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PROCESS FOR PREPARING ALKYL TERTIARY-ALKYL ETHER

The invention relates to a process for preparing alkyl tertiary-alkyl ethers such as methyl tert-butyl ether ("MTBE"), ethyl tert-butyl ether ("ETBE"), tert-amyl methyl ether ("TAME"), etc. Such ethers are popular
5 high-octane additives for liquid fuels, especially gasoline, replacing the environmentally controversial organolead antiknock compounds.

Processes for preparing MTBE and other ethers are known in the art. Thus, they may be made by reacting an
10 alcohol (typically a primary alcohol such as methanol, hereinafter "MeOH") with an iso-olefin (e.g., isobutene) or the corresponding tertiary alcohol (e.g., tert-butanol) in the presence of an acid catalyst. As 100% conversion is not achieved, the reaction mixture
15 comprises the product ether but also starting reagents. Unfortunately, MTBE and MeOH are hard to separate by distillation as an MeOH/MTBE azeotrope is formed.

Initially, the product ethers were separated from the reaction mixture by washing and/or distilling
20 (repeatedly, under pressure or combinations thereof). Subsequently, in German patent application No. 2,705,538 and US patent No. 4,198,530 it is taught to distil in the presence of a hydrocarbon, whereby a new azeotrope of hydrocarbons and MeOH is formed and separated. A next
25 improvement is taught in European patent application No. 78,422, wherein an amount of hydrocarbons is used that is higher than the content in the hydrocarbons/MeOH azeotrope, thereby resulting in the separation of 99% pure or more MTBE. In the processes of each of these
30 specifications, the hydrocarbons/MeOH azeotrope is separated into its components MeOH, respectively



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hydrocarbons. Thus, an additional separation unit (washing unit, fractionator, etc.) is required. This makes these processes complex and less attractive. In case the elevated temperature of the azeotrope is not used, these processes are even less attractive for economical reasons. Therefore, it remains desirable to find a process for preparing alkyl tertiary-alkyl ethers in an economically attractive manner, which process allows simple recovery of high purity product streams produced at low energy consumption.

It has now been discovered that this objective may be achieved by heating at least part of the iso-olefin reagent in the distillation column, where it assists in fractionating the reaction mixture, and using at least part of the overhead mixture (product obtained at the top of the distillation column, containing the iso-olefin reagent and alcohol) without separation into its components, to feed the reaction. Accordingly, the invention provides a process for preparing an alkyl tertiary-alkyl ether by

- (a) feeding an iso-olefin reagent-containing stream and an alcohol reagent to a reactor and allowing these reagents to react under etherification conditions to form an alkyl tertiary-alkyl ether-containing reaction mixture,
- (b) passing the reaction mixture produced in (a) and a feed stream comprising C4 to C9 hydrocarbons (hereinafter, the "hydrocarbon feed stream") to a distillation column,
- (c) fractionating the reaction mixture and hydrocarbons to obtain a bottom product comprising alkyl tertiary-alkyl ether and an overhead mixture comprising alcohol and hydrocarbons, and
- (d) recycling at least part of the overhead mixture to the reactor,

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wherein the hydrocarbon feed stream comprises iso-olefin reagent, and wherein at least part of the iso-olefin reagent-containing stream supplied into the reactor is formed by the overhead mixture (hereinafter, the "distillation recycle").

The iso-olefin reagent-containing stream is formed by the distillation recycle and, optionally, a stream of fresh reagent. Preferably (since economically more attractive), at least 50 %wt, more preferably at least 80 %wt, of the iso-olefin reagent-containing stream is formed by the distillation recycle. Most preferably, all of the iso-olefin reagent that is fed into the reactor stems from the distillation recycle.

Besides the iso-olefin, the hydrocarbon feed stream may further comprise inert hydrocarbons such as butane, pentane, etc., and essentially inert hydrocarbons such as 1-butene, etc. Preferably, the hydrocarbon feed stream comprises at least 50 %wt of the iso-olefin reagent. To avoid build-up of inert hydrocarbons, a bleed stream may be introduced downstream of the reactor and/or the distillation column. Optionally, a conventional isomerization unit (as disclosed in for instance US patents Nos. 5,243,090, 5,254,748 and 5,254,764) may be used to isomerize (part of) the inert hydrocarbons into the iso-olefin reagent. There is no advantage in using hydrocarbon feed streams comprising C3- or C9+ hydrocarbons as these components do not facilitate the fractionation of the reaction mixture in the distillation column.

