

Green Chemistry

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard [Terms & Conditions](#) and the [ethical guidelines](#) that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Synthesis of glycerol 1,2-carbonate by transesterification of glycerol with dimethyl carbonate using triethylamine as a facile separable homogeneous catalyst

José R. Ochoa-Gómez,^{*a,b} Olga Gómez-Jiménez-Aberasturi^a, Camilo Ramírez-López^a and Belén Maestro-Madurga^a

Received (in XXX, XXX) Xth XXXXXXXXX 200X, Accepted Xth XXXXXXXXX 200X

DOI: 10.1039/b000000x

The synthesis of glycerol 1,2-carbonate (GC) by transesterification of glycerol with dimethyl carbonate (DMC) using triethylamine (TEA) as a facile separable homogeneous catalyst has been studied at 10 different temperatures, DMC/glycerol molar ratios and TEA/glycerol molar ratios. Reaction rate increases dramatically with temperature and TEA/glycerol molar ratio but reaction is difficult to stop in the target molecule at the highest TEA/glycerol molar ratios because GC undergoes further transesterification to glycerol dicarbonate (GDC). However, a good reaction control can be achieved by working at a TEA/glycerol molar ratio of 0.1: a 99% glycerol conversion and a 98% GC yield are obtained in 2.5 h 15 with a DMC/glycerol molar ratio of 4 at refluxing temperature (88°C → 68°C). At 90°C glycidol is also formed in 6-10% yields. A mechanism to justify its synthesis is proposed. GDC formation can be avoided at conversions below 100% but in this case GC is highly impurified with glycerol after solvent removal by evaporation. To separate both chemicals a liquid-liquid extraction method has been developed. Selective extraction solvents for GC, such as methyl isobutyl ketone (MIBK) or DMC, were found using 20 the method of miscibility numbers. GC is selectively extracted at room temperature in MIBK in a 100% yield with purity higher than 98% from a glycerol/GC mixture consisting of 80 wt% GC by using a MIBK/mixture mass ratio of 1.6 and three extraction steps.

Introduction

As it is well known, the increasing use of glycerol in the last 15 25 years as a building block is a consequence of its greater availability at lower prices due to its production surplus associated to the biodiesel manufacturing. Glycerol 1,2-carbonate (4-hydroxymethyl-1,3-dioxolan-2-one, CAS #931-40-8) is one of its valuable derivatives which has been already incorporated to 30 the portfolio of companies such as Huntsman and Ube Industries Limited.

The increasing industrial attention for glycerol 1,2-carbonate (GC) is based on both its physical and chemical (reactivity) properties. GC is a multifunctional, not flammable (f.p. > 204°C), 35 water soluble, readily biodegradable, non toxic and slightly viscous (85.4 mPa.s at 25°C) liquid molecule with a very low evaporation rate (b.p. 110-115°C at 0.1 mm Hg). Additionally, it has a high renewable content (the mass percentage of the molecule coming from renewable sources) ranging between 76%, 40 if obtained from glycerol and another raw material apart from CO₂, and 100%, if it could be manufactured directly from glycerol and CO₂. All these features make GC a green chemical which is or can be used as a solvent, as a component in beauty & 45 ecocomposites, electrolytes for lithium and lithium-ion batteries, carrier in pharmaceutical preparations, and in the manufacturing

