

DESCRIPTION

PROCESS FOR PRODUCTION OF 4-ALKYLPHENOLS

5 TECHNICAL FIELD

The present invention relates to a process for the production of 4-alkylphenols.

4-alkylphenols produced in accordance with the present invention can be used as synthetic raw materials of every
10 kind, and particularly 4-tert-butylphenol (hereafter abbreviated as 4-TBP) is useful as a molecular weight controlling agent for polycarbonate resins, or as a raw material for producing phenol resins or surfactants.

15 BACKGROUND ART

Conventional processes for the production of 4-alkylphenols, in which a phenol is reacted with an olefin, an alcohol, or an ether in the presence of a catalyst, thereby alkylating the phenol, are already known. One known process
20 for producing a 4-alkylphenol from a phenol and an olefin involves conducting an addition reaction between the phenol and the olefin in the presence of an acid catalyst, and then conducting a disproportionation reaction (see Japanese Patent Laid-Open Publication No. Hei 8-12610). In the case of this
25 process, an olefin having very high purity must be used in

order to suppress the generation of by-products derived from the raw material olefin. Particularly in those cases where an olefin having a boiling point is used, obtaining a sufficiently pure olefin by distillation is difficult, meaning an alcohol or an ether that functions as the raw material for the olefin must be purified, the dehydration reaction or dealcoholization of this raw material must be performed with a high selectivity level, and the resulting olefin must then be purified to the desired purity level using a purification procedure such as distillation, making the production process expensive and uneconomic. In contrast, in those cases where an alcohol or an ether is used as the raw material, the preparation costs are cheaper, and handling of the materials is simpler than in the process using a highly pure olefin. However, on the other hand, if either the water generated in the case of an alcohol raw material, or the alcohol generated in the case of an ether raw material, causes a deterioration in the catalytic activity, then that the water or the alcohol must be removed from the reaction system.

Examples of processes for producing a 4-alkylphenol by reacting a phenol and an alcohol in the presence of a catalyst include (1) a process in which a phenol and a secondary or tertiary alcohol are reacted together at a pressure not exceeding 4 atmospheres (typically at a pressure close to atmospheric pressure, and at a temperature of approximately

135 to 180°C), in the presence of a dehydration and
condensation catalyst such as activated clay and sulfuric acid,
while generated water is vaporized (see U.S. Pat. No.
2,140,782), (2) a process in which tert-butanol (hereafter
5 abbreviated as TBA) with an approximately 12 to 30% content of
water by weight is reacted with a phenol, in the presence of a
synthetic silica-alumina based catalyst, and at a temperature
of 220 to 300°C (see Japanese Patent Laid-Open Publication No.
Sho 56-57727), and (3) a process for alkylating a phenol with
10 TBA in the presence of a cation exchange resin [Catalysis
Letters, 19 (1993), pp. 309 to 317].

Each of the above processes (1) through (3) enables the
production of a 4-alkylphenol in a single step. The properties
of the activated clay used in the aforementioned process (1)
15 vary depending on the locality and the site from which it was
mined, and as a result, the reproducibility of the catalytic
effect is poor. Furthermore, the generated water tends to
adsorb between layers of the clay, making the clay prone to be
reduced in acidity, which leads to a fall in the catalytic
20 activity. If sulfuric acid is used, then the proton acidity of
the sulfuric acid varies markedly depending on the quantity of
water that is generated, causing large variations in the
catalytic activity. Accordingly, in the process (1), water
must be vaporized and removed from the reaction system, but in
25 the case where TBA is used as the alcohol, the TBA vaporizes

azeotropically with water, meaning a large quantity of TBA must be used, making the process economically disadvantageous. In the aforementioned process (2), because the proportion of the ortho isomer increases rapidly at temperatures less than 220°C, the reaction must be conducted at a high temperature. Furthermore, in order to maintain the liquid phase state of the reaction mixture, the reaction must also be conducted under pressurized conditions, meaning a special pressure apparatus is required. Operation of the aforementioned process (3) can be complex, as the durability of the cation exchange resin is too low to enable a continuous, long-term reaction at the temperature that promotes the dehydration reaction of TBA. Furthermore, the cation exchange resin also undergoes gradual decomposition, causing acidic components such as sulfonic acid to gradually contaminate the reaction solution, meaning the reaction product must be neutralized prior to the distillation step that is used to obtain the final product.

Examples of processes for producing a 4-alkylphenol by reacting a phenol and an ether in the presence of a catalyst include (4) a process in which a phenol is alkylated using methyl tert-butyl ether (hereafter abbreviated as MTBE) in the presence of a cation exchange resin (see Catalysis Letters, 19 (1993), pp. 309 to 317), and (5) a process in which a hydroxylated aromatic compound undergoes tertiary butylation, by reacting a hydroxylated aromatic compound such as phenol or

pyrocatechol with an alkyl tert-butyl ether, at a temperature of 60 to 130°C, in the presence of sulfuric acid or an ion exchange resin, and removing the generated alcohol, so that the reaction is completed in an environment free of alcohol
5 (see Japanese Laid-Open Publication No. Sho 57-67529).

Operation of the aforementioned processes (4) and (5) can be complex because the durability of the cation exchange resin is too low in the presence of the generated alcohol, at the temperature at which the cation exchange resin decomposes the
10 ether to generate an olefin, the cation exchange resin undergoes gradual decomposition, causing acidic components such as sulfonic acid to gradually contaminate the reaction solution, meaning the reaction product must be neutralized prior to the distillation step that is used to obtain the
15 final product. Furthermore, if sulfuric acid is used, then the generated olefin isomerizes in the presence of the sulfuric acid, causing the reaction product to become a complexed mixture.

In recent years, synthetic zeolites have been attracting
20 considerable interest as catalysts, not only because they display excellent alkylation activity and selectivity for aromatic compounds, but also because they are non-corrosive, environmentally friendly, and offer excellent durability. Examples of reported processes that use synthetic zeolites in
25 the alkylation of phenol with TBA include (6) gas phase

alkylation processes using a zeolite catalyst (see U.S. Pat. No. 4,391,998, U.S. Pat. No. 4,532,368, and Japanese Patent Publication No. Sho 52-12181), (7) processes for alkylating a phenol with an alcohol and/or an ether, in the presence of a metal-containing Y-type zeolite in the liquid phase, and preferably at a temperature within a range from 200 to 320°C (see Japanese Patent Laid-Open Publications Nos. Sho 62-240637 and Sho 62-246532), and (8) processes for alkylating a phenol with TBA using a synthetic zeolite, such as a process for conducting the reaction in carbon tetrachloride in the presence of an HY-type zeolite [see J. Chem. Research (S), (1988) pp. 40 to 41], and processes that use large pore zeolites such as HY-type and H β -type zeolites [Applied Catalysis A: General, 166 (1998), pp. 89 to 95, and 207 (2001), pp. 183 to 190].

