# PROCESS FOR REMOVING AN ALKANOL IMPURITY FROM AN ORGANIC CARBONATE STREAM

The present invention relates to a process for removing an alkanol impurity from a stream containing an organic carbonate and the alkanol impurity.

Examples of organic carbonates are cyclic alkylene carbonates (such as ethylene carbonate) and non-cyclic dialkyl carbonates (such as diethyl carbonate). It is well known to make cyclic alkylene carbonate by reaction of alkylene oxide (such as ethylene oxide) with carbon dioxide in the presence of a suitable catalyst. Such processes have been described for example in US4508927 and US5508442.

Dialkyl carbonates can be produced by reaction of alkylene carbonate with alkanol. Where alkylene carbonate (such as ethylene carbonate) is reacted with alkanol (such as ethanol), the products are dialkyl carbonate (such as diethyl carbonate) and alkanediol (such as monoethylene glycol). Such process is well-known and an example thereof is disclosed in US5359118. This document discloses a process in which di($C_1$-$C_4$ alkyl) carbonates alkanediols are prepared by transesterification of an alkylene carbonate with a $C_1$-$C_4$ alkanol.

At various points within said total process producing dialkyl carbonate from alkylene oxide via alkylene carbonate, organic carbonate streams containing one or more alkanol impurities may be produced. An example of such alkanol impurity is an ether alkanol, for example an alkoxy alkanol. For example, in a reactor where ethanol and ethylene carbonate are reacted into diethyl carbonate and monoethylene glycol, a side-reaction of ethanol with

ethylene oxide, formed by back-reaction of ethylene carbonate into ethylene oxide and carbon dioxide, into 2-ethoxyethanol (ethyl oxitol) may take place. Further, ethyl oxitol may be formed by a side-reaction of ethanol with ethylene carbonate in such a way that carbon dioxide is released and ethyl oxitol is produced. Still further, a side-reaction between ethanol and monoethylene glycol may take place producing ethyl oxitol and water. Still even further, ethyl oxitol may be formed via decarboxylation of hydroxyethyl ethyl carbonate.

Therefore, the product stream from a reactor where ethanol and ethylene carbonate are reacted into diethyl carbonate and monoethylene glycol, may comprise unconverted ethanol, unconverted ethylene carbonate, diethyl carbonate, monoethylene glycol and the above-mentioned ethyl oxitol impurity. The presence of said alkoxy alkanol impurity may be detrimental in any subsequent production process. Said alkoxy alkanol impurity may for example end up in the dialkyl carbonate that is used as a starting material for the synthesis of diphenyl carbonate from said dialkyl carbonate and phenol. For example, in a case where the dialkyl carbonate is diethyl carbonate and the alkoxy alkanol impurity is ethyl oxitol, said ethyl oxitol may react with the phenol starting material and/or with the diphenyl carbonate product.

Direct reaction of phenol and ethyl oxitol may result in the production of phenyl 2-ethoxyethyl ether, and hence in the loss of valuable phenol reactant. Further, such reaction results in the introduction of undesired chemicals in the process and therefore to separation issues.

Reaction of diphenyl carbonate with ethyl oxitol results in product loss as phenyl 2-ethoxyethyl carbonate is produced. Further, the latter product acts as a "poison" in any subsequent polymerisation of diphenyl carbonate into polycarbonate material. For example, when diphenyl carbonate is reacted with bis-phenol A (BPA), polycarbonate and phenol are formed. Diphenyl carbonate can react with BPA since phenol is a relatively good leaving group. Dialkyl carbonates (such as diethyl carbonate) however cannot be used to produce polycarbonate by reaction with BPA, since alkanols are not good leaving groups. Alkoxy alkanols (such as ethyl oxitol) are neither good leaving groups. Therefore, in case phenyl 2-ethoxyethyl carbonate is present in a diphenyl carbonate feed to be reacted with BPA, phenol will be released easily from said phenyl 2-ethoxyethyl carbonate but not ethyl oxitol which will consequently stop the polymerization process at one end of the chain. Consequently, phenyl 2-ethoxyethyl carbonate has to be removed from diphenyl carbonate before the latter is contacted with BPA.

The above exemplifies that in a case where an organic carbonate stream containing an alkanol impurity is formed, it is desired to remove said alkanol impurity before any subsequent process takes place wherein the organic carbonate is transformed into a valuable end product. For example, it is needed to remove any ethyl oxitol impurity from a diethyl carbonate stream containing said impurity before reaction of the diethyl carbonate with phenol takes place.