More preferably the hydrocarbon feed stream comprises at least 80 %wt, most preferably at least 99 %wt of the iso-olefin reagent. Build-up of inert hydrocarbons in this most preferred embodiment is very small, if any. Accordingly, the overhead mixture may be recycled in total to the reactor without need of a bleed stream. Loss



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of reagents/products is than negligible, whereas the elevated temperature of this overhead mixture is optimally used.

5 The hydrocarbon feed stream may be passed into the distillation column together with the reaction mixture, or through a separate inlet. Preferentially, it is passed into the distillation column through a separate inlet that is located below the inlet of the reaction mixture, whereby nearly all of the alcohol reagent may be removed
10 from the bottom product comprising the alkyl tertiary-alkyl ether.

Preferably, the amount of hydrocarbon feed stream is such as to introduce at least sufficient hydrocarbons into the distillation column to separate the alcohol in
15 the form of an azeotrope of the alcohol and the hydrocarbons from the produced alkyl tertiary-alkyl ether. This amount is related to the internal pressure in the distillation column. For instance, from US patent No. 4,198,530 it is known that at a pressure of 5 atm
20 (5.07 bar a), the MeOH contents in the azeotrope is about 4 mol%, but at a pressure of 10 atm (10.1 bar a), it is about 9 mol%. The amount is also related to the content of hydrocarbons in the reaction mixture, for instance, of excess iso-olefin reagent and inert hydrocarbons due to
25 build-up, if any.

Suitable iso-olefin reagents used in the present process have up to 8 carbon atoms and are more suitably selected from isobutene and isoamylenes (2-methyl-1-butene, 2-methyl-2-butene and dimethylpropene).

30 The alcohol reagent suitably has up to 8 carbon atoms and is more suitable a primary alcohol, such as methanol and ethanol, but may also be a secondary, tertiary or aromatic alcohol. Tertiary-alkyl ethers of primary alcohols generally have the better combustion properties
35 and are therefore preferred.



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Preferably, the molar ratio wherein the iso-olefin reagent and the alcohol reagent are allowed to react ranges from 1:0.9 to 1:1.1, and is more preferably about 1:1.02. Using more than the stoichiometric amount of one of the reagents allows improved conversion in respect of the other reagent. However, in case excess alcohol reagent is used, the difficulty in obtaining sufficiently pure alkyl tertiary-alkyl ether is aggravated, whereas in case excess iso-olefin reagent is used, large volumes thereof will be recirculated, increasing the costs of equipment.

The catalyst typically is an acidic solid catalyst such as a sulfonic acid substituted ion exchange resin or an acidic natural or synthetic silicate (e.g., amorphous silica-alumina or acid zeolites). Preferably, the catalyst is an ion exchange resin, e.g., produced by polymerization of aromatic vinyl compounds to which catalytically active functional groups are covalently bonded. Suitable sulfonic acid substituted ion exchange resins are disclosed in European patent application No. 102,840 and in International application No. 90/08758. A very suitable catalyst is a sulfonic acid substituted ion exchange resin having at least 1.2, more preferably about 1.2 to 1.8 sulfonic acid groups for each aromatic ring system. Typical examples of very suitable catalysts are sulfonic acid substituted divinylbenzene-styrene resins sold under the trademarks DUOLITE C20, DUOLITE C26, AMBERLYST 15, AMBERLITE IR-120, AMBERLITE 200 and DOWEX 50.

The reaction usually is conducted at a temperature between 30 and 120 °C, preferably between 45 and 100 °C, and a pressure between 5 and 40 bar g, preferably between 10 and 20 bar g. Typically, the reagents are supplied and made to flow continuously through the sulfonic acid substituted ion exchange resin which is disposed in the

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form of a fixed bed, at a liquid hourly space velocity (LHSV) that is generally less than 80 hr^{-1} . The conditions are all known to those skilled in the art. Indeed, similar conditions and catalysts may be used without departing from the gist of the invention.

5 The distillation is suitably carried out in a distillation tower having 30 to 50 theoretical plates ("TPs") that is, for instance, operated at a pressure between 6 and 12 bar g, a bottom temperature (T_B) between
10 130 and 150 °C, and a top temperature (T_T) between 50 and 70 °C. The invention may quite suitably be carried out with a distillation tower of 40 TPs, operating at a pressure of 9 bar g, a T_B of 140 °C, and a T_T of 65 °C (all approximations).