In the aforementioned processes (6), because the reaction is conducted in the gas phase, not only is a large quantity of heat required, but because the reaction temperature is close to the decomposition point of 4-TBP, a fall in the selectivity is unavoidable, and moreover, carbon deposits from the phenol cause a significant deterioration in the catalytic activity. In the aforementioned processes (7), the selectivity of the generated 4-alkylphenol is poor, and the generation of 2-alkylphenol by-products, which are difficult to separate from 4-alkylphenol, tends to be a problem. The contents of the

references describing the aforementioned processes (8) detail investigations of the effects that the state of the zeolite, including the micropore structure and the acidity, and specific reaction conditions, including the temperature, the feed rate of the raw material, and the ratio of the raw materials, have on the catalytic activity and the reaction selectivity. In the reaction examples, because C4 hydrocarbon oligomers are generated, the selectivity of 4-TBP is poor, and no mention is made of an industrially useful process for producing a high yield of 4-TBP.

An object of the present invention is to provide an industrially useful process that enables the production of 4-alkylphenols with good selectivity and a high yield.

DISCLOSURE OF THE INVENTION

The present invention is a process for the production of a 4-alkylphenol, comprising the steps of: reacting a 4-unsubstituted phenol with an alkyl alcohol or an alkyl ether in the presence of a synthetic zeolite, at a temperature of 50 to 110°C (a first step); either removing the generated water contained within the liquid phase of the produced reaction mixture in the case where an alkyl alcohol is used in the first step, or removing the generated alcohol contained within the liquid phase of the produced reaction mixture in the case where an alkyl ether is used in the first step (a second

step)); and subsequently conducting a rearrangement reaction in the reaction mixture from which the generated water or the generated alcohol has been removed, at a temperature of 90 to 150°C and in the presence of an acid catalyst (a third step).

5 In a preferred embodiment of the present invention, in the third step, the water concentration of the liquid phase of the reaction mixture is adjusted to no more than 0.5% by weight for those cases where an alkyl alcohol is used in the first step, or alternatively, the alcohol concentration of the
10 liquid phase of the reaction mixture is adjusted to no more than 0.5% by weight for those cases where an alkyl ether is used in the first step, and then the rearrangement reaction is conducted with the quantity of the 4-unsubstituted phenol adjusted so as to represent a 1 to 10-fold molar ratio
15 relative to the quantity of the alkyl alcohol or the alkyl ether that is consumed during the alkylation reaction of the first step. In addition, 4-TBP can be produced by using phenol as the 4-unsubstituted phenol, and using either TBA as the alkyl alcohol, or MTBE as the alkyl ether.

20 The characteristic features of the present invention are that an alkylation reaction of a 4-unsubstituted phenol is conducted in the presence of a synthetic zeolite and at a temperature within a range from 50 to 110°C (the first step), the water or the alcohol generated by the alkylation reaction
25 and contained within the liquid phase of the produced reaction

mixture is removed (the step 2), and the by-products such as the 2-alkylated phenols, 3-alkylated phenols, 2,4-dialkylated phenols, 2,6-dialkylated phenols, and 2,4,6-trialkylated phenols contained within the reaction mixture following the removal of the water or the alcohol can then be efficiently converted into the 4-alkylphenol, at a temperature within a range from 90 to 150°C, and in the presence of an acid catalyst (the third step).

As a result of the above characteristic features, there is no marked reduction in the catalytic activity caused by the generated water, as is observed in the aforementioned process (1), and TBA with an approximately 12 to 30% content of water by weight can be used as a raw material. Furthermore, the type of catalyst deterioration observed in the aforementioned processes (3) through (5) can be suppressed, and because the reaction mixture contains no acidic components, complex operations such as neutralization operations can be avoided. In addition, the above characteristic features ensure a high 4-alkylphenol selectivity, meaning the generation of the type of inseparable 2-alkylphenols observed in the above processes (7) can be suppressed. Generation of the C4 hydrocarbon oligomers observed in the above processes (8) can also be suppressed. In addition, within the temperature range described above, the reaction mixture exists in the liquid phase, meaning the type of catalyst deterioration caused by

carbon deposits observed in the aforementioned processes (6) can be suppressed. Moreover, by removing the water or the alcohol generated in the second step, any reduction in the activity of the acid catalyst during the third step can be suppressed, meaning the alkyl group rearrangement reaction from 2,4-dialkylated phenols, 2,6-dialkylated phenols, and 2,4,6-trialkylated phenols and the like to the 4-alkylphenol proceeds with good selectivity in a relatively short period of time. Even in those cases where an acidic cation exchange resin is used as the acid catalyst, the 4-alkylphenol can still be produced with a high level of selectivity, and in these cases, the temperature of the rearrangement reaction can be lowered to 90°C, and because the generated water or the generated alcohol has been removed, elution of the acid components, leading to a deterioration of the ion exchange resin, can be prevented.

BEST MODE FOR CARRYING OUT THE INVENTION

First is a description of the first step.

In the first step, a 4-unsubstituted phenol is reacted with an alkyl alcohol or an alkyl ether in the presence of a synthetic zeolite at a temperature of 50 to 110°C, thereby alkylating the 4-unsubstituted phenol.

Examples of the 4-unsubstituted phenol include phenol, 2-cresol, 3-cresol, 2-ethylphenol, 3-ethylphenol, 2-propylphenol,

3-propylphenol, 2-isopropylphenol, 3-isopropylphenol, 2-tert-butylphenol, and 3-tert-butylphenol.

An alkyl alcohol comprising the required alkyl group to be introduced is used in the present invention, and suitable examples include methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, TBA, pentanol, hexanol, cyclohexanol, and benzyl alcohol. The quantity used of the alkyl alcohol is preferably within a range from 0.1 to 2 moles, and even more preferably from 0.2 to 1 mole, per 1 mole of the 4-
10 unsubstituted phenol.

