METHOD FOR CONTINUOUSLY PRODUCING TERTIARY BUTYL ETHERS OF GLYCEROL

Inventors: Arno Behr, Dortmund (DE); Alexander Kleyenstein, Hemer (DE)

Assignee: TECHNISCHE UNIVERSITAET DORTMUND, DORTMUND (DE)

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The invention relates to a method for producing a mixture of substances comprising a higher tertiary butyl ether of glycerol, comprising the steps: acid-catalyzed reaction of isobutene with glycerol to form a reaction mixture, and extraction of at least part of the reaction mixture from step a by means of at least one solvent, wherein the solvent or the mixture of solvents comprises an ET(30) value of $\approx 35.0$. 

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ABSTRACT
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FIELD OF TECHNOLOGY

[0001] The present invention relates to a method for producing a mixture of substances comprising higher tertiary butyl ethers of glycerol. Moreover, the invention relates to a fuel which is obtainable by this method.

BACKGROUND

[0002] Glycerol is a very versatile educt which is prevalently produced from regrowing raw materials. Glycerol is formed in the production of biodiesel as a co-product of its transesterification. Should the demand for biodiesel be growing within the next years then glycerol were available at too low prices in amounts that would argue for employing it in industrial-scale products.

[0003] Thus, distillatively separating a product mixture of glycerol and of a mixture of high-boiling substances does not make sense for both, energy and technology reasons. The spectrum of GTBE (tertiary butyl ethers of glycerol) comprises three different etherification steps of which only the higher ethers (di- and triethers), also referred to as h-GTBE, can be employed as an octane enhancer in fuel. The mono-ether has less favorable combustion properties and also tends to sediment in fuel.

[0004] U.S. Pat. No. 5,731,476 describes a sulfonic acid-catalyzed homogeneous etherification. At this, reaction is carried on only to a low conversion rate at which the reaction mixture still is in bi-phase form. Unreacted glycerol, the catalyst and parts of the resulting mono-ethers are separated in a decanter and are cycled back. Isobutene is stripped out of the organic phase and the liquid phase is extracted with water. Then, the extract is discarded and the raffinate of higher ethers is recovered at the head of the extraction unit.

[0005] The method shows disadvantages in that the reaction is carried out at low conversion rates to ensure a two-phase stream at the exit of the reactor. Furthermore, the stream entering the extraction phase consists of less than 50% of mono-ethers; thus, almost half of the separated reaction products gets discarded.

[0006] Thus, one object is to provide an improved method for producing and/or purifying tertiary butyl ethers of glycerol which overcomes the existing disadvantages at least partially and is in particular able to provide a higher yield in many applications.

SUMMARY

[0007] According to the invention, a method for producing a mixture of substances comprising higher tertiary butyl ethers of glycerol is proposed, comprising the steps:

[0008] a) Acid-catalyzed reaction of isobutene with glycerol to form a reaction mixture;

[0009] b) extraction of at least part of the reaction mixture from step a) by means of at least one solvent, wherein the solvent or the mixture of solvents comprises an $E_{(30)}$ value of $\leq 35.0$.

[0010] In applying the method according to the invention at least one of the following advantages can be achieved for a multitude of applications:

[0011] The glycerol ether resulting from the method may be extracted with a fuel and may be used as a mixture for combustion engines,

[0012] the glycerol ether may be obtained directly if a further purification step is added,

[0013] the formation of by-products such as mono-tertiary butyl ethers (ultimately to be discarded) may be reduced significantly (if necessary by appropriate additional measures),

[0014] an inconvenient thermal separation of water and glycerol is avoided,

[0015] an inconvenient separation of the mono-ethers from the h-GTBE is avoided.