15 In a preferred embodiment of the invention, the reaction mixture is employed in indirect heat transfer with the (hot) bottom product comprising the alkyl tertiary-alkyl ether. In a more preferred embodiment the bottom product is also employed in indirect heat transfer
20 with the hydrocarbon feed stream further downstream of the distillation column.

Referring now to Figure 1, a schematic process flow diagram is presented for a specific embodiment (A) of the instant invention. In this embodiment and subsequent
25 embodiments of the present invention, the hydrocarbon feed stream, introduced via inlet 21, is composed of isobutene.

In Figure 1, the reagents introduced via inlet 11 essentially comprise isobutene as iso-olefin and MeOH as
30 primary alcohol in a molar ratio of 1:1.02. It is passed to reactor 1 containing an acid catalyst (e.g., "AMBERLYST 15") for etherification at an LHSV of about 20 hr^{-1} , a pressure of 20 bar g and a temperature of 50 °C. Via pipe 12, the reaction mixture, essentially
35 comprising isobutene, MeOH and MTBE (conversion of about

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99%), is passed to the mid-portion of distillation column 2 (a column counting 37 TPs). The distillation is carried out at an internal pressure of 9 bar g, a T_B of 141 °C and a T_T of 63 °C. The inlet 21 of the hydrocarbon feed stream is below the inlet of the reaction mixture. The amount of hydrocarbon feed stream is sufficient to compensate the amount of isobutene converted into MTBE (about 40 ton per hour). The overhead mixture obtained at the top of the distillation column 2, via outlet 22, is essentially composed of isobutene and MeOH (about 47 ton per hour, ratio isobutene to MeOH of about 97:3 m/m). An alcoholic feed stream of fresh MeOH is introduced via inlet 23 in an amount sufficient to change the molar ratio to that of the reaction feedstock (about 23 ton per hour). The bottom product, obtained at outlet 24 is essentially composed of the alkyl tertiary-alkyl ether, MTBE (about 63 ton per hour).

A preferred embodiment (B) of the present invention is illustrated as a schematic diagram in Figure 2. In Figure 2, the bottom product, obtained at outlet 24, is cooled in heat exchanger 3 by indirect heat exchange with the hydrocarbon feed stream, introduced via inlet 21. In an alternative embodiment (C) (Figure 3), the bottom product is cooled in heat exchanger 4 by indirect heat exchange with the reaction mixture, transported via pipe 12. In the most preferred embodiment (D) of the present invention (Figure 4), the bottom product is first cooled in heat exchanger 4 by indirect heat exchange with the reaction mixture and subsequently (downstream) in heat exchanger 3 with the hydrocarbon feed stream.

The virtue of each of the embodiments (A) to (D) is that no extraction of recycle methanol is required. In addition, the labour (i.e., energy consumption per second, expressed in Watts) required to prepare 1000 kg of MTBE per hour for embodiment (A) is small, and that of

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embodiments (B) to (D) smaller still. The results of a computer simulation have been summarized in the Table.

5 The Table is completed with results of computer simulations that are based on a process (C1) wherein the iso-olefin reagent is heated to the same temperature as in embodiments (A) to (D), however now heating the iso-olefin externally (requiring about 1 MW to bring the 40 ton isobutene to the same temperature as that of the distillation recycle). Moreover, the distillation column
10 is fed with a separate flow of liquid hydrocarbons. The overhead mixture is then led to a separation unit (i.e., a washing unit with a duty of about 3.5 MW) where the alcohol and the liquid hydrocarbons are separated. The alcohol is recirculated to the reactor, the liquid
15 hydrocarbons are reused in the distillation column. Other conditions are kept identical to those of embodiment (A). Also included are the results based on a process (C2) similar to that of (C1), wherein the bottom product is in indirect heat exchange with the reaction mixture (cf.
20 European patent application No. 0,323,134, Fig. 1 or 2). Other conditions are kept identical to those of embodiment (C).

Advantageously, in the present process no separation unit for the methanol is needed. Moreover, the present
25 process is clearly more energy-efficient (less energy per ton MTBE per hour).