An alkyl ether comprising the required alkyl group to be introduced is used in the present invention, and suitable examples include dimethyl ether, diethyl ether, di-n-propyl ether, diisopropyl ether, di-n-butyl ether, diisobutyl ether, 15 MTBE, ethyl tert-butyl ether, n-propyl tert-butyl ether, isopropyl tert-butyl ether, n-butyl tert-butyl ether, and isobutyl tert-butyl ether. The quantity used of the alkyl ether is preferably within a range from 0.1 to 2 moles, and even more preferably from 0.2 to 1 mole, per 1 mole of the 4-
20 unsubstituted phenol.

Suitable examples of the synthetic zeolite include large pore zeolites such as X-type, Y-type, β -type, L-type, and mordenite zeolites, medium pore zeolites such as ZSM and SAPO zeolites, and mesoporous silicates such as MCM. Of these, Y-
25 type, β -type, L-type, and mordenite zeolites are preferred.

Typically, the synthetic zeolite comprises ions of alkali metals or alkaline earth metals within the zeolite structure. In the present invention, a zeolite is used in which at least a portion of these ions have been replaced with at least one ion selected from the group consisting of transition metal ions, aluminum ions, and protons.

In order to improve the reaction efficiency, the acidity of the synthetic zeolite, namely the silica/alumina ratio, is preferably small, and the alkali metals and alkaline earth metals contained in the zeolite have preferably been substituted with hydrogen atoms. Furthermore, in order to improve the selectivity of the 4-alkylphenol, a zeolite with a pore size that best suits the molecular size of the 4-alkylphenol is preferred. For example, in the production of 4-TBP, either mordenite or β -type zeolite is preferably used as the zeolite, and the silica/alumina ratio preferably falls within a range from 1 to 200, and even more preferably from 5 to 150, and most preferably from 5 to 50.

There are no particular restrictions on the form of the synthetic zeolite, and powders, granules, or lumps can be used. Furthermore, powders or granules can also be molded prior to use, and suitable shapes for these molded forms include spheres, circular cylinders, rings, or star shapes.

Furthermore, there are no particular restrictions on the size of the synthetic zeolite particles, although smaller particles

generally result in an increased surface area and improved reactivity. The particle size is normally selected so as to have no effect on normal operations, and is typically within a range from 1 to 800 microns.

5 The quantity of the synthetic zeolite to be used varies depending on the reaction system. For example, in the case of a batch system, the quantity of the synthetic zeolite is preferably within a range from 1 to 100% by weight relative to the weight of the 4-unsubstituted phenol. If reaction
10 efficiency is also considered, then quantities within a range from 5 to 25% by weight are even more desirable. If the quantity of the synthetic zeolite is too small, then the rate of reaction tends to decline, whereas if the quantity is too large, the reaction becomes uneconomic, and both of these
15 scenarios are undesirable.

 The alkylation reaction may be conducted either in the presence of a solvent or in a solvent-free environment. There are no particular restrictions on the solvent, provided it is inert with respect to the reaction, and suitable examples
20 include aliphatic hydrocarbons such as hexane, heptane, octane, nonane, decane, and cyclohexane; aromatic hydrocarbons such as benzene, toluene, xylene, and mesitylene; and halogenated hydrocarbons such as carbon tetrachloride, 1,2-dichloroethane, and chlorobenzene. Of these solvents, the use of toluene is
25 preferred. In those cases where a solvent is used, there are

no particular restrictions on the quantity of the solvent, although from the viewpoints of reaction efficiency, ease of operation, and economic viability, a 1 to 20-fold weight relative to the quantity of the 4-unsubstituted phenol is preferred.

The alkylation reaction is conducted at a comparatively low temperature within a range from 50 to 110°C. If the reaction temperature is less than 50°C, then the reaction slows markedly, and the reaction efficiency deteriorates. In contrast, if the reaction temperature exceeds 110°C, then not only does the selectivity of the target 4-alkylphenol fall, but the alkyl alcohol or the alkyl ether, and the 4-unsubstituted phenol as the raw material can also undergo polymerization, increasing the production of high boiling point by-products.

The alkylation reaction can be conducted under normal pressure, under reduced pressure, or under pressurized conditions. The reaction system can employ either a batch system or a continuous system. The reaction can use a fixed bed system, where the 4-unsubstituted phenol and the alkyl alcohol or the alkyl ether are passed through a synthetic zeolite-filled layer, or fluidized bed or moving bed systems.

The reaction time for the alkylation is preferably within a range from 1 to 30 hours, and preferably from 5 to 10 hours. If the reaction time is less than 1 hour, then the reaction is

unable to proceed sufficiently, and the reaction efficiency tends to fall, whereas if the time exceeds 30 hours, the quantity of by-products having high boiling points tends to increase, and both of these scenarios are undesirable.

5 If required, the synthetic zeolite can be removed from the reaction mixture obtained after the alkylation reaction, and the left mixture is then supplied to the second step.

Next is a description of the second step.

10 In the second step, either the generated water is removed from the liquid phase of the produced reaction mixture in those cases where an alkyl alcohol was used in the first step, or the generated alcohol is removed from the liquid phase of the produced reaction mixture in those cases where an alkyl ether was used in the first step.

15 Examples of suitable methods of removing the water include distillation, bubbling an inert gas such as nitrogen or argon through the reaction mixture, and conducting dehydration using a water adsorbent such as a molecular sieve, zeolite, alumina, or activated carbon and so on. Examples of
20 suitable methods of removing the alcohol include distillation, bubbling an inert gas such as nitrogen or argon through the reaction mixture, and removal by adsorption using an alcohol adsorbent such as a molecular sieve, zeolite, alumina, or activated carbon and so on. In order to ensure maximum
25 activity for the acid catalyst used in the third step

described below, the concentration of residual water or residual alcohol within the liquid phase of the reaction mixture subjected to the rearrangement reaction is preferably reduced to no more than 0.5% by weight. If this concentration
5 exceeds 0.5% by weight, then the activity of the acid catalyst does not attain satisfactorily, and the rate of the rearrangement reaction of the third step declines markedly.

Next is a description of the third step.

In the third step, an "alkyl group rearrangement
10 reaction" is initiated in which the alkyl groups are eliminated from the 2-alkylated phenols, 3-alkylated phenols, 2,4-dialkylated phenols, 2,6-dialkylated phenols, and 2,4,6-trialkylated phenols produced in the first step, and are subsequently added to the 4-position of the 4-unsubstituted
15 phenols, thereby obtaining the 4-alkylphenol.