[0016] As defined by the present invention, higher tertiary butyl ethers of glycerol are those ethers which may result from the reaction of isobutene with glycerol. In particular, isobutene and glycerol may be used in the form of pure substances. In this process, a catalyst may be used to accelerate the reaction. Tertiary butyl ethers of glycerol include in particular those ethers, selected from the group consisting of 3-tert-butoxy-propane-1,2-diol, 2-tert-butoxy-propane-1,3-diol, 1,3-di-tert-butoxy-propane-2-ol, 2,3-di-tert-butoxy-propane-1-ol, 1,2,3-tri-tert-butoxy-propane. Among the range of these ethers, di-ethers and tri-ethers are referred to as so-called higher ethers.

[0017] In the present invention, the mixture of substances may consist of at least one component of the tertiary butyl ethers of glycerol, a solvent and/or a further compound. The mixture of substances may be in a homogeneous or a heterogeneous state. Preferably, the mixture of substances is used in the form of a solution.

[0018] The first step of the method according to the invention comprises an acid-catalyzed reaction of isobutene with glycerol to yield a reaction mixture. As defined by the present invention, an acid-catalyzed reaction means in particular the sub-stoichiometrical use of a proton donor together with the respective educts isobutene and glycerol. At this, the catalyst may be present in a molar concentration, based on the initial concentration of glycerol, in the range of $\geq 0.5$ mol-% to $\leq 10$ mol-%, preferably in a range of $\geq 2$ mol-% to $\leq 8$ mol-%, and particularly preferred in a range of $\geq 3$ mol-% to $\leq 6$ mol-%. The catalyst may be in a homogeneous or a heterogeneous state. Preferably, the fraction of glycerol and mono-ether in the mixture of substances is within a range of $\geq 0$ wt-% to $\leq 5$ wt-%, preferably within a range of $\geq 0.1$ wt-% to $\leq 3$ wt-%, and particularly preferred within a range of $\geq 0.5$ wt-% to $\leq 2$ wt-%.

[0019] As defined by the present invention, the reaction mixture resulting from this means in particular the reaction mixture in the state from the beginning of the reaction until the equilibrium state and/or the termination of the reaction. The reaction mixture may be in a homogeneous or a heterogeneous state. As defined by the present invention, the educts used in the method for producing tertiary butyl ethers of glycerol are in a liquid phase and are preferably selected from the group consisting of the raw materials of the educts, glycerol and an isobutene containing material stream, raw glycerol and isobutene or raw glycerol and an isobutene containing material stream. Reacting pure glycerol with pure isobutene or isobutene containing streams may be particularly preferred in this process.

[0020] The reaction may be carried out in a reaction unit. In particular, the reaction unit is comprised of an stirred vessel, a cascade of stirred vessels, a tube reactor, a liquid jet mixer.
and/or a static mixer. An individual stirred vessel or a cascade of stirred vessels may be particularly preferred in this process.

[0021] In a variant of the invention, the reaction mixture, after having been reacted at least partially, is freed from unreacted isobutene by stripping and/or by flushing at leaving the reaction unit in the form of a material stream. According to a preferred embodiment of the invention, the separated isobutene may be cycled back into the reaction at least partially. According to an alternative preferred embodiment of the invention, the isobutene or isobutene containing gas stream may be discharged off the reaction unit.

[0022] Step b) of the method according to the invention comprises an extraction of at least part of the reaction mixture from step a) by means of at least one solvent, wherein the solvent or the mixture of solvents comprises an $E_{30}(30)$ value of $\leq 35.0$.

[0023] Herein, an extraction is in particular defined as the process of selectively dissolving, washing or leaching out certain substances as transition components of solid or liquid mixtures of substances by means of liquid solvents. As defined by the present invention, extraction may in particular refer to a liquid-liquid-extraction.

[0024] It is important to point out that in case, a mixture of solvents is used in step b), individual components of this mixture (depending on the method’s application) may have a higher $E_{30}(30)$ value. These mixtures are explicitly included within the scope of the method of the invention as long as the $E_{30}(30)$ value of the mixture as a whole comprises a value of $\leq 35.0$.