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Table

Embodiment	A	B	C	D	C1	C2
Duty of column 2 (MW)	13.1	13.1	13.1	13.1	13.1	13.1
Heat recovery in 3 (MW)	n.a.	1.9	n.a.	1.9	n.a.	1.9
Heat recovery in 4 (MW)	n.a.	n.a.	2.0	1.7	n.a.	n.a.
External heating of isobutene (MW)	n.a.	n.a.	n.a.	n.a.	1.0	1.0
Duty of additional separation unit (MW) ¹⁾	n.a.	n.a.	n.a.	n.a.	3.5	3.5
Total duty (MW) ²⁾	13.1	11.2	11.1	9.5	17.6	15.7
Energy efficiency (KW/ton MTBE)	208	178	176	150	280	250

1) Estimated value, based on heats of vaporisation

2) Relative value, based on identical conditions and parameters

n.a. Not applicable

C L A I M S

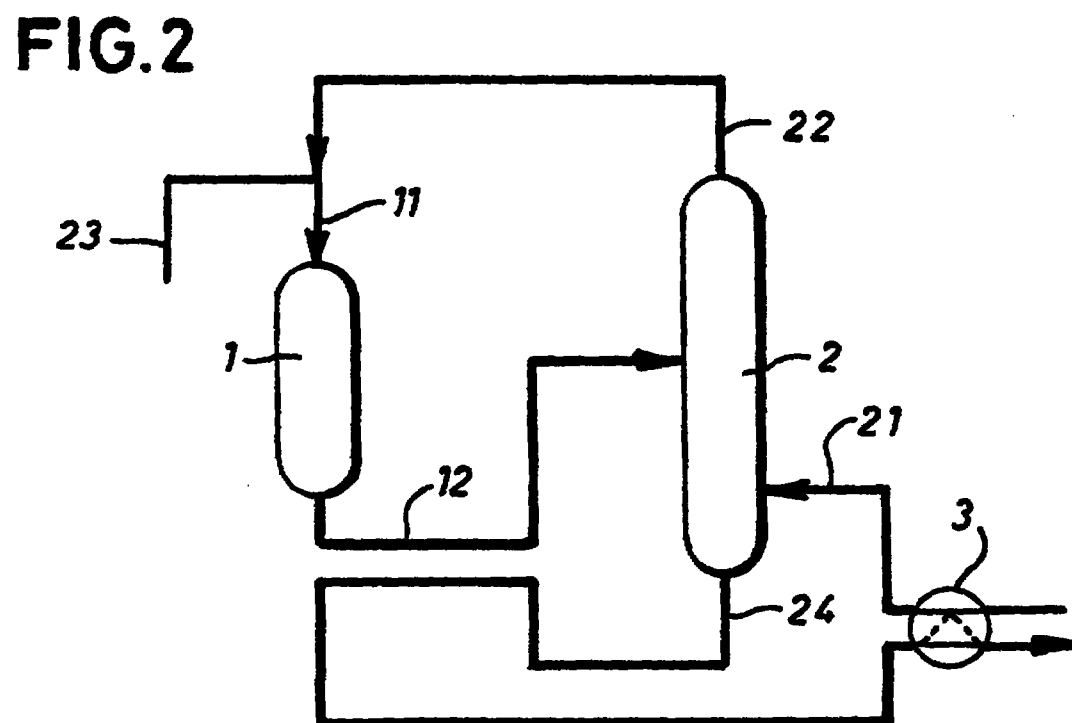
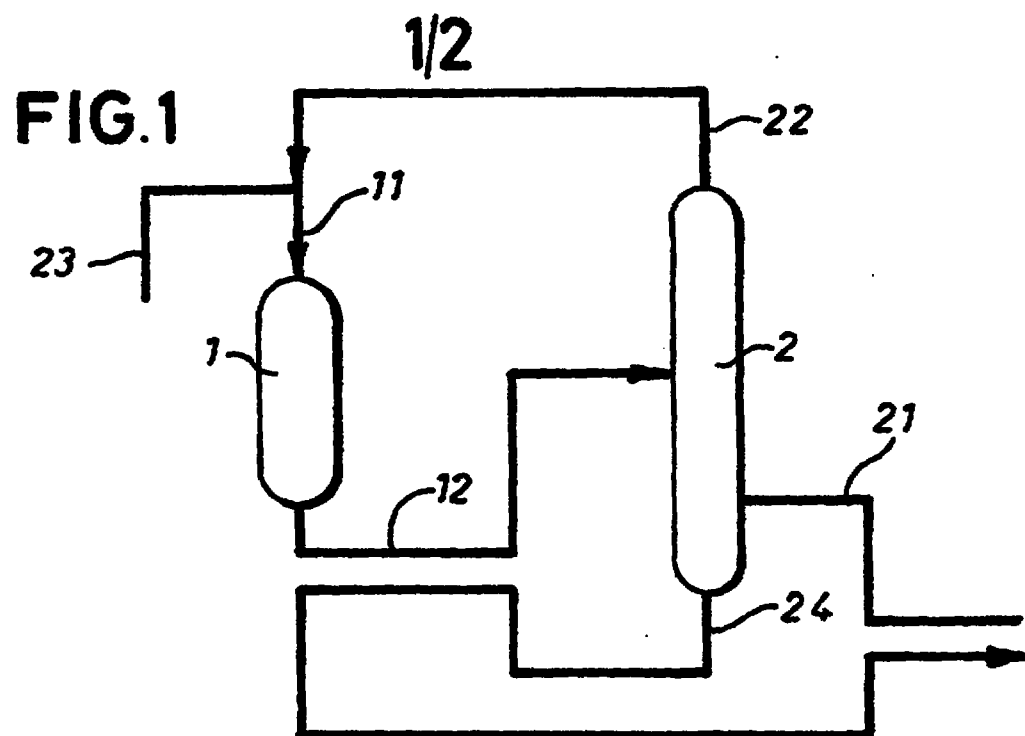
1. A process for preparing an alkyl tertiary-alkyl ether by
- 5 (a) feeding an iso-olefin reagent-containing stream and an alcohol reagent to a reactor and allowing these reagents to react under etherification conditions to form an alkyl tertiary-alkyl ether-containing reaction mixture,
- 10 (b) passing the reaction mixture produced in (a) and a feed stream comprising C4 to C9 hydrocarbons (hereinafter, the "hydrocarbon feed stream") to a distillation column,
- 15 (c) fractionating the reaction mixture and hydrocarbons to obtain a stream comprising alkyl tertiary-alkyl ether at the bottom of the distillation column and a stream comprising alcohol and hydrocarbons at the top of the distillation column, and
- (d) recycling at least part of the overhead mixture to the reactor,
- 20 wherein the hydrocarbon feed stream comprises iso-olefin reagent, and wherein at least part of the iso-olefin reagent-containing stream supplied into the reactor is formed by the overhead mixture.
- 25 2. A process as claimed in claim 1, wherein at least 50 %wt of the iso-olefin reagent-containing stream is formed by the overhead mixture.
3. A process as claimed in claim 1 or 2, wherein the hydrocarbon feed stream comprises at least 80 %wt of iso-olefin reagent.
- 30 4. A process as claimed in any one of claims 1 to 3, wherein the iso-olefin reagent has up to 8 carbon atoms.