A synthetic zeolite or an acidic cation exchange resin is used as the acid catalyst.

In order to ensure that the alkyl group is introduced at the 4-position of the 4-unsubstituted phenol, the synthetic
20 zeolite preferably contains a pore size that best suits the molecular size of the target 4-alkylphenol. Furthermore, the acidity (the silica/alumina ratio) of the zeolite is preferably small, and the alkali metals and alkaline earth metals within the zeolite have preferably been substituted
25 with hydrogen atoms. If the acidity of the synthetic zeolite

is too high, then the decomposition reaction of the target 4-alkylphenol is promoted, and the selectivity of the 4-alkylphenol tends to decrease. For example, in the production of 4-TBP, either β -type or Y-type zeolite is preferably used as the zeolite, and the silica/alumina ratio preferably falls within a range from 1 to 200, and even more preferably from 5 to 150, and most preferably from 5 to 50.

Because the synthetic zeolite adsorbs water, it is preferably subjected to a dehydration treatment prior to use.

Dehydration can be conducted by heating at a temperature of 100 to 300°C for a period of several hours. Dehydration can also be achieved under a stream of nitrogen or air. The synthetic zeolite may be the same zeolite as that used during the alkylation reaction, but may also be different. The rearrangement reaction may be conducted after the synthetic zeolite used in the alkylation reaction is removed, or be conducted with the zeolite still present.

The quantity of the synthetic zeolite to be used varies depending on the reaction system. For example, in the case of a batch system, the quantity of the synthetic zeolite is preferably within a range from 1 to 100% by weight relative to the total weight of the 4-unsubstituted phenol and the product 4-alkylphenol as the raw material. If reaction efficiency is also considered, then quantities within a range from 5 to 25% by weight are even more desirable. If the quantity of the

synthetic zeolite is too small, then the rate of reaction tends to decline, whereas if the quantity is too large, the reaction becomes uneconomic, and both of these scenarios are undesirable.

5 Suitable acidic cation exchange resins include any cation exchange resin that displays acidity, including styrene-based sulfonic acid resins.

 There are no particular restrictions on the form of the acidic cation exchange resin, provided it functions
10 satisfactorily as a catalyst, although typically, minute particles with an average particle size of 0.01 to 10 mm, or spherical or cylindrical particles, can be used.

 The quantity of the acidic cation exchange resin to be used varies depending on the reaction system. For example, in
15 the case of a batch system, the quantity of the acidic cation exchange resin is preferably within a range from 1 to 100% by weight relative to the total weight of the 4-unsubstituted phenol as the raw material and 4-alkylphenol as the product. If reaction efficiency is also considered, then quantities
20 within a range from 5 to 25% by weight are even more desirable. If the quantity of the acidic cation exchange resin is too small, then the rate of reaction tends to decline, whereas if the quantity is too large, the reaction becomes uneconomic, and both of these scenarios are undesirable.

25 The rearrangement reaction may be conducted either in the

presence of a solvent or in a solvent-free environment. There are no particular restrictions on the solvent, provided it is inert with respect to the reaction, and suitable examples include aliphatic hydrocarbons such as heptane, octane, nonane, 5 decane, and methylcyclohexane; aromatic hydrocarbons such as toluene, xylene, and mesitylene; and halogenated hydrocarbons such as chlorobenzene. Of these solvents, the use of toluene is particularly preferred. In those cases where a solvent is used, there are no particular restrictions on the quantity of 10 the solvent, although from the viewpoints of reaction efficiency, ease of operation, and economic viability, a 1 to 20-fold weight excess relative to the total weight of the 4-unsubstituted phenol as the raw material and the 4-alkylphenol as the product is preferred.

15 The rearrangement reaction is conducted at a temperature within a range from 90 to 150°C. If the reaction temperature is too high, then the introduced alkyl group tends to dissociate and return to the raw material, causing a reduction in the conversion ratio of the alkylated phenol, and a 20 reduction in the selectivity of 4-alkylphenol. In contrast, if the reaction temperature is too low, then the rate of the rearrangement reaction slows markedly, making the reaction uneconomic.

 The rearrangement reaction can be conducted under normal 25 pressure, under reduced pressure, or under pressurized

conditions. The reaction system can employ either a batch system or a continuous system. The reaction can be conducted by a fixed bed system, where the reaction mixture obtained at the second step is passed across the acid catalyst, or
5 fluidized bed or moving bed systems.

From the viewpoints of suppressing the generation of by-products, and improving the selectivity of the 4-alkylphenol, the reaction time for the rearrangement reaction is preferably within a range from 1 to 20 hours.

10 During the rearrangement reaction, the proportion of 4-unsubstituted phenol within the reaction mixture can be adjusted to a value within a specific range by adding the 4-unsubstituted phenol to the reaction solution as required, thereby improving the selectivity of the 4-alkylphenol and
15 increasing the rate of reaction. The quantity of the 4-unsubstituted phenol within the reaction mixture is preferably equivalent to a 1 to 10-fold moles relative to the quantity of alkyl groups introduced within the first step, namely, the quantity of alkyl alcohol or alkyl ether consumed during the
20 alkylation reaction of the first step. If this quantity is less than 1-fold mole, then initiating an alkyl group rearrangement reaction from 2,4-dialkylated phenols, 2,6-dialkylated phenols, and 2,4,6-trialkylated phenols becomes difficult, whereas if the quantity is larger than a 10-fold
25 moles, then the conversion ratio of the 4-unsubstituted phenol

tends to decline.

The reactions and operations from the first step through to the third step can be conducted within the same reaction vessel, or may also be conducted within consecutive reaction
5 vessels.

The 4-alkylphenol produced in accordance with the present invention can be isolated and purified using normal isolation and purification procedures of organic compounds. For example, the acid catalyst can be filtered from the reaction mixture as
10 required, and the 4-alkylphenol is then isolated and purified from the resulting filtrate using procedures such as distillation, recrystallization, and chromatography and so on.