[0025] As defined by the present invention, a solvent mixture is a mixture of at least two partially miscible components. That means that one component may dissolve into the other at a fraction of $\geq 90$ vol%, preferably of $\geq 98$ vol%, and particularly preferred of $\geq 99$ vol%. Preferably, the obtained solvent mixture comprises an $E_{30}(30)$ value of $\leq 35.0$.

[0026] Two liquid phases are participating in a liquid-liquid-extraction (LLE), in which the substance to be extracted, i.e. the valuable substance S, is dissolved out of the existent carrier liquid mixture by means of a solvent L. After a completed transfer of the valuable substance from the donor phase to the receiving solvent, a mechanical phase separation yields the raffinate R, which is depleted of the valuable substance, and the extract phase E, which is rich in valuable substance. In contrast to other separation processes, LLE does not result in an individually separated mixture component but in a solvent-loaded mixture. In most cases, this mixture may further be separated in subsequent process steps.


[0028] Preferably, the extraction is carried out with at least one solvent which has an $E_{30}(30)$ value of $\geq 33$, and/or wherein the solvent preferably has a miscibility gap with water.

[0029] Preferably, the extraction is carried out with at least one solvent which has an $E_{30}(30)$ value of $\geq 32.0$, even more preferably of $\geq 31.5$.

[0030] Particularly preferred solvents are those, selected from the group of alcanes, cycloalkanes, alcanes, cycloalkenes, alcanes, cycloalkanes and/or the aromatic C6-C14 carbons.

[0031] As defined by the present invention, solvents are in particular selected from the group, comprising 2-methylbutane, n-pentane, n-hexane, 1-hexene, 1-hexene, n-heptane, n-octane, n-nonane, benzene, methylbenzene, toluene, (trifluoromethyl)benzene, 1,4-dimethylbenzene, p-xylene, 1,3,5-trimethylbenzene, n-decane, n-dodecane, cyclohexane, cyclohexene, cis-decahydrocyclopentylalene, 1,2,3,4-tetrahydrocyclopentylalene, vinylbenzene, diethyl ether, bis(2-chloroethyl)ether, tetrahydrofurane, ethyl vinyl ether, di-n-propyl ether, disopropyl ether, di-n-butyl ether, tert-butyl methyl ether, tert-amyl methyl ether, 2-methoxy-2-methylbutane and/or carbon disulfide.

[0032] In a variant, the solvent may be selected from the group of diesel fuel, kerosine, petrol, light petrol, synthetic petrol, alkylate based petrol, biodiesel, ethanol-fuel, cellulosic-ethanol, butanol, liquid gas, methanol, plant oil, heavy fuel oil, benzene, petrol and benzene mixtures, gasoil, motor petroleum.

[0033] In one embodiment of the method according to the present invention, the volume ratio of solvent and reaction mixture of step a) is within a range of $\geq 0.8:1$ and $\leq 1.5:1$. In a liquid-liquid-extraction, the mono-ether compounds may be more easily separated from the mixture by means of the glycerol phase such that the mono-ether may preferably stay in the polar phase.

[0034] In a further variant of the invention, the molar ratio (mol/mol) of the educts isobutene and glycerol may be in a range of $\geq 1:0.5$ and $\leq 1:5$, preferably in a range of $\geq 1:1$ and $\leq 4$, and particularly preferred in a range of $\geq 1:1.5$ and $\leq 1:3$. Like this, the conversion of isobutene may be increased. This proves to be particularly favorable with mixtures such as raffinate I. As one advantage, the gas exhaust contains little isobutene because, as in the production of ethyl tertiary butyl ether, for example, an isobutene conversion of 99% may be obtained only by a very laborious twofold reactive rectification.

[0035] As defined by the present invention, “raffinate I” is in particular a mixture of isobutene plus at least one further substance, selected from the group of isobutene, n-butane, 2-butene (cis and/or trans), 1-butene and butadiene.