Referring to the above example where ethanol and ethylene carbonate have been reacted into diethyl carbonate and monoethylene glycol, the product stream

also containing unconverted ethanol and ethylene carbonate and ethyl oxitol side-product, may be separated by means of distillation. The boiling points for the various components in said product stream are mentioned in the table below.

| Component | Boiling point (°C) |
|---|---|
| ethanol | 78.4 |
| diethyl carbonate | 126-128 |
| ethyl oxitol | 135 |
| monoethylene glycol | 197.3 |
| ethylene carbonate | 260.4 |

The distillation as referred to above may result in a top stream containing diethyl carbonate and unconverted ethanol and a bottom stream containing monoethylene glycol and unconverted ethylene carbonate. Most likely, all of the ethyl oxitol ends up in the top stream. However, depending on the specific conditions under which distillation is carried out, part of the ethyl oxitol may end up in the bottom stream. Subsequently, said top stream may be further separated by means of distillation into a top stream containing unconverted ethanol which can be recycled to the reactor where diethyl carbonate and monoethylene glycol are produced, and a bottom stream containing diethyl carbonate and the ethyl oxitol impurity.

As discussed above, before an organic carbonate is transformed into a valuable end product in any subsequent process, the alkanol impurity has to be removed therefrom as that might interfere said subsequent process and/or any further processes. For the above example, this means that the ethyl oxitol impurity should be removed from the bottom stream containing diethyl carbonate and the ethyl

oxitol impurity. In principle, ethyl oxitol and diethyl carbonate could be separated by means of a further distillation step. However because of the small difference in boiling point between diethyl carbonate and ethyl oxitol (see above table), such separation is very cumbersome requiring many distillation steps and stages. Therefore, there is a need to find a simple method of removing an alkanol impurity from an organic carbonate stream containing such alkanol impurity.

Surprisingly it was found that by contacting the organic carbonate stream with an extraction solvent and separating the extraction solvent phase from the organic carbonate phase, such alkanol impurity is removed from such stream by extraction of the alkanol impurity into the extraction solvent phase.

Accordingly, the present invention relates to a process for removing an alkanol impurity from a stream containing an organic carbonate and the alkanol impurity, comprising contacting the stream with an extraction solvent and separating the extraction solvent phase from the organic carbonate phase.

The organic carbonate in the stream from which the alkanol impurity has to be removed in accordance with the present invention, may be a di($C_1$-$C_5$)alkyl carbonate, wherein the alkyl groups (straight, branched and/or cyclic) may be the same or different, such as methyl, ethyl and propyl; or a di($C_5$-$C_7$)aryl carbonate, wherein the aryl groups may be the same or different, such as phenyl; or a ($C_1$-$C_5$)alkyl ($C_5$-$C_7$)aryl carbonate, wherein the alkyl group and the aryl group are as defined above; or a cyclic ($C_1$-$C_{10}$) alkylene carbonate, such as the carbonate of ethylene, propylene, butadiene or styrene; or a mixture of such organic carbonates. Specifically,

the organic carbonate is a dialkyl carbonate, more specifically diethyl carbonate.

The alkanol impurity which has to be removed from the stream containing the organic carbonate and said impurity in accordance with the present invention, may be an ether alkanol, more specifically an alkoxy alkanol, most specifically 2-ethoxyethanol, as described above.

The amount of the alkanol impurity in the stream containing the organic carbonate and said impurity may be comprised in the range of from 0.1 to 10 wt.%, specifically 0.3 to 8 wt.%, more specifically 0.5 to 6 wt.% and most specifically 0.5 to 5 wt.%.

The contacting of the stream containing the organic carbonate and the alkanol impurity with the extraction solvent in the present process, results in the formation of an extraction solvent phase and an organic carbonate phase. In order to achieve that the extraction solvent phase contains said alkanol impurity, the alcohol impurity should be more soluble in the extraction solvent than in the organic carbonate. Preferably, the extraction solvent is a polar extraction solvent. More preferably, the extraction solvent is selected from the group consisting of water, $C_1$-$C_4$ aliphatic ketones, $C_1$-$C_4$ aliphatic alcohols and $C_1$-$C_4$ aliphatic carboxylic acids. More preferably, the extraction solvent is water or a $C_1$-$C_4$ aliphatic carboxylic acid, such as formic acid, acetic acid, propionic acid or butyric acid. Most preferably, the extraction solvent is water.