of chemical intermediates and polymers.¹⁻⁶

GC has been synthesized by a number of methods which have been reviewed by Ochoa-Gómez et al., with special emphasis on 50 those with industrial feasibility.⁷ Among these methods, transesterification of glycerol with an organic carbonate is the most studied, at least in the last 5 years. Ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) have been used as carbonylating sources using basic catalysts. As 55 stated by Ochoa-Gómez et al., the key for using one or other carbonate as raw material lies in most cases in using a cheap and/or easily recyclable catalyst. Thus, starting from EC, CaO, Al/Ca or Mg-mixed oxides and Li-hydrotalcite,⁸ basic resins and zeolites,⁹ and immobilized ionic liquids¹⁰ have been used as 60 catalysts with glycerol conversions of 85-100% and GC selectivities of 84-99%. Typical catalysts from DMC are K₂CO₃,¹¹ CaO,¹²⁻¹⁴ Ca(OH)₂ and calcium diglyceroxide,¹⁵ K₂CO₃/MgO,¹⁶ Mg-Al hydrotalcite in DMF as solvent,¹⁷ KF-hydroxyapatite,¹⁸ Mg/Al/Zr mixed oxide¹⁹, lipases²⁰ and ionic 65 liquids,²¹ with conversions of 95-100% and selectivities of 95-99%. Finally, MgAl hydrotalcites supported on α- and γ-Al₂O₃ have been used as catalysts starting from diethyl carbonate in a continuous system (tubular reactor) using dimethyl sulfoxide as solvent, with conversions of 20-100% and selectivities of 60-

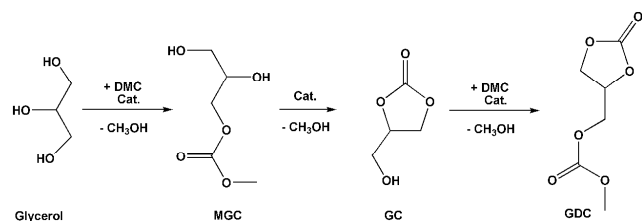
100% depending on the hydrotalcite type and operating conditions.²²

Of the above catalysts, K_2CO_3 is the only homogeneous one although another homogeneous catalysts such as NaOH have been also reported leading to a 100% conversion and a 95% yield.¹² A primary advantage of homogeneous catalysts is that reaction rates are generally higher than those with heterogeneous ones. However, a strong drawback of basic homogeneous solid catalysts used for synthesizing GC is that their separation from the reaction medium requires a neutralization step and the product must be recovered by distillation under reduced pressure. This why an overwhelming majority of the catalysts above mentioned are heterogeneous, which are claimed to be easily separable and recyclable by filtration. However, this is not true in many cases because, with the exception of the cheap and broadly commercially available CaO, they frequently require a cumbersome synthetic procedure, including consecutive steps of precipitation, aging, drying and calcination. Likewise, a costly regeneration step by washing and calcination is also too often needed after a few reaction cycles. It would therefore be desirable to have a homogeneous catalyst which satisfies the advantages of both homogeneous (high reaction rate) and heterogeneous (ease of separation and recycling) catalysts.

Amines have been used as homogeneous catalysts in transesterification reactions, e.g. for manufacturing biodiesel,²³ methyl acetate and methyl benzoate²⁴, and 1,4-butanediyl dimethacrylate.²⁵ Among them, triethylamine (TEA) is specially interesting because it has a boiling point (89.5 °C) high enough to provide a wide temperature window for reaction at ambient pressure but, at the same time, neither so low as to lead to handling problems nor so high as to preclude its easy separation by distillation at atmospheric pressure.

In this paper, the solvent-free synthesis of glycerol 1,2-carbonate from glycerol and DMC by transesterification using TEA as a facile separable homogeneous catalyst is reported as well as a method to separate glycerol and GC by liquid-liquid extraction.

Currently, it is well known that glycerol transesterification with DMC proceeds through a series of consecutive steps as depicted in Scheme 1. First, glycerol reacts with DMC to give methyl glyceryl carbonate (MGC) which subsequently undergoes a fast intramolecular transesterification to yield GC. Under suitable conditions (large excess of DMC and MeOH removal) GC reacts with DMC resulting in methyl (1,3-dioxolan-2-one-4-yl)methyl carbonate (glycerol dicarbonate, GDC) which may evolve to glycerol tricarbonate (not shown in Scheme 1) under DMC in large excess and long reaction times (48 h) as shown by Rokicki et al.¹¹



Scheme 1. Steps and intermediates in the transesterification of glycerol with DMC.