EXAMPLES

Hereinafter, the present invention will be described in
15 detail by way of examples, although the present invention is in no way limited by the following examples. In the tables, 2-TBP represents 2-tert-butylphenol, and 2,4-DTBP represents 2,4-di-tert-butylphenol. The composition values (%) following reaction each represent a percentage value determined from the
20 relative area of the peak for each component observed in a gas chromatographic analysis [column: G-100 (manufactured by Chemicals Evaluation and Research Institute, Japan), detector: FID (flame ionization detector), temperature of detector and vaporization chamber: 270°C, pattern of temperature increase:
25 held at 80°C for 3 minutes, raised to 250°C at a rate of

10°C/minute, and then held at 250°C for 15 minutes]. The selectivity (%) of the 4-TBP is derived with reference to phenol, and the yield (%) of the 4-TBP is derived with reference to either TBA or MTBE.

5 Reference Example 1

(First Step)

A 4-neck flask with an internal capacity of 100 mL, fitted with a stirrer, a condenser, and a thermometer was charged with 50.0 g (531 mmol) of phenol and 12.5 g of a
10 proton-substituted β -type zeolite (H- β , manufactured by N.E. Chemcat Corporation), and the resulting mixture was stirred. The mixture was heated to 100°C, and 22.6 g (266 mmol) of TBA with 13% content of water by weight was added dropwise to the mixture over a period of 3 hours using a syringe. The
15 resulting mixture was stirred for a further 3 hours at the same temperature, thus effecting an alkylation reaction. Analysis of the reaction solution by gas chromatography revealed a product composition comprising phenol (42.0%), 4-TBP (50.1%), 2-TBP (4.7%), and 2,4-DTBP (3.1%), representing
20 the conversion ratio of phenol is 46.2%, the selectivity of 4-TBP is 81.9%, and the yield of 4-TBP is 75.9%.

Example 1

(First Step)

A 4-neck flask with an internal capacity of 100 mL,
25 fitted with a stirrer, a condenser, and a thermometer was

charged with 50.0 g (531 mmol) of phenol and 12.5 g of a proton-substituted β -type zeolite (H-BEA-25, manufactured by Süd Chemie Group), and the resulting mixture was stirred. The mixture was heated to 90°C, and 22.6 g (266 mmol) of TBA with
5 13% content of water by weight was added dropwise to the mixture over a period of 3 hours using a syringe. The resulting mixture was stirred for a further 5 hours at the same temperature, thus effecting an alkylation reaction. The resulting reaction solution was analyzed by gas chromatography,
10 and the relative proportions of the various compounds, the conversion ratio of phenol, and the selectivity and yield of the 4-TBP were determined. The results are shown in Table 1.

(Second Step)

The β -type zeolite was removed by filtration from the
15 reaction mixture obtained in the first step. The resulting filtrate was then subjected to distillation under reduced pressure [26.7 to 4.7 kPa (200 to 35 mmHg), internal temperature 90 to 120°C], thereby removing water. Measurement of the water concentration within the mixture following this
20 water removal revealed a value of 0.1% by weight. Furthermore, the quantity of phenol, recorded as a molar ratio relative to the TBA consumed in the alkylation reaction of the first step, was 1.1.

(Third Step)

25 A 4-neck flask with an internal capacity of 100 mL,

fitted with a stirrer, a condenser, and a thermometer was charged with the dehydrated mixture obtained in the second step, and 12.5 g of proton-substituted Y-type zeolite (HSZ-360HUA, manufactured by Tosoh Corporation), and the resulting mixture was heated to 120°C, and then stirred for 1 hour to effect a rearrangement reaction. The resulting reaction solution was analyzed by gas chromatography, and the relative proportions of the various compounds, and the selectivity and yield of 4-TBP were determined. The results are shown in Table 1.

Table 1

Item		Example 1	
		First step	Third step
Reaction solution composition (%)	Phenol	39.4	39.4
	4-TBP	54.2	58.0
	2-TBP	3.8	1.5
	2,4-DTBP	2.6	1.2
Conversion ratio(%) of phenol		42.5	
Selectivity(%) of 4-TBP		61.2	95.6
Yield(%) of 4-TBP		52.1	81.3

Example 2

(Second Step)

The β -type zeolite was removed by filtration from the reaction mixture obtained in the first step of the example 1. The resulting filtrate was then subjected to distillation under reduced pressure [26.7 to 4.7 kPa (200 to 35 mmHg), internal temperature 90 to 120°C], thereby removing water. Measurement of the water concentration within the mixture following this water removal revealed a value of 0.1% by

weight. Furthermore, the quantity of phenol, recorded as a molar ratio relative to the TBA consumed in the alkylation reaction of the first step, was 1.1.

(Third Step)

5 A 4-neck flask with an internal capacity of 200 mL, fitted with a stirrer, a condenser, and a thermometer was charged with the dehydrated mixture obtained in the second step, and 100 g of phenol. This enabled the quantity of phenol, recorded as a molar ratio relative to the TBA consumed in the alkylation reaction of the first step, to be adjusted to a value of 6. 12.5 g of proton-substituted Y-type zeolite (as described above) was then added, and the resulting mixture was heated to 120°C, and then stirred for 1 hour to effect a rearrangement reaction. The resulting reaction solution was
10 analyzed by gas chromatography, and the relative proportions of the various compounds, and the selectivity and yield of 4-TBP were determined. The results are shown in Table 2.

Table 2

Item		Example 2	
		First step	Third step
Reaction solution composition (%)	Phenol	39.4	80.9
	4-TBP	54.2	18.5
	2-TBP	3.8	0.46
	2,4-DTBP	2.6	0.005
Conversion ratio(%) of phenol		42.5	
Selectivity(%) of 4-TBP		61.2	97.3
Yield(%) of 4-TBP		52.1	82.7

20 Example 3

(Second Step)

The β -type zeolite was removed by filtration from the reaction mixture obtained in the first step of the example 1. The resulting filtrate was then subjected to distillation under reduced pressure [26.7 to 4.7 kPa (200 to 35 mmHg),
5 internal temperature 90 to 120°C], thereby removing water. Measurement of the water concentration within the mixture following this water removal revealed a value of 0.1% by weight. Furthermore, the quantity of phenol, recorded as a molar ratio relative to the TBA consumed in the alkylation
10 reaction of the first step, was 1.1.

(Third Step)

A 4-neck flask with an internal capacity of 100 mL, fitted with a stirrer, a condenser, and a thermometer was charged with the dehydrated mixture obtained in the second
15 step, and 12.5 g of acidic cation exchange resin (Amberlyst 15E, manufactured by Organo Corporation), and the resulting mixture was heated to 90°C, and then stirred for 1 hour to effect a rearrangement reaction. The resulting reaction solution was analyzed by gas chromatography, and the relative
20 proportions of the various compounds, and the selectivity and yield of 4-TBP were determined. The results are shown in Table 3.