The time for contacting the stream containing the organic carbonate and the alkanol impurity with the extraction solvent in the present process should be sufficient to complete the extraction process. Said

contacting time may be in the order of 1 minute to 24 hours, for example 3 minutes to 12 hours.

The temperature at which the present invention is performed, that is to say the temperature of the biphasic mixture of extraction solvent and organic carbonate, may be comprised in the range of from -50 to 100 °C. Surprisingly, it has been found that at relatively low temperature the alcohol impurity is extracted into the extraction solvent to the greatest extent in the present process. This is illustrated in the Examples below. Therefore, in the present invention, said temperature is preferably comprised in the range of from 0 to 40 °C, more preferably 1 to 30 °C, more preferably 2 to 25 °C, and most preferably 2 to 10 °C. In accordance with the invention, the temperature is preferably at least 0 °C, more preferably at least 1 °C, more preferably at least 2 °C, and most preferably at least 3 °C. Further, in accordance with the invention, the temperature is preferably at most 40 °C, more preferably at most 35 °C, more preferably at most 30 °C, more preferably at most 25 °C, more preferably at most 20 °C, more preferably at most 15 °C, and most preferably at most 10 °C.

A suitable weight ratio of extraction solvent to the stream containing the organic carbonate and the alkanol impurity, is comprised in the range of from 10:1 to 1:10. Preferably, said weight ratio is comprised in the range of from 5:1 to 1:5, more preferably 3:1 to 1:3, even more preferably 2:1 to 1:2. Most preferably, said weight ratio amounts to 1:1.

The pressure at which the present process is carried out, may be subatmospheric, atmospheric or superatmospheric pressure. Preferably, said pressure is atmospheric pressure.

After said extraction, the extraction solvent phase should be separated from the organic carbonate phase, in accordance with the invention, so that a stream containing the organic carbonate from which stream alcohol impurity has been removed, remains. In the case where water is the extraction solvent, an aqueous phase has to be separated from an organic phase. Any skilled person can find a suitable method of separating the extraction solvent phase from the organic carbonate phase in the present process.

In a case where the stream containing the organic carbonate and the alkanol impurity, is a stream containing a dialkyl carbonate that has been produced from reacting an alkanol with an alkylene carbonate, the stream usually contains unconverted alkanol reactant in addition to the alkanol impurity. Reference is made to the introduction of the present specification wherein the formation of such organic carbonate stream is described.

In a case where the stream containing the organic carbonate and the alkanol impurity, is a stream containing dialkyl carbonate, unconverted alkanol and an alkanol impurity, contacting of said stream with an extraction solvent to extract and remove the alkanol impurity in accordance with the present invention, is preferably performed after the step wherein dialkyl carbonate is separated from unconverted alkanol.

Separation of the dialkyl carbonate from unconverted alkanol may be effected by means of distillation. Such distillation results in a top stream containing the unconverted alkanol (such as ethanol) and a bottom stream containing the dialkyl carbonate (such as diethyl carbonate), in a case where the unconverted alkanol has been reacted in a preceding step with an alkylene

carbonate to produce the dialkyl carbonate and an alkanediol.

The present invention advantageously results in the removal of an alkanol impurity in organic carbonate streams, which alkanol impurity might have interfered in any subsequent process using said organic carbonate if it would not have been removed.

Accordingly, the present invention also relates to a process for the preparation of a dialkyl carbonate and an alkanediol comprising:

(a) reacting an alkylene carbonate and an alkanol in the presence of a transesterification catalyst to obtain a product mixture containing unconverted alkylene carbonate, unconverted alkanol, dialkyl carbonate, alkanediol and an alkanol impurity;

(b) separating unconverted alkylene carbonate and alkanediol from the product mixture to obtain a top stream containing unconverted alkanol, dialkyl carbonate and the alkanol impurity;

(c) recovering the alkanediol; and

(d) separating unconverted alkanol from the top stream containing unconverted alkanol, dialkyl carbonate and the alkanol impurity obtained in step (b) to obtain a bottom stream containing dialkyl carbonate and the alkanol impurity, which process further comprises

(e) contacting the bottom stream containing dialkyl carbonate and the alkanol impurity obtained in step (d) with an extraction solvent and separating the extraction solvent phase from the organic carbonate phase.