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5. A process as claimed in any one of claims 1 to 4, wherein the alcohol reagent has up to 8 carbon atoms.
6. A process as claimed in any one of claims 1 to 5, wherein the iso-olefin reagent and the alcohol reagent
5 are allowed to react in a molar ratio ranging from 1:0.9 to 1:1.1.
7. A process as claimed in any one of claims 1 to 6, wherein the etherification is carried out in the presence of an acidic solid catalyst.
- 10 8. A process as claimed in any one of claims 1 to 7, wherein the reaction is conducted at a temperature between 30 and 120 °C and under a pressure between 5 and 40 bar g.
- 15 9. A process as claimed in any one of claims 1 to 8, wherein the distillation is carried out in the distillation column of 30 to 50 theoretical plates.
10. A process as claimed in any one of claims 1 to 9, wherein indirect heat transfer is provided between the stream comprising alkyl tertiary-alkyl ether recovered at
20 the bottom of the distillation column and (i) the reaction mixture and/or (ii) the hydrocarbon feed stream.





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FIG.3

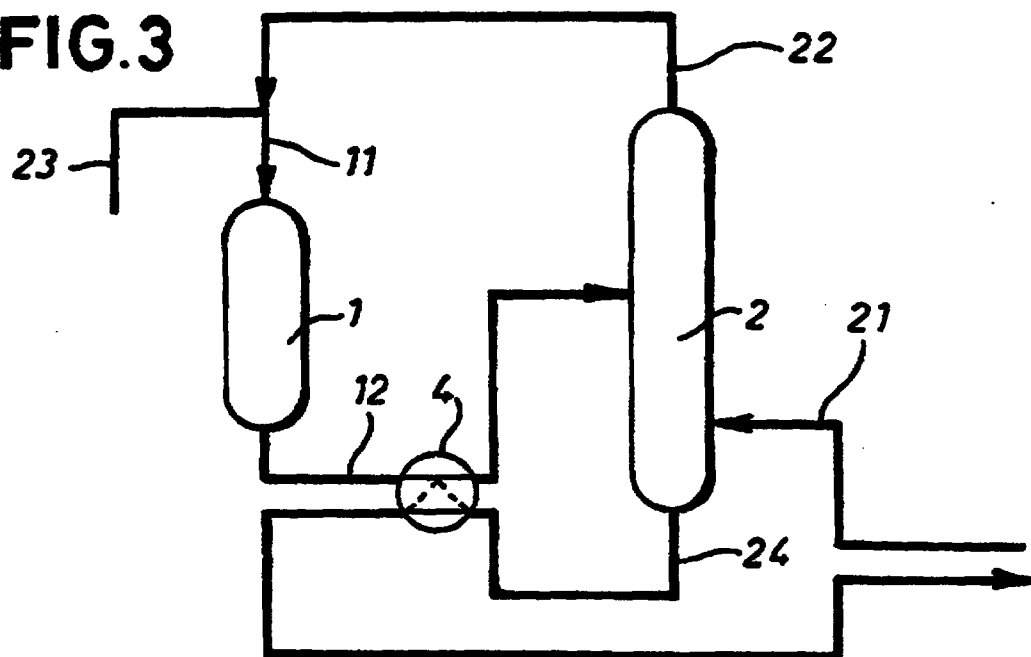
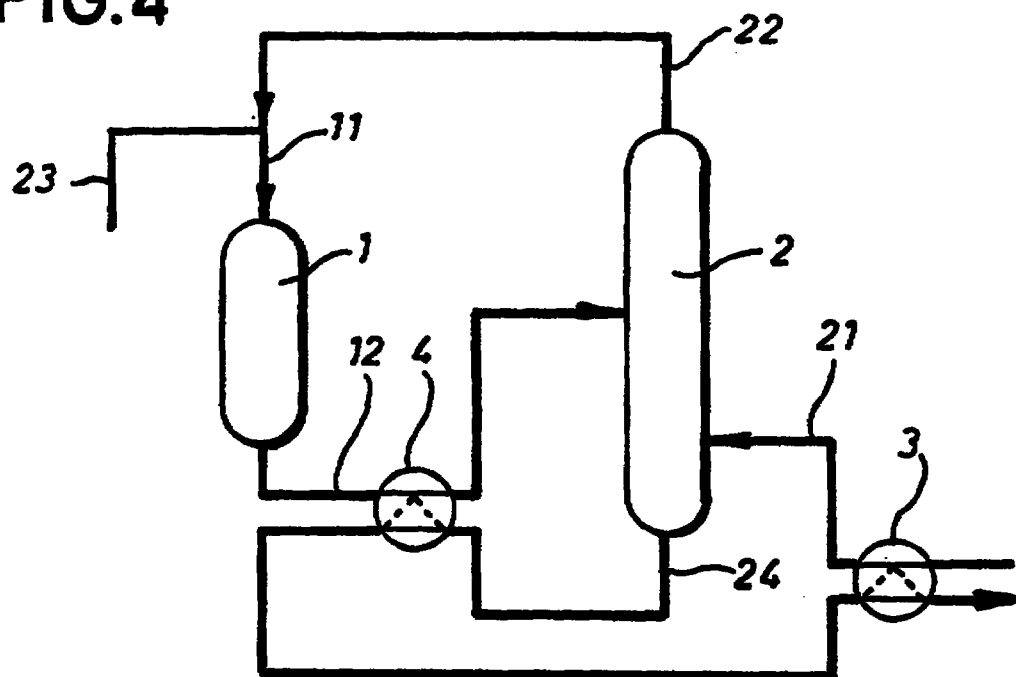


FIG.4



hydrocarbons. Thus, an additional separation unit (washing unit, fractionator, etc.) is required. This makes these processes complex and less attractive. In case the elevated temperature of the azeotrope is not used, these processes are even less attractive for economical reasons. Therefore, it remains desirable to find a process for preparing alkyl tertiary-alkyl ethers in an economically attractive manner, which process allows simple recovery of high purity product streams produced at low energy consumption.

