PROCESS FOR PREPARING ALKANEDIOL AND DIALKYL CARBONATE

The present invention relates to a process for the preparation of an alkanediol and a dialkyl carbonate from an alkylene carbonate and an alkanol.

Such transesterification processes are known. According to these known transesterification processes, the reaction of the alkanol with the alkylene carbonate has to be effected in the presence of a transesterification catalyst. US5359118 discloses a process in which di(C_1-C_4 alkyl) carbonates and alkanediols are prepared by transesterification of an alkylene carbonate with a C_1-C_4 alkanol. Thereto, the process is carried out in the presence of a transesterification catalyst. The catalyst is usually homogeneous, although the use of heterogeneous catalysts is also suggested.

In general, heterogeneous catalysts are less active than their homogeneous counterparts. Further, they suffer from deactivation due to leaching of active species. Therefore, after some time, heterogeneous catalysts need to be replaced. This leaching also leads to problems in the purification section due to the presence of active species in the product.

According to US5359118, suitable homogeneous transesterification catalysts include hydrides, oxides, hydroxides, alcoholates, amides or salts of alkali metals. It is generally suggested to use such alkali metal compounds in amounts comprised in the broad range of from 0.001 to 2 wt.%, based on the reaction mixture to be reacted. More specifically, it is disclosed that in the process according to the invention of US5359118, in

fact relatively high concentrations of the active catalyst based on alkali metal compounds can be used without the occurrence of the yield-reducing and reaction course-impeding developments of carbon dioxide and the formation of polyols. The use of such high catalyst concentration is illustrated in the Example of US5359118, wherein a stream containing 4 wt.% of catalyst (potassium hydroxide) is recycled to reesterification column (I).

It is desirable, in a process for the preparation of an alkanediol and a dialkyl carbonate from an alkylene carbonate and an alkanol, to be able to perform the reaction in the presence of a relatively small amount of homogeneous transesterification catalyst while still achieving optimal conversion of the alkylene carbonate.

A drawback of using homogeneous transesterification catalysts is that they leave the reactor with one or more of the products. When entering the product purification section, their presence can cause detrimental side-reactions as well as induce reverse reactions, which prevent optimal overall conversion of the alkylene carbonate. Homogeneous transesterification catalysts are usually recycled, as is for example the case in the process as disclosed in US5359118. Such recycling involves complex and costly procedures.

It is an object of the present invention, in a process for the preparation of an alkanediol and a dialkyl carbonate from an alkylene carbonate and an alkanol, to achieve an optimal overall conversion of the alkylene carbonate when performing the process in the presence of only a relatively small amount of homogeneous transesterification catalyst, by preventing the catalyst from entering the product purification section.

Surprisingly, it was found that the above object is achieved by a process wherein the transesterification reaction is carried out in the presence of only 20 to 2,000 ppmw of the homogeneous transesterification catalyst, and in which process the reaction mixture is contacted with a solid sorbent, which latter treatment advantageously results in the removal or substantial removal of the catalyst before the product mixture is sent to the product purification section.

Accordingly, the present invention 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 homogeneous transesterification catalyst to obtain a mixture containing unconverted alkylene carbonate, unconverted alkanol, dialkyl carbonate, alkanediol and catalyst, wherein the catalyst amount is of from 20 to 2,000 ppmw based on the amount of the mixture;

(b) contacting the mixture from step (a) with a solid sorbent to obtain a mixture containing unconverted alkylene carbonate, unconverted alkanol, dialkyl carbonate and alkanediol and further containing either no catalyst or a substantially reduced amount of catalyst;

(c) separating the mixture from step (b) into a bottom stream containing unconverted alkylene carbonate and alkanediol and a top stream containing unconverted alkanol and dialkyl carbonate;

(d) recovering the alkanediol from the bottom stream from step (c); and

(e) recovering the dialkyl carbonate from the top stream from step (c).