[0036] In a further alternative embodiment of the method according to the present invention, the molar ratio (mol/mol) of isobutene and the higher tertiary butyl ethers of glycerol from step a) is within a range of $\geq 0.1:1$ and $\leq 1:1$. Like this, the conversion of isobutene may be increased. This proves to be particularly advantageous with mixtures such as raffinate I, for example. As one advantage, the gas exhaust contains little isobutene because, as in the production of ethyl tertiary butyl ether, for example, an isobutene conversion of 99% may be obtained only by a very laborious twofold reactive rectification.

[0037] In another embodiment of the method according to the present invention, the temperature of the reaction mixture of step a) is between $\geq 60^\circ$ C. and $\leq 130^\circ$ C., preferably in a temperature range of between $\geq 70^\circ$ C. and $\leq 120^\circ$ C., and particularly preferred in a temperature range of between $\geq 80^\circ$ C. and $\leq 110^\circ$ C. At this temperature, the reaction progress with respect to the yield and reaction time is improved in many applications.

[0038] In another embodiment of the method according to the present invention, the conversion is effected at a pressure of $\geq 10$ bar to $\leq 20$ bar. Advantageously, the compounds, which are in the form of gases under normal conditions, may be liquified and used as solvents in this pressure range.
Another advantage in many applications of the invention lies in the fact that this pressure range is favorable for economically operating the reaction system because it corresponds to its internal pressure and, thus, does not have to be produced by compression or pump performance.

In a further embodiment of the method according to the present invention, the acid from step a) has a pKa value of \( \leq 2 \). As defined by the present invention, the term “acid” comprises substances which can act as a proton donor. It may also refer to a mixture of acids which have a pKa value of \( \leq 2 \). In particular, the acid is one, comprising hydrochloric acid, sulfuric acid and/or sulfonic acid. Preferably, p-toluene-sulfonic acid, methanesulfonic acid and/or benzenesulfonic acid may be used.

In one variant, the higher ethers may be extracted with petrol plus an addition of a glycerol containing stream or with pure hydrocarbon plus an addition of a glycerol containing stream. The extraction unit may be realized by means of several mixer-settler-units, by extraction columns or by interconnecting both of them. The stream condution may be by cross flow, counter flow or by counter flow distribution.

In a further variant, the extract stream may be processed thermally, and the extraction medium may be cycled back into the extraction process. Advantageously, this leads to savings in extraction medium and, thus, to a more cost-effective production of the substance mixture of the invention.

In a further embodiment of the method according to the present invention, the acid-catalyzed reaction is a homogenous catalysis, wherein the catalyst and the educts may be in solution at least during the catalytic step of the reaction.

Further, an object of the invention is a fuel which can be obtained by the method of the invention, comprising at least part of the reaction mixture from step a) and at least one solvent.

Another object of the invention relates to the use of the fuel in combustion engines, turbines or combustion plants.

The aforementioned and claimed method of the invention, as described in the embodiment examples, is not subject to specific exclusion provisions with respect to its size, system design, material selection and technical concept such that the selection criteria known to the application field may be applied unrestrictedly.

Further details, features and advantages of the object of the invention may be derived from the subclaims and the following description of the drawings relating thereto, in which several embodiments of the method according to the present invention are depicted by way of example.

**BRIEF DESCRIPTION**

The present invention will be further explained by means of specific embodiments of the method with reference to the following drawings, without being restricted to this, wherein:

**FIG. 1** shows a method for producing a fuel comprising higher ethers; and

**FIG. 2** shows an alternative method for producing higher ethers.

**DETAILED DESCRIPTION**

**[0051]** FIG. 1 shows an assembly of the various process steps according to a preferred embodiment of the method. Following an optional precleansing, the educt isobutene is conducted to an appropriate reaction unit (A) via the stream (1), together with recycled isobutene (4) and recycled glycerol, mono-ether and catalyst (14). In a downstream process step, the reaction product (3) is freed of unreacted isobutene in a stripping column (B) (or alternatively a flash), which is then recycled to the reaction (4).