It has now been discovered that this objective may be achieved by heating at least part of the iso-olefin reagent in the distillation column, where it assists in fractionating the reaction mixture, and using at least part of the overhead mixture (product obtained at the top of the distillation column, containing the iso-olefin reagent and alcohol) without separation into its components, to feed the reaction. Accordingly, the invention provides a process for preparing an alkyl tertiary-alkyl ether by

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and wherein the hydrocarbon feed stream is passed into the distillation column through a separate inlet located below that of the reaction mixture.

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wherein the hydrocarbon feed stream comprises iso-olefin reagent, ~~and~~ wherein at least part of the iso-olefin reagent-containing stream supplied into the reactor is formed by the overhead mixture (hereinafter, the "distillation recycle"),

The iso-olefin reagent-containing stream is formed by the distillation recycle and, optionally, a stream of fresh reagent. Preferably (since economically more attractive), at least 50 %wt, more preferably at least 80 %wt, of the iso-olefin reagent-containing stream is formed by the distillation recycle. Most preferably, all of the iso-olefin reagent that is fed into the reactor stems from the distillation recycle.

Besides the iso-olefin, the hydrocarbon feed stream may further comprise inert hydrocarbons such as butane, pentane, etc., and essentially inert hydrocarbons such as 1-butene, etc. Preferably, the hydrocarbon feed stream comprises at least 50 %wt of the iso-olefin reagent. To avoid build-up of inert hydrocarbons, a bleed stream may be introduced downstream of the reactor and/or the distillation column. Optionally, a conventional isomerization unit (as disclosed in for instance US patents Nos. 5,243,090, 5,254,748 and 5,254,764) may be used to isomerize (part of) the inert hydrocarbons into the iso-olefin reagent. There is no advantage in using hydrocarbon feed streams comprising C3- or C9+ hydrocarbons as these components do not facilitate the fractionation of the reaction mixture in the distillation column.

More preferably the hydrocarbon feed stream comprises at least 80 %wt, most preferably at least 99 %wt of the iso-olefin reagent. Build-up of inert hydrocarbons in this most preferred embodiment is very small, if any. Accordingly, the overhead mixture may be recycled in total to the reactor without need of a bleed stream. Loss

of reagents/products is than negligible, whereas the elevated temperature of this overhead mixture is optimally used.

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~~distillation column together with the reaction mixture, /~~
~~/or through a separate inlet. Preferentially, it~~ is passed
into the distillation column through a separate inlet
that is located below the inlet of the reaction mixture,
whereby nearly all of the alcohol reagent may be removed
10 from the bottom product comprising the alkyl tertiary-
alkyl ether.

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such as to introduce at least sufficient hydrocarbons
into the distillation column to separate the alcohol in
15 the form of an azeotrope of the alcohol and the
hydrocarbons from the produced alkyl tertiary-alkyl
ether. This amount is related to the internal pressure in
the distillation column. For instance, from US patent
No. 4,198,530 it is known that at a pressure of 5 atm
20 (5.07 bar a), the MeOH contents in the azeotrope is about
4 mol%, but at a pressure of 10 atm (10.1 bar a), it is
about 9 mol%. The amount is also related to the content
of hydrocarbons in the reaction mixture, for instance, of
excess iso-olefin reagent and inert hydrocarbons due to
25 build-up, if any.

Suitable iso-olefin reagents used in the present
process have up to 8 carbon atoms and are more suitably
selected from isobutene and isoamylenes (2-methyl-1-
butene, 2-methyl-2-butene and dimethylpropene).

30 The alcohol reagent suitably has up to 8 carbon atoms
and is more suitable a primary alcohol, such as methanol
and ethanol, but may also be a secondary, tertiary or
aromatic alcohol. Tertiary-alkyl ethers of primary
alcohols generally have the better combustion properties
35 and are therefore preferred.