Although the process of the present invention is described as a sequence of process steps, it is possible to carry out further process steps in between each of the process steps described.

In step (a) of the process of the present invention, the catalyst amount is of from 20 to 2,000 ppmw ("parts per million by weight"). Said amount is based on the amount (i.e. weight) of the mixture that is obtained in step (a) and which contains unconverted alkylene carbonate, unconverted alkanol, dialkyl carbonate, alkanediol and catalyst. Said catalyst amount is preferably of from 20 to 1,500 ppmw, more preferably of from 30 to 1,000 ppmw, more preferably of from 30 to 750 ppmw, more preferably of from 40 to 500 ppmw, more preferably of from 40 to 300 ppmw, more preferably of from 50 to 150 ppmw, and most preferably of from 60 to 100 ppmw.

Said catalyst amount in step (a) is at most 2,000 ppmw, preferably at most 1,750 ppmw, more preferably at most 1,500 ppmw, more preferably at most 1,250 ppmw, more preferably at most 1,000 ppmw, more preferably at most 750 ppmw, more preferably at most 500 ppmw, more preferably at most 400 ppmw, more preferably at most 300 ppmw, more preferably at most 200 ppmw, more preferably at most 150 ppmw, more preferably at most 120 ppmw, more preferably at most 100 ppmw, and most preferably at most 80 ppmw.

Said catalyst amount in step (a) is at least 20 ppmw, preferably at least 25 ppmw, more preferably at least 30 ppmw, more preferably at least 35 ppmw, more preferably at least 40 ppmw, more preferably at least 45 ppmw, more

preferably at least 50 ppmw, more preferably at least 55 ppmw, and most preferably at least 60 ppmw.

Suitable transesterification conditions for step (a) of the process of the present invention include a temperature of from 40 to 200 °C, and a pressure of from 50 to 5000 kPa (0.5 to 50 bar). The temperature at which step (a) of the process of the present invention is carried out, is preferably of from 50 to 150 °C, more preferably of from 60 to 140 °C, more preferably of from 80 to 140 °C, and most preferably of from 100 to 140 °C. Said temperature is preferably at most 200 °C, more preferably at most 180 °C, more preferably at most 160 °C, more preferably at most 150 °C, more preferably at most 145 °C, more preferably at most 140 °C, and most preferably at most 135 °C. Said temperature is preferably at least 40 °C, more preferably at least 50 °C, more preferably at least 60 °C, more preferably at least 70 °C, more preferably at least 80 °C, more preferably at least 90 °C, more preferably at least 100 °C, and most preferably at least 110 °C.

The homogeneous transesterification catalyst to be used in step (a) of the process of the present invention may be one of many suitable homogeneous 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, that is to say lithium, sodium, potassium, rubidium and cesium. In the present invention, the homogeneous transesterification catalyst is preferably an alkali metal hydroxide or alkanolate, wherein said alkali metal is preferably potassium or

sodium. More preferably, said catalyst is an alkali metal alkanolate, wherein said alkali metal is preferably sodium. Where the catalyst is an alkali metal alkanolate, such as a sodium alkanolate, it is advantageous to use the alkanolate of the alkanol that is being used as feedstock to step (a). For example, where the alkanol is ethanol, it is advantageous to use sodium ethoxide as the catalyst.

Other suitable homogeneous transesterification catalysts to be used in step (a) of the process of the present invention 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. Thus, the transesterification catalyst is generally a basic catalyst.

In step (b) of the process of the present invention, the mixture from step (a) is contacted with solid sorbent. This may be achieved by passing said mixture through a guard bed containing solid sorbent. It was found that solid sorbent removes the catalyst substantially, to such a level that it no longer is harmful in any subsequent purification procedure.