Table 3

Item		Example 3	
		First step	Third step
Reaction solution composition (%)	Phenol	39.4	38.2
	4-TBP	54.2	60.0
	2-TBP	3.8	1.0
	2,4-DTBP	2.6	0.8
Conversion ratio(%) of phenol		42.5	
Selectivity(%) of 4-TBP		61.2	97.4
Yield(%) of 4-TBP		52.1	87.7

Example 4

(First Step)

5 A 4-neck flask with an internal capacity of 200 mL, fitted with a stirrer, a condenser, and a thermometer was charged with 125.0 g (1.33 mol) of phenol and 12.5 g of a proton-substituted β -type zeolite (H-BEA-25, manufactured by Sd-Chemie Catalysts Japan, Inc.), and the resulting mixture

10 was stirred. The mixture was heated to 100°C, and 22.6 g (266 mmol) of TBA with 13% content of water by weight was added dropwise to the mixture over a period of 3 hours using a syringe. The resulting mixture was stirred for a further 3

15 hours at the same temperature, thus effecting an alkylation reaction. The resulting reaction solution was analyzed by gas chromatography, and the relative proportions of the various compounds, the conversion ratio of phenol, and the selectivity and yield of 4-TBP were determined. The results are shown in Table 4.

20 (Second Step)

The β -type zeolite was removed by filtration from the

reaction mixture obtained in the first step. The resulting filtrate was then subjected to distillation under reduced pressure [26.7 to 4.7 kPa (200 to 35 mmHg), internal temperature 90 to 120°C], thereby removing water. Measurement of the water concentration within the mixture following this water removal revealed a value of 0.15% by weight.

(Third Step)

A 4-neck flask with an internal capacity of 100 mL, fitted with a stirrer, a condenser, and a thermometer was charged with the dehydrated mixture obtained in the second step, and 12.5 g of proton-substituted Y-type zeolite (as described above), and the resulting mixture was heated to 120°C, and then stirred for 1 hour to effect a rearrangement reaction. The resulting reaction solution was analyzed by gas chromatography, and the relative proportions of the various compounds, and the selectivity and yield of 4-TBP were determined. The results are shown in Table 4.

Table 4

Item		Example 4	
		First step	Third step
Reaction solution composition (%)	Phenol	73.6	69.5
	4-TBP	23.4	29.6
	2-TBP	1.8	0.8
	2,4-DTBP	1.2	0.2
Conversion ratio(%) of phenol		18.4	
Selectivity(%) of 4-TBP		90.9	96.7
Yield(%) of 4-TBP		83.9	89.0

Comparative Example 1

A 4-neck flask with an internal capacity of 100 mL,

fitted with a stirrer, a condenser, and a thermometer was charged with 50.0 g (531 mmol) of phenol and 12.5 g of a proton-substituted β -type zeolite (H-BEA-25, manufactured by Süd-Chemie Catalysts Japan, Inc.), and the resulting mixture
5 was stirred. The mixture was heated to 100°C, and 22.6 g (266 mmol) of TBA with 13% content of water by weight was added dropwise to the mixture over a period of 3 hours using a syringe. The resulting mixture was stirred for a further 2 hours at the same temperature, thus effecting an alkylation
10 reaction. Analysis of the reaction solution by gas chromatography revealed a product composition comprising phenol (39.0%), 4-TBP (54.0%), 2-TBP (4.0%), and 2,4-DTBP (3.0%), representing the conversion ratio of phenol is 44.5%, the selectivity of 4-TBP is 88.8%, and the yield of 4-TBP is
15 79.0%. Measurement of the water concentration of the reaction solution revealed a value of 5.0% by weight. The β -type zeolite was subsequently removed by filtration.

A 4-neck flask with an internal capacity of 100 mL, fitted with a stirrer, a condenser, and a thermometer was then
20 charged with the filtrate obtained above, and 12.5 g of proton-substituted Y-type zeolite (as described above), and the resulting mixture was heated to 120°C and stirred for 5 hours, but no rearrangement reaction took place.

25 Comparative Example 2

A 4-neck flask with an internal capacity of 100 mL, fitted with a stirrer, a condenser, and a thermometer was charged with 50.0 g (531 mmol) of phenol and 12.5 g of proton-substituted β -type zeolite (H-BEA-25, manufactured by Süd-Chemie Catalysts Japan, Inc.), and the resulting mixture was stirred. The mixture was heated to 90°C, and 19.7 g (266 mmol) of TBA was added dropwise to the mixture over a period of 3 hours using a syringe. The resulting mixture was stirred for a further 5 hours at the same temperature, thus effecting an alkylation reaction. The resulting reaction solution was analyzed by gas chromatography, and the relative proportions of the various compounds, the conversion ratio of phenol, and the selectivity and yield of 4-TBP were determined. The results are shown in Table 5. Measurement of the water concentration of the reaction solution revealed a value of 1.0% by weight. The β -type zeolite was subsequently removed by filtration.

A 4-neck flask with an internal capacity of 100 mL, fitted with a stirrer, a condenser, and a thermometer was then charged with the filtrate obtained above, and 12.5 g of proton-substituted Y-type zeolite (as described above), and the resulting mixture was heated to 120°C, and then stirred to effect a rearrangement reaction. The reaction solution was analyzed by gas chromatography after stirring for 1 hour, and then again after stirring for 5 hours, and at each stage the

relative proportions of the various compounds, the conversion ratio of phenol, and the selectivity and yield of 4-TBP were determined. The results are shown in Table 5.

Table 5

Item		Comparative Example 2		
		Alkylation reaction	Rearrangement reaction	
			After 1 hour	After 5 hours
Reaction solution composition (%)	Phenol	39.0	40.7	40.4
	4-TBP	54.6	54.4	56.5
	2-TBP	3.9	3.0	1.8
	2,4-DTBP	2.5	1.9	1.3
Conversion ratio(%) of phenol		40.2	42.3	43.4
Selectivity(%) of 4-TBP		89.5	91.7	94.8
Yield(%) of 4-TBP		71.9	77.6	82.3

5

Example 5

(First Step)

A 4-neck flask with an internal capacity of 100 mL, fitted with a stirrer, a condenser, and a thermometer was charged with 50.0 g (531 mmol) of phenol and 12.5 g of a proton-substituted β -type zeolite (H-BEA-25, manufactured by Sd-Chemie Catalysts Japan, Inc.), and the resulting mixture was stirred. The mixture was heated to 100°C, and 24.2 g (266 mmol) of MTBE was added dropwise to the mixture over a period of 3 hours using a syringe. The resulting mixture was stirred for a further 5 hours at the same temperature, thus effecting an alkylation reaction. The resulting reaction solution was analyzed by gas chromatography, and the relative proportions of the various compounds, the conversion ratio of phenol, and the selectivity and yield of 4-TBP were determined. The

results are shown in Table 6.