C L A I M S

1. A process for preparing an alkyl tertiary-alkyl ether by

(a) feeding an iso-olefin reagent-containing stream and an alcohol reagent to a reactor and allowing these reagents to react under etherification conditions to form an alkyl tertiary-alkyl ether-containing reaction mixture,

(b) passing the reaction mixture produced in (a) and a feed stream comprising C4 to C9 hydrocarbons (hereinafter, the "hydrocarbon feed stream") to a distillation column,

(c) fractionating the reaction mixture and hydrocarbons to obtain a stream comprising ^{substantially pure} alkyl tertiary-alkyl ether at the bottom of the distillation column and a stream comprising alcohol and hydrocarbons at the top of the distillation column, and

(d) recycling at least part of the overhead mixture to the reactor,

wherein the hydrocarbon feed stream comprises iso-olefin reagent, ~~and~~ wherein at least part of the iso-olefin reagent-containing stream supplied into the reactor is formed by the overhead mixture, L

2. A process as claimed in claim 1, wherein at least 50 %wt of the iso-olefin reagent-containing stream is formed by the overhead mixture.

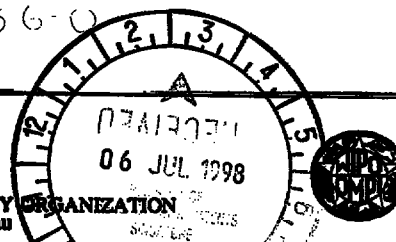
3. A process as claimed in claim 1 or 2, wherein the hydrocarbon feed stream comprises at least 80 %wt of iso-olefin reagent.

4. A process as claimed in any one of claims 1 to 3, wherein the iso-olefin reagent has up to 8 carbon atoms.

L and wherein the hydrocarbon feed stream is passed into the distillation column through a separate inlet located below that of the reaction mixture.

AMENDED SHEET

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6: C07C 43/04, 41/06, 41/42	A1	(11) International Publication Number: WO 96/21635
		(43) International Publication Date: 18 July 1996 (18.07.96)

(21) International Application Number: PCT/EP96/00264

(22) International Filing Date: 11 January 1996 (11.01.96)

(30) Priority Data:
95200086.7 13 January 1995 (13.01.95) EP

(34) Countries for which the regional or international application was filed: GB et al.

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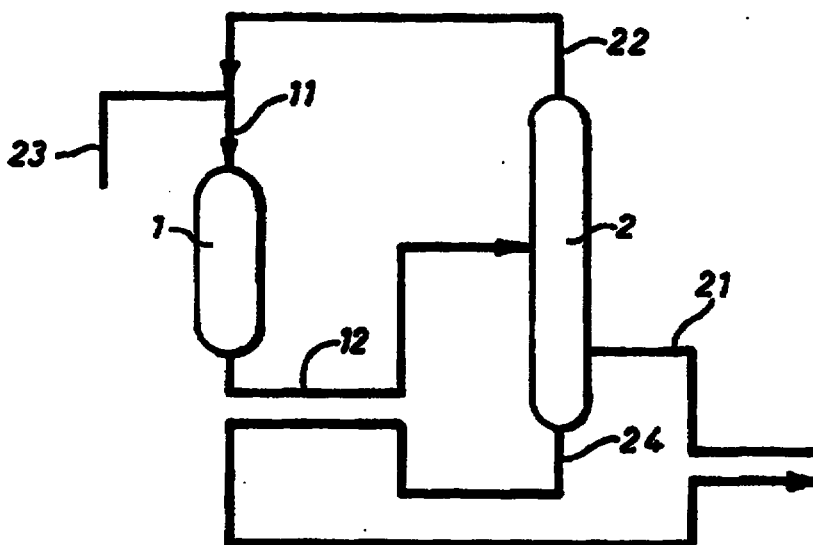
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(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AZ, BY, KZ, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: PROCESS FOR PREPARING ALKYL TERTIARY-ALKYL ETHER



(57) Abstract

The invention relates to a process for preparing an alkyl tertiary-alkyl ether by (a) feeding an iso-olefin reagent-containing stream and an alcohol reagent via inlet (11) to reactor (1) and allowing these reagents to react under etherification conditions to form an alkyl tertiary-alkyl ether-containing reaction mixture, (b) passing the reaction mixture produced in (a) via pipe (12) and a hydrocarbon feed stream via inlet (21) to distillation column (2), (c) fractionating the reaction mixture and hydrocarbons to obtain a stream comprising alkyl tertiary-alkyl ether at outlet (24) at the bottom of the distillation column (2) and a stream comprising alcohol and hydrocarbons at outlet (22) at the top of the distillation column (2), and (d) recycling at least part of the overhead mixture obtained at outlet (22) to the reactor (1), wherein the hydrocarbon feed stream comprises iso-olefin reagent, and wherein at least part of the iso-olefin reagent-containing stream supplied into the reactor is formed by the overhead mixture.