alkanol runs to the
- 30 bottom.

The alkanol/isoolefin azeotrope taken off at the top can contain a small proportion of the ether.

- 5 In another embodiment of the process, the reactive distillation apparatus has a plurality of distillation zones, with one distillation zone being located above (i.e. downstream in the direction of gas flow) the reaction zone (e.g. Fig. 5 and Fig. 6).
- 10 In another variant of the invention, it is possible for the alkyl tert-alkyl ether to be fed into the reactive distillation apparatus between distillation and reaction zones (e.g. Fig. 1). In Fig. 3, the starting material is fed in between two distillation zones. Furthermore, the ether can be fed into the apparatus in a distillation zone (Fig. 4).
- 15 Surprisingly and advantageously, location of the catalyst packing or the reaction zone above the inlet for the starting material prevents catalyst poisons such as metal ions from reaching the reaction zone, so that deactivation of the catalyst is at least reduced. Furthermore, fractionation of an alkyl tert-alkyl ether/alkanol mixture as far as the azeotropic point is
- 20 possible in the rectification section, so that alkyl tert-alkyl ether/alkanol mixtures of any composition can be processed. This ensures that an ether-containing liquid phase always reaches the reaction zone, so that the cleavage reaction does not stop.
- 25 Suitable column pressures for operation of the reactive distillation apparatus are in the range from 1 to not more than 10 bar. For the cleavage of MTBE, a column pressure of 3-7 bar has been found to be useful. If the catalyst used is, for example, a cation exchange resin, considerable elimination of sulfonic acid groups from the resin surface has to be expected at above 125°C, so that deactivation of the catalyst
- 30 gradually takes place. In this case, a reaction temperature of from 105 to 115°C is advisable.

The operating temperature which is optimal for the catalyst can be set via the column pressure.

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Other catalysts which can be used in the process of the invention are, for example, acid-activated bentonites and/or aluminas, zeolites, sulfonated zirconium oxides or montmorillonites. These catalysts can be employed at higher temperatures.

Location of the catalyst packing above the feed point prevents poisoning of the catalyst by metal ions which may be present in the feed stream. It is also possible to use ether/alkanol mixtures of any composition, since
 5 distillative fractionation of the mixture as far as the azeotrope can occur between the feed point and the reaction packing. This also enables the reaction temperature within the reaction zone to be controlled via the vaporization equilibrium, so that damage to the catalyst can be prevented. In this respect, processes which operate with the catalyst located in the
 10 bottom section have a considerable disadvantage because of possible overheating in the bottom section, so that damage to the catalyst can occur.

The following example of the cleavage of MTBE into methanol and isobutene is intended to illustrate the present invention. The cleavage
 15 according to the invention of ethers such as ETBE, TAME, TAE, TBIPE, TBSBE or TBTBE is carried out analogously.

The cleavage of MTBE is carried out in a pressure column which is equipped with distillation packing and reaction-distillation packing. The
 20 column, which is operated adiabatically, has the following dimensions and packing locations:

- Internal diameter = 80 mm
- location of the packing elements:
 - 2nd-6th tray: distillation packing
 - 7th-13th tray: reaction packing
 - 14th-30th tray: distillation packing

The starting material, consisting of 99% by weight of MTBE and 1% by
 25 weight of methanol, is subcooled to a temperature of 68°C and fed at this temperature to the 20th tray at a rate of 2 kg/h. The subcooling of the starting material mixture is necessary for purely engineering reasons and has no influence on the reaction.

30 The column pressure set is 6.5 bar. At the top of the column, the condenser is operated at about 52-53°C, so that the vapor stream can be completely condensed. Part of the condensed stream is discharged from the column while another part is returned to the column as runback. The reflux ratio is 9.

The temperature in the reaction zone under these boundary conditions is from 95 to 110°C and should therefore lead to no damage to the styrene-divinylbenzene-based cation exchange resin installed in the reaction packing. The temperature at the bottom is about 120°C.

Fig. 6 schematically depicts the example described here; the composition of the feed stream and of the distillate and bottoms streams are summarized in Table 1. The MTBE conversion in this example is over 99%.

The starting material is fed in via line F. The reactive distillation apparatus has two distillation zones (D and D3), a heatable bottom zone B and a reaction zone R. Isobutene is taken off as distillate stream O, and methanol is taken off as bottoms stream A.

	kg/h	MTBE	Isobutene	Methanol
Feed stream	2.00	99.0% by mass	0.0% by mass	1.0% by mass
Distillate stream	1.32	1.4% by mass	95.5% by mass	3.1% by mass
Bottoms stream	0.68	0.2% by mass	0.0% by mass	99.8% by mass

Table 1: Mass flows and main constituents of the streams (rounded values)

Claims

1. A process for the cleavage of alkyl tert-alkyl ethers into the corresponding isoolefins and alkanols by acid-catalyzed reactive distillation, wherein the reactive distillation apparatus has, in an upward direction, a bottom zone, at least one distillation zone and a reaction zone and the alkyl tert-alkyl ether is fed into the reaction zone via an azeotrope of the alkyl tert-alkyl ether and the corresponding alkanol, wherein the azeotrope of the alkyl tert-alkyl ether is fed into the reactive distillation apparatus below the reaction zone of the reactive distillation apparatus.
2. The process as claimed in claim 1, wherein the alkyl tert-alkyl ether is fed into the reaction distillation apparatus between the reaction zone and the bottom zone.
3. The process as claimed in claim 1 or 2, wherein the alkyl tert-alkyl ether is fed into the reactive distillation apparatus between distillation zone and reaction zone.
4. The process as claimed in any of claims 1 to 3, wherein the reactive distillation apparatus has a plurality of distillation zone, with one distillation zone being located above the reaction zone.
5. The process as claimed in any of claims 1 to 4, wherein the alkyl tert-alkyl ether is fed into the reaction distillation apparatus in a distillation zone.
6. The process as claimed in any of claims 1 to 5, wherein n-alkyl tert-alkyl ethers are cleaved into n-alkanols and isoolefins.
7. The process as claimed in any of claims 1 to 5, wherein sec-alkyl tert-alkyl ethers are cleaved into secondary alkanols and isoolefins.
8. The process as claimed in any of claims 1 to 6, wherein tert-alkyl tert-alkyl ethers are cleaved into tertiary alkanols and isoolefins.

9. The process as claimed in any of claims 1 to 6, wherein methyl tert-butyl ether is cleaved into isobutene and methanol.
10. The process as claimed in any of claims 1 to 6, wherein ethyl tert-butyl ether is cleaved into isobutene and ethanol.
11. The process as claimed in any of claims 1 to 6, wherein tert-amyl methyl ether is cleaved into isopentene and methanol.
12. The process as claimed in any of claims 1 to 6, wherein tert-amyl ethyl ether is cleaved into isopentene and ethanol.
13. The process as claimed in any of claims 1 to 5 and 7, wherein tert-butyl isopropyl ether is cleaved into isobutene and isopropanol.
14. The process as claimed in any of claims 1 to 5 and 7, wherein tert-butyl sec-butyl ether is cleaved into isobutene and 2-butanol.
15. The process as claimed in any of claims 1 to 5 and 8, wherein tert-butyl tert-butyl ether is cleaved into isobutene and isobutanol.