(Second Step)

The β -type zeolite was removed by filtration from the reaction mixture obtained in the first step. The resulting
5 filtrate was then subjected to distillation under reduced pressure [26.7 kPa (200 mmHg), internal temperature 30 to 40°C], thereby removing methanol. Measurement of the methanol concentration within the mixture following this methanol removal revealed a value of 0.1% by weight. Furthermore, the
10 quantity of phenol, recorded as a molar ratio relative to the MTBE consumed in the alkylation reaction of the first step, was 1.1.

(Third Step)

A 4-neck flask with an internal capacity of 100 mL,
15 fitted with a stirrer, a condenser, and a thermometer was charged with the substantially methanol-removed mixture obtained in the second step, and 12.5 g of proton-substituted Y-type zeolite (as described above), and the resulting mixture was heated to 120°C, and then stirred for 1 hour to effect a
20 rearrangement reaction. The resulting reaction solution was analyzed by gas chromatography, and the relative proportions of the various compounds, and the selectivity and yield of 4-TBP were determined. The results are shown in Table 6.

Table 6

Item		Example 5	
		First step	Third step
Reaction solution composition (%)	Phenol	49.2	39.4
	4-TBP	45.9	58.0
	2-TBP	2.5	1.5
	2,4-DTBP	2.4	1.2
Conversion ratio(%) of phenol		46.0	
Selectivity(%) of 4-TBP		73.0	95.6
Yield(%) of 4-TBP		67.3	81.3

Example 6

(Second Step)

- 5 The β -type zeolite was removed by filtration from the reaction mixture obtained in the first step of the example 5. The resulting filtrate was then subjected to distillation under reduced pressure [26.7 kPa (200 mmHg), internal temperature 30 to 40°C], thereby removing methanol.
- 10 Measurement of the methanol concentration within the mixture following this methanol removal revealed a value of 0.1% by weight. Furthermore, the quantity of phenol, recorded as a molar ratio relative to the MTBE consumed in the alkylation reaction of the first step, was 1.1.

15 (Third Step)

- A 4-neck flask with an internal capacity of 200 mL, fitted with a stirrer, a condenser, and a thermometer was charged with the substantially methanol-removed mixture obtained in the second step, and 100 g of phenol. This enabled
- 20 the quantity of phenol, recorded as a molar ratio relative to the MTBE consumed in the alkylation reaction of the first step,

to be adjusted to a value of 6. 12.5 g of proton-substituted Y-type zeolite (as described above) was then added, and the resulting mixture was heated to 120°C, and then stirred for 1 hour to effect a rearrangement reaction. The resulting reaction solution was analyzed by gas chromatography, and the relative proportions of the various compounds, and the selectivity and yield of 4-TBP were determined. The results are shown in Table 7.

Table 7

Item		Example 6	
		First step	Third step
Reaction solution composition (%)	Phenol	49.2	80.9
	4-TBP	45.9	18.5
	2-TBP	2.5	0.46
	2,4-DTBP	2.4	0.005
Conversion ratio(%) of phenol		46.0	
Selectivity(%) of 4-TBP		73.0	97.3
Yield(%) of 4-TBP		67.3	82.7

Example 7

(Second Step)

The β -type zeolite was removed by filtration from the reaction mixture obtained in the first step of the example 5.

The resulting filtrate was then subjected to distillation under reduced pressure [26.7 kPa (200 mmHg), internal temperature 30 to 40°C], thereby removing methanol.

Measurement of the methanol concentration within the mixture following this methanol removal revealed a value of 0.1% by weight. Furthermore, the quantity of phenol, recorded as a molar ratio relative to the MTBE consumed in the alkylation

reaction of the first step, was 1.1.

(Third Step)

A 4-neck flask with an internal capacity of 100 mL, fitted with a stirrer, a condenser, and a thermometer was charged with the substantially methanol-removed mixture obtained in the second step, and 12.5 g of β -type zeolite (H-BEA-25, manufactured by Süd-Chemie Catalysts Japan, Inc.), and the resulting mixture was heated to 120°C, and then stirred for 1 hour to effect a rearrangement reaction. The resulting reaction solution was analyzed by gas chromatography, and the relative proportions of the various compounds, and the selectivity and yield of 4-TBP were determined. The results are shown in Table 8.

Table 8

Item		Example 7	
		First step	Third step
Reaction solution composition (%)	Phenol	49.2	39.5
	4-TBP	45.9	58.6
	2-TBP	2.5	1.1
	2,4-DTBP	2.4	0.81
Conversion ratio(%) of phenol		46.0	
Selectivity(%) of 4-TBP		73.0	96.8
Yield(%) of 4-TBP		67.3	89.1

Example 8

(Second Step)

The β -type zeolite was removed by filtration from the reaction mixture obtained in the first step of the example 5. The resulting filtrate was then subjected to distillation under reduced pressure [26.7 kPa (200 mmHg), internal

temperature 30 to 40°C], thereby removing methanol.

Measurement of the methanol concentration within the mixture following this methanol removal revealed a value of 0.1% by weight. Furthermore, the quantity of phenol, recorded as a molar ratio relative to the MTBE consumed in the alkylation reaction of the first step, was 1.1.

(Third Step)

A 4-neck flask with an internal capacity of 100 mL, fitted with a stirrer, a condenser, and a thermometer was charged with the substantially methanol-removed mixture obtained in the second step, and 12.5 g of acidic cation exchange resin (Amberlyst 15E, manufactured by Organo Corporation), and the resulting mixture was heated to 90°C, and then stirred for 1 hour to effect a rearrangement reaction. The resulting reaction solution was analyzed by gas chromatography, and the relative proportions of the various compounds, and the selectivity and yield of 4-TBP were determined. The results are shown in Table 9.