Results and discussion

All reactions were carried out in a batchwise mode because results from some preliminary experiments showed that if continuous distillation of methanol to shift quickly the equilibrium on right is carried out by using a rectifying column, it is very difficult to stop the reaction in GC since it is converted in a greater or lesser degree into GDC as it is formed. On a matter of fact, this is the way of obtaining GDC in very good yields as described in the *Experimental section*.

Influence of temperature

The variation of the OH/C=O FTIR peak absorbance ratio ($A_{OH}/A_{C=O}$) with reaction time at different temperatures is depicted in Fig. 1 at 4 and 0.3 DMC/glycerol and TEA/glycerol molar ratios, respectively. Conversions and yields are given in Table 1. As it can be seen, reaction rate increases dramatically with temperature, as expected. A > 99% glycerol conversion and a 91% GC yield were achieved at reflux (reflux temperature shifts from 88°C to 68-70°C as reaction proceeds as a consequence of methanol formation) in 1.25 h but under these conditions GDC was also obtained in 8% yield. GDC was not detected at lower temperatures. Likewise, in none of the reactions glycidol was detected.

The synthesis of 4-methyl-1,3-dioxolan-2-one and ethylene carbonate by reacting 2-methyl-1,3-propanediol and ethylene glycol, respectively, with DMC using TEA as a catalyst has been reported.²⁶ A temperature of 120°C and reactions times of 4-16 h were needed for obtaining conversions ranging from 81 to 99% with selectivities between 63% and 83%. However, high temperatures can not be used in the synthesis of GC as we shown in a previous paper, in which we reported the synthesis of GC from 3-chloro-1,2-propanediol and CO_2 using TEA as both solvent and CO_2 fixation-activation agent.²⁷ Above 100°C, GC yield decreases dramatically from 90% to 58% (135°C) due to GC polymerization. We hypothesized that GC polymerization could occur either through the formation of an alkoxide ion by reaction between the hydroxyl moiety of GC and TEA (see Scheme 2), which could initiate the glycerol 1,2-carbonate ring opening polymerization, or by the conversion of GC in glycidol which, in turn, can subsequently polymerize to polyglycerols. The first possibility is supported from results by Rokicki et al. who described the base-catalyzed ring opening polymerization of glycerol 1,2-carbonate at 170°C which proceeds with CO_2 evolution and yields hyperbranched aliphatic polyethers,¹¹ and the second one from results by Sandler and Berg who reported a vigorous polymerization of glycidol in the presence of TEA.²⁸

Table 1. Influence of temperature at a DMC/glycerol molar ratio of 4 and a TEA/glycerol molar ratio of 0.3.

T (°C)	t_R (h)	C	Y_{GC}	Y_{GDC}
25	24	35	34	0
40	22	60	58	0
55	8	62	60	0
Reflux	1.1	>99	91	8

t_R : reaction time; C: glycerol conversion (%); Y_{GC} : glycerol 1,2-carbonate yield (%); Y_{GDC} : glycerol dicarbonate yield (%).

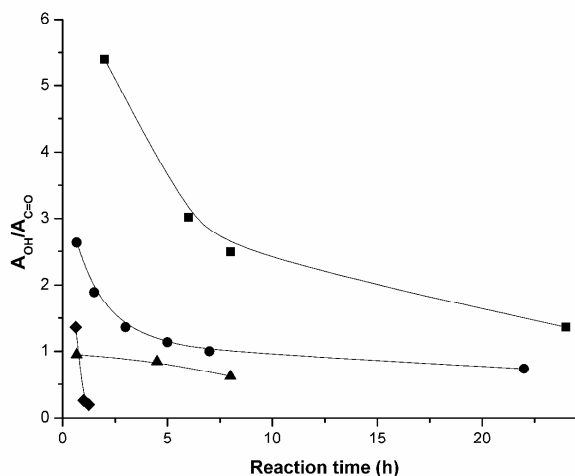
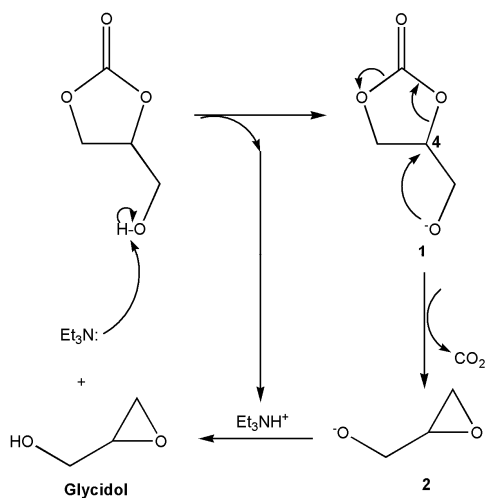