**[0052]** The liquid phase (5), which is led off the stripping column (B), is conducted further to a process step of liquid-liquid-extracting in a continuous extraction unit (C). As an extraction medium, which is supplied via stream (7), the fuel to be upgraded qualitatively may be employed directly.

**[0053]** To enhance the polar phase of the extraction, at least part of the glycerol to be supplied to the system is fed into the continuous extraction unit (C) via stream (6), if applicable, as this is not absolutely necessary for the process and dependent on the application. From the extraction unit (C), mixture (8) is supplied to the settling unit (C'). Depending on the design, this may occur via pumps from one container to the next (mixer-settler) or simply via an overflow weir (decanter).

**[0054]** In this embodiment, the head stream (10) of the continuous extraction unit is supplied to the extraction column and is extracted with a further stream of fresh glycerol (11). The head stream (13) of the system unit (D) may be used directly as a fuel or may be diluted to the corresponding volume fraction of the higher ethers. The extracts rich in glycerol (9), (12) are cycled back into the reactor (14).

**[0055]** It should be noted that the head stream (10) may be made further use of directly, without further extraction, which depends on the application.

**[0056]** FIG. 2 shows a variant of the process according to an alternative preferred embodiment of the invention, in order to isolate the higher ethers. Herein, the streams and system units of FIG. 2 correspond to the process of FIG. 1, if not indicated otherwise.

**[0057]** In the process of FIG. 2, the unpoluble raffinate (13) is supplied to a rectification unit (E), or optionally a flash, to thermally separate the extraction medium in order to recycle it. The separated, low-boiling extraction medium is recycled via stream (7) into the continuous extraction unit (C), and the higher ethers as high boiling components are recovered via stream (15).

**[0058]** The individual combinations of the components and the features of the aforementioned embodiments are exemplary only; the exchange and the substitution of these teachings with other teachings, which are included in this disclosure, and with the cited disclosures are also explicitly contemplated. It will be apparent to those skilled in the art that variations, modifications and other embodiments than those described herein may be made thereto without departing from the spirit and scope of the invention. Accordingly, the above description is by way of example and not to be construed as limiting. The word “comprising”, as used in the claims, does not preclude other constituents or steps. The indefinite article “a/an” does not preclude the meaning of a plural. The mere fact that certain measures are cited in mutually different claims does not illustrate that a combination of these measures may not be utilized in an advantageous manner. The scope of the invention is defined by the following claims and the associated equivalents. Furthermore, the used reference signs are not limiting the claimed scope of the invention.
1. A method for producing a mixture of substances comprising higher tertiary butyl ethers of glycerol, comprising the steps:
a) reacting an acid-catalyzed reaction of isobutene with glycerol to form a reaction mixture; and
b) extracting at least part of the reaction mixture from step a) by means of at least one solvent, wherein the at least one solvent or a mixture of solvents comprises an ∊<sup>r</sup>(30) value of ≤0.35.
2. A method according to claim 1, wherein a volume ratio of the at least one solvent and the reaction mixture of step a) is within a range of ≤0.8:1 and ≤1.5:1.
3. A method according to claim 1, wherein a molar ratio of the educts isobutene and glycerol is in a range of ≥1:0.5 and ≤1:5.
4. A method according to claim 1, wherein the temperature of the reaction mixture of step a) is between ≥60° C. and ≤130° C.

5. A method according to claim 1, wherein a conversion is effected at a pressure of ≥10 bar to ≤20 bar.
6. A method according to claim 1, wherein the acid from step a) has a pKa value of ≤2.
7. A method according to claim 1, wherein the higher tertiary butyl ethers of glycerol are extracted out of a liquid reaction product by means of a carbon containing stream.
8. A method according to claim 1, wherein the acid-catalyzed reaction from step a) is a homogenous catalysis.
9. A fuel, obtainable by a method according to claim 1, comprising at least part of the reaction mixture from step a) and at least one solvent.
10. The fuel of claim 9, wherein a use of the fuel includes combustion engines, turbines or combustion plants.

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