The solid sorbent may have a void content of from 50 to 98 vol.%. The void content of the solid sorbent is considered to be the void volume between the solid particles. Potential pores inside the solid particles are not taken into account. The void content is based on total volume of solid sorbent particles and volume between these particles. Preferably, the solid sorbent has a void content of at least 55 vol.%, more preferably at least 60 vol.%. The upper limit depends on the desired

strength of the solid sorbent particles. Usually, the void content can be at most 98 vol.%, more specifically at most 90 vol.%, most specifically at most 80 vol.%.

Many solid sorbents are suitable for use in the present invention. It is preferred that the solid sorbent does not react to a substantial degree with the other components in the reaction mixture which mixture includes unconverted alkylene carbonate, unconverted alkanol, dialkyl carbonate, alkanediol. Therefore, from this point of view, the sorbent is preferably an inert solid, more preferably one or more solids chosen from the group consisting of silica, silica gel, glass, alumina, more especially alpha-alumina, molecular sieves, clay and minerals. However, as in step (a) the transesterification catalyst is generally a basic catalyst, it is preferred that the solid sorbent to be used in step (b) contains acid groups. Preferably, the solid sorbent is a clay or ion exchange resin which contains acid groups such as for example sulfonic acid groups or carboxylic acid groups. Carboxylic acid groups are preferred because they do not react with the mixture to be treated. An acidic activated clay or weakly acidic ion exchange resin may thus be used as the solid sorbent. It has been found that with such acidic solid sorbents it is possible to prevent the other components in the reaction mixture from further reacting and at the same time to substantially remove the transesterification catalyst.

Although the solid sorbent can be present in one or more separate reactors which may be arranged in parallel or in series, it is preferred from an economic point of view that the solid sorbent is present in the

transesterification reactor used in step (a) near the outlet for the reaction mixture in said latter reactor.

In the present specification, sorption means a process in which one substance (the sorption agent or sorbent) takes up or holds another substance by absorption, adsorption or a combination of both.

In step (b) of the present process, a mixture is obtained which contains unconverted alkylene carbonate, unconverted alkanol, dialkyl carbonate and alkanediol and which further contains either no catalyst or a substantially reduced amount of catalyst. By "substantially reduced amount of catalyst" it is meant an amount less than 50, preferably less than 40, more preferably less than 30, more preferably less than 25, more preferably less than 20, more preferably less than 15, and most preferably less than 10 ppmw of catalyst, based on the amount (i.e. weight) of said mixture obtained in step (b).

Not all of the reaction mixture from step (a) needs to be subjected to step (b). However, from an efficiency point of view, preferably all of said reaction mixure is subjected to step (b), as in such case the residual catalyst amount can be minimized as much as possible.

The solid sorbent preferably sorbs the catalyst reversibly so that the solid sorbent, after having removed the catalyst therefrom, can be re-used. However, the solid sorbent may also be used only once and then discarded.

In step (c) of the process of the present invention, the mixture from step (b) is separated into a bottom stream containing unconverted alkylene carbonate and alkanediol and a top stream containing unconverted

alkanol and dialkyl carbonate. Any skilled person knows how to effect such separation, for example by means of distillation.

In step (d) of the process of the present invention, the alkanediol is recovered from the bottom stream from step (c). Any skilled person knows how to effect such recovery, for example by means of distillation.

In step (e) of the process of the present invention, the dialkyl carbonate is recovered from the top stream from step (c). Any skilled person knows how to effect such recovery, for example by means of distillation.

The invention is further illustrated by the following Examples.

Examples

A. Preparation of dialkyl carbonate

The following procedure was used to prepare diethyl carbonate (DEC) from the cyclic carbonate ethylene carbonate (eC) or propylene carbonate (pC) and ethanol (EtOH) at low catalyst concentrations.