All of the above-described embodiments and preferences in relation to the above-described general process for removing an alkanol impurity from a stream containing an organic carbonate and the alkanol impurity,

comprising contacting the stream with an extraction solvent and separating the extraction solvent phase from the organic carbonate phase, also apply to the above-mentioned specific process for the preparation of a dialkyl carbonate and an alkanediol, more in particular to step (e), respectively, of said process.

The transesterification catalyst to be used in step (a) of the above-mentioned process may be one of many suitable homogeneous and heterogeneous transesterification catalysts known from prior art.

For example, suitable homogeneous transesterification catalysts have been described in US5359118 and include hydrides, oxides, hydroxides, alkanolates, amides, or salts of alkali metals, i.e., lithium, sodium, potassium, rubidium and cesium. Preferred homogeneous transesterification catalysts are hydroxides or alkanolates of potassium or sodium. Other suitable homogeneous transesterification catalysts are alkali metal salts, such as acetates, propionates, butyrates, or carbonates. Suitable catalysts are described in US5359118 and the references mentioned therein, such as EP274953A, US3803201, EP1082A, and EP180387A.

Suitable heterogeneous transesterification catalysts to be used in step (a) of the above-mentioned process include ion exchange resins that contain functional groups. Suitable functional groups include tertiary amine groups and quaternary ammonium groups, and also sulphonic acid and carboxylic acid groups. Further suitable catalysts include alkali metal and alkaline earth metal silicates. Suitable catalysts have been disclosed in US4062884 and US4691041. The heterogeneous catalyst may be selected from ion exchange resins comprising a polystyrene matrix and tertiary amine functional groups.

An example is Amberlyst A-21 (ex Rohm & Haas) comprising a polystyrene matrix to which N,N-dimethylamine groups have been attached. Eight classes of transesterification catalysts, including ion exchange resins with tertiary amine and quaternary ammonium groups, are disclosed in J F Knifton et al., J. Mol. Catal, 67 (1991) 389ff.

Further transesterification conditions for step (a) of the above-mentioned process are known in the art and suitably include a temperature from 40 to 200 °C, and a pressure from 50 to 5000 kPa (0.5 to 50 bar).

Further, the present invention relates to a process for making a diaryl carbonate, comprising contacting, in the presence of a transesterification catalyst, an aryl alcohol with a stream containing a dialkyl carbonate from which stream an alkanol impurity has been removed in accordance with any one of the above-described processes.

Still further, the present invention relates to a process for making a diaryl carbonate, comprising contacting a stream containing a dialkyl carbonate and an alkanol impurity with an extraction solvent and separating the extraction solvent phase from the organic carbonate phase in accordance with any one of the above-described processes, and then contacting, in the presence of a transesterification catalyst, an aryl alcohol with the stream containing the dialkyl carbonate.

Preferably, said diaryl carbonate is diphenyl carbonate and said aryl alcohol is phenol.

In addition, the above-described transesterification catalyst and other transesterification conditions are equally applicable to said process for making a diaryl carbonate.

The invention is further illustrated by the following Examples.

Examples

A certain amount of a solution A containing 99.16 wt.% of diethyl carbonate (DEC), 0.76 wt.% of ethyl oxitol (EtOx; 2-ethoxyethanol) and 0.04 wt.% of ethanol (EtOH) was placed in a glass vial. A certain amount of deionised water (extraction solvent) was then added to said vial. The temperature, the amounts of solution A and water added, and the weight ratio of amount of added water to amount of added solution A, in Experiments 1-5 are mentioned in the table below.

| Exp. | T (°c) | $H_2O$ (g) | Sol. A (g) | $H_2O$:sol. A (wt.) |
|---|---|---|---|---|
| 1 | 3.0 | 3.7 | 3.8 | 1:1 |
| 2 | 21.2 | 14.9 | 15.0 | 1:1 |
| 3 | 64.0 | 4.0 | 4.1 | 1:1 |
| 4 | 64.0 | 3.06 | 4.15 | 0.7:1 |

The vial was then closed and homogenized by shaking for 5 minutes before it was allowed to phase separate at the above-mentioned temperature for one day. During said one-day period, the contents of the vials was re-homogenized three times. At the end of the experiment, the aqueous phase was separated from the organic phase and the composition of the samples was analyzed by means of gas chromatography, the results of which are shown in the table below.