Table 9

Item		Example 8	
		First step	Third step
Reaction solution composition (%)	Phenol	49.2	38.2
	4-TBP	45.9	60.0
	2-TBP	2.5	1.0
	2,4-DTBP	2.4	0.8
Conversion ratio(%) of phenol		46.0	
Selectivity(%) of 4-TBP		73.0	97.4
Yield(%) of 4-TBP		67.3	87.7

Example 9

(First Step)

A 4-neck flask with an internal capacity of 200 mL, fitted with a stirrer, a condenser, and a thermometer was charged with 125.0 g (1.33 mol) of phenol and 12.5 g of
5 proton-substituted β -type zeolite (H-BEA-25, manufactured by Süd-Chemie Catalysts Japan, Inc.), and the resulting mixture was stirred. The mixture was heated to 100°C, and 24.2 g (266 mmol) of MTBE was added dropwise to the mixture over a period of 3 hours using a syringe. The resulting mixture was stirred
10 for a further 5 hours at the same temperature, thus effecting an alkylation reaction. The resulting reaction solution was analyzed by gas chromatography, and the relative proportions of the various compounds, the conversion ratio of phenol, and the selectivity and yield of 4-TBP were determined. The
15 results are shown in Table 10.

(Second Step)

The β -type zeolite was removed by filtration from the reaction mixture obtained in the first step. The resulting filtrate was then subjected to distillation under reduced
20 pressure [26.7 kPa (200 mmHg), internal temperature 30 to 40°C], thereby removing methanol. Measurement of the methanol concentration within the mixture following this methanol removal revealed a value of 0.15% by weight.

(Third Step)

25 A 4-neck flask with an internal capacity of 100 mL,

fitted with a stirrer, a condenser, and a thermometer was charged with the substantially methanol-removed mixture obtained in the second step, and 12.5 g of proton-substituted Y-type zeolite (as described above), and the resulting mixture was heated to 120°C, and then stirred for 1 hour to effect a rearrangement reaction. The resulting reaction solution was analyzed by gas chromatography, and the relative proportions of the various compounds, and the selectivity and yield of 4-TBP were determined. The results are shown in Table 10.

Table 10

Item		Example 9	
		First step	Third step
Reaction solution composition (%)	Phenol	73.6	69.5
	4-TBP	23.4	29.6
	2-TBP	1.8	0.8
	2,4-DTBP	1.2	0.2
Conversion ratio(%) of phenol		18.4	
Selectivity(%) of 4-TBP		90.9	96.8
Yield(%) of 4-TBP		83.9	89.0

Comparative Example 3

(Second Step)

The β -type zeolite was removed by filtration from the reaction mixture obtained in the first step of the example 5. Measurement of the methanol concentration within the resulting reaction solution revealed a value of 5.0% by weight.

A 4-neck flask with an internal capacity of 100 mL, fitted with a stirrer, a condenser, and a thermometer was then charged with the filtrate obtained above, and 12.5 g of proton-substituted Y-type zeolite (as described above), and

the resulting mixture was heated to 120°C and stirred for 5 hours, but no rearrangement reaction took place.

INDUSTRIAL APPLICABILITY

5 The present invention enables an industrially useful production of 4-alkylphenols with good selectivity and a high yield. As a result, highly pure 4-alkylphenols can be produced.

CLAIMS

1. A process for production of a 4-alkylphenol, comprising the steps of: reacting a 4-unsubstituted phenol with an alkyl
5 alcohol or an alkyl ether in the presence of a synthetic zeolite, at a temperature of 50 to 110°C (a first step); either removing the generated water contained within the liquid phase of the produced reaction mixture in the case where an alkyl alcohol is used in the first step, or removing the generated
10 alcohol contained within the liquid phase of the produced reaction mixture in the case where an alkyl ether is used in the first step (a second step); and subsequently conducting a rearrangement reaction in the reaction mixture from which the generated water or the generated alcohol has been removed, at
15 a temperature of 90 to 150°C and in the presence of an acid catalyst (a third step).

2. The process for production of a 4-alkylphenol according to claim 1, comprising the steps of: reacting a 4-unsubstituted phenol with an alkyl alcohol in presence of a
20 synthetic zeolite, at a temperature of 50 to 110°C (the first step); removing generated water contained within the liquid phase of the thus produced reaction mixture (the second step); and subsequently conducting a rearrangement reaction in the reaction mixture from which the generated water has been
25 removed, at a temperature of 90 to 150°C, and in presence of an

acid catalyst (the third step).

3. The process for production of a 4-alkylphenol according to claim 2, wherein in the third step, the concentration of water of the liquid phase of the reaction mixture is adjusted to no more than 0.5% by weight.

4. The process for production of a 4-alkylphenol according to either one of claim 2 and claim 3, wherein in the third step, the rearrangement reaction is conducted with a quantity of the 4-unsubstituted phenol within the reaction mixture adjusted so as to represent a 1 to 10-fold molar ratio relative to a quantity of the alkyl alcohol consumed during an alkylation reaction of the first step.

5. The process for production of a 4-alkylphenol according to any one of claim 2 to claim 4, wherein the 4-unsubstituted phenol is phenol, and the alkyl alcohol is tert-butanol.

6. The process for production of a 4-alkylphenol according to claim 1, comprising the steps of: reacting a 4-unsubstituted phenol with an alkyl ether in presence of a synthetic zeolite, at a temperature of 50 to 110°C (the first step); removing the generated alcohol contained within the liquid phase of the thus produced reaction mixture (the second step); and subsequently conducting a rearrangement reaction in the reaction mixture from which the generated alcohol has been removed, at a temperature of 90 to 150°C, and in presence of an acid catalyst (the third step).

7. The process for production of a 4-alkylphenol according to claim 6, wherein in the third step, the alcohol concentration of the liquid phase of the reaction mixture is adjusted to no more than 0.5% by weight.

5 8. The process for production of a 4-alkylphenol according to claim 6 or claim 7, wherein in the third step, the rearrangement reaction is conducted with a quantity of the 4-unsubstituted phenol within the reaction mixture adjusted so as to represent a 1 to 10-fold molar ratio relative to a
10 quantity of the alkyl ether consumed during an alkylation reaction of the first step.

9. The process for production of a 4-alkylphenol according to any one of claim 6 to claim 8, wherein the 4-unsubstituted phenol is phenol, and the alkyl ether is methyl tert-butyl
15 ether.