The reactions were performed in a temperature controlled multitube autoclave. Agitation was obtained by mechanical shaking of the autoclave. Sodium ethoxide (NaOEt) catalyst, ethanol and cyclic carbonate (eC or pC) were mixed in a sealed vial prior to heat treatment in the autoclave. The catalyst was added as a solution in ethanol (made from 250 mg of NaOEt and 100 g of EtOH). After 4 hours of heat treatment, the vials were cooled down to 4 °C and samples of the reaction mixtures in the vials were analyzed by means of gas chromatography.

Three different autoclave temperatures were investigated: 65, 120 and 130 °C. Target yields of 30% DEC from eC and 10% DEC from pC were set. The yield of

DEC was calculated as the molar concentration of DEC at the end of the experiment divided by the molar concentration of cyclic carbonate (eC or pC) at the beginning of the experiment. EtOH was used in 4 times molar excess over the cyclic carbonate.

It was determined which minimum catalyst concentration (in ppmw, based on total weight of the reaction mixture) was needed at each of said autoclave temperatures to achieve the above-mentioned target yields. These minimum catalyst concentrations are shown in the table below.

	T = 65 °C		T = 120 °C		T = 130 °C	
	eC	pC	eC	pC	eC	pC
Catalyst concentration	900	1,200	200	250	70	100

From the above table it appears that the minimum catalyst concentrations needed to achieve the target yields were only in the ppm region, thus resulting in the use of less catalyst. When the temperature was raised to 120 °C and further to 130 °C, said concentrations needed to achieve the target yields were significantly dropped as shown above.

B. Removal of catalyst from carbonate containing mixture

A solution of 180 g of a carbonate containing mixture, the composition of which is shown in the table below, and 116 ppmw of NaOEt catalyst (based on said weight of 180 g), was treated with a solid sorbent.

Component in carbonate containing mixture	Amount (in wt.%)
ethanol	75.3
ethylene carbonate	12.9
diethyl carbonate	7.4
monoethylene glycol	4.1
hydroxyethyl ethyl carbonate	0.3

The following two sorbents were tested (separately): (1) 1.02 g of BASF acidic activated clay F24, and (2) 1.09 g of DOWEX MAC 3 ion weakly acidic ion exchange resin.

During the treatment, < 2 ml samples were taken and analysed by means of Inductively Coupled Plasma (ICP) spectrometry. The measured catalyst concentrations were plotted against time for the two sorbents tested. The concentrations at t = 1,200 minutes is shown in the table below for both treatments.

Solid sorbent	Catalyst concentration (ppmw)	
	t = 0	t = 1,200 min.
BASF F24 clay	116	22
DOWEX MAC3 resin	116	7

From the above table it appears that both said solid sorbents were capable of effectively reducing the catalyst conentrations to levels at which they are no longer considered to be harmful in any subsequent purification procedure.

C L A I M S

1. 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 homogeneous transesterification catalyst to obtain a mixture containing unconverted alkylene carbonate, unconverted alkanol, dialkyl carbonate, alkanediol and catalyst, wherein the catalyst amount is of from 20 to 2,000 ppmw based on the amount of the mixture;

(b) contacting the mixture from step (a) with a solid sorbent to obtain a mixture containing unconverted alkylene carbonate, unconverted alkanol, dialkyl carbonate and alkanediol and further containing either no catalyst or a substantially reduced amount of catalyst;

(c) separating the mixture from step (b) into a bottom stream containing unconverted alkylene carbonate and alkanediol and a top stream containing unconverted alkanol and dialkyl carbonate;

(d) recovering the alkanediol from the bottom stream from step (c); and

(e) recovering the dialkyl carbonate from the top stream from step (c).

2. Process according to claim 1, wherein the homogeneous transesterification catalyst is an alkali metal hydroxide or alkanolate.

3. Process according to any one of the preceding claims, wherein the solid sorbent is a clay or ion exchange resin which contains acid groups.

4. Process according to claim 3, wherein the acid groups are carboxylic acid groups.

5. Process according to any one of the preceding claims, wherein the mixture from step (b) contains less than 50 ppmw of catalyst based on the amount of the mixture.