| | DEC (wt.%) | EtOx (wt.%) | EtOH (wt.%) | |
|---|---|---|---|---|
| Solution A | 99.16 | 0.76 | 0.04 | % of EtOx removed **(*)** |
| Organic phase from Exp. | | | | |
| 1 | 99.97 | 0.00 | 0.00 | 100 |
| 2 | 99.90 | 0.06 | 0.003 | 92 |
| 3 | 99.67 | 0.26 | 0.03 | 66 |
| 4 | 99.59 | 0.34 | 0.04 | 55 |

**(*)** % of EtOx removed = {([wt.% EtOx in sol. A]-[wt.% EtOx in organic phase])/[wt.% EtOx in sol. A]}*100%

From the results in the above table it appears that the use, at a relatively low temperature, of water as an extractive solvent to extract ethyl oxitol out of a mixture containing diethyl carbonate and said ethyl oxitol, is an efficient means of removing alcohol impurity from an organic carbonate.

# C L A I M S

1. Process for removing an alkanol impurity from a stream containing an organic carbonate and the alkanol impurity, comprising contacting the stream with an extraction solvent and separating the extraction solvent phase from the organic carbonate phase.

2. Process according to claim 1, wherein the organic carbonate is a di($C_1$-$C_5$)alkyl carbonate, preferably diethyl carbonate; or a di($C_5$-$C_7$)aryl carbonate; or a ($C_1$-$C_5$)alkyl ($C_5$-$C_7$)aryl carbonate; or a cyclic ($C_1$-$C_{10}$) alkylene carbonate; or a mixture thereof.

3. Process according to any one of the preceding claims, wherein the alkanol impurity is an ether alkanol, more specifically an alkoxy alkanol, most specifically 2-ethoxyethanol.

4. Process according to claim 3, wherein the organic carbonate is diethyl carbonate and the alkanol impurity is 2-ethoxyethanol.

5. Process according to any one of the preceding claims, wherein the extraction solvent is selected from the group consisting of water, $C_1$-$C_4$ aliphatic ketones, $C_1$-$C_4$ aliphatic alcohols and $C_1$-$C_4$ aliphatic carboxylic acids.

6. Process according to any one of the preceding claims, wherein the temperature is comprised in the range of from 0 to 40 °C, preferably 1 to 30 °C, more preferably 2 to 25 °C, and most preferably 2 to 10 °C.

7. Process according to any one of the preceding claims, wherein the stream containing an organic carbonate and the alkanol impurity is obtained by a process for the

preparation of a dialkyl carbonate and an alkanediol comprising:

(a) reacting an alkylene carbonate and an alkanol in the presence of a transesterification catalyst to obtain a product mixture containing unconverted alkylene carbonate, unconverted alkanol, dialkyl carbonate, alkanediol and an alkanol impurity;

(b) separating unconverted alkylene carbonate and alkanediol from the product mixture to obtain a top stream containing unconverted alkanol, dialkyl carbonate and the alkanol impurity;

(c) recovering the alkanediol; and

(d) separating unconverted alkanol from the top stream containing unconverted alkanol, dialkyl carbonate and the alkanol impurity obtained in step (b) to obtain a bottom stream containing dialkyl carbonate and the alkanol impurity,

which process further comprises

(e) contacting the bottom stream containing dialkyl carbonate and the alkanol impurity obtained in step (d) with an extraction solvent and separating the extraction solvent phase from the organic carbonate phase.

8. Process according to claim 7, wherein the alkylene carbonate is ethylene carbonate, the unconverted alkanol is ethanol, the dialkyl carbonate is diethyl carbonate, the alkanediol is monoethylene glycol and the alkanol impurity is 2-ethoxyethanol.

9. Process for making a diaryl carbonate, comprising contacting, in the presence of a transesterification catalyst, an aryl alcohol with a stream containing a dialkyl carbonate from which stream an alkanol impurity has been removed in accordance with the process of any one of claims 1-8.

10. Process for making a diaryl carbonate, comprising contacting a stream containing a dialkyl carbonate and an alkanol impurity with an extraction solvent and separating the extraction solvent phase from the organic carbonate phase in accordance with the process of any one of claims 1-8, and then contacting, in the presence of a transesterification catalyst, an aryl alcohol with the stream containing the dialkyl carbonate.

11. Process according to claim 9 or 10, wherein the diaryl carbonate is diphenyl carbonate and the aryl alcohol is phenol.