Fig. 1. Variation of the OH/C=O peak absorbance ratio with reaction time at different temperatures: 25°C (■); 40°C (●); 55°C (▲); Reflux (◆). DMC/glycerol molar ratio = 4; TEA/glycerol molar ratio = 0.3.

In fact, some reactions were carried out above the boiling temperature of the reaction mixture in closed vessels under autogeneous pressure, to determine whether GDC synthesis could be precluded or not by slowing down the reaction between GC and DMC as a consequence of the higher methanol concentration in the liquid phase under pressure. Experimental conditions were as follow: a TEA/glycerol molar ratio of 0.3, 90°C, 2 h and DMC/glycerol molar ratios ranging from 4 to 6. GDC synthesis could not be prevented but glycidol was additionally obtained in yields of 6-10%.



Scheme 2. Proposed mechanism for glycidol formation.

The formation of glycidol at 90°C can be explained through a mechanism as that depicted in Scheme 2. At a high enough temperature, TEA can abstract a proton from the hydroxyl moiety of GC resulting in the formation of the strong nucleophile 1,3-dioxolan-2-one-4-methoxide **1** and TEAH⁺, the conjugated acid of TEA. The negatively charged oxygen atom of **1** attacks intramolecularly to the carbon atom **4** in the ring resulting in the electron displacement shown in said Scheme thereby giving the 2,3-epoxy-1-propanolate **2** with CO₂ evolution. Finally, glycidol

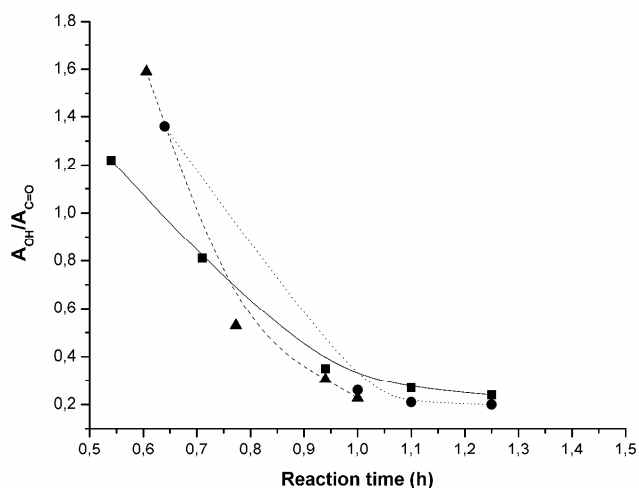


Fig. 2. Variation of the OH/C=O peak absorbance ratio with reaction time at different DMC/glycerol molar ratios: 2 (■); 4 (●); 6 (▲). T: reflux; TEA/glycerol molar ratio: 0.3.

is obtained by acid-base reaction between TEAH⁺ and **2**.

The above discussed dramatic drop in GC yield at temperatures above 90-100°C has interesting implications on the feasibility of the direct synthesis of GC from glycerol and CO₂. It is apparent that this route is at first the obvious choice for synthesizing GC because both reagents are green chemicals commercially available at a low price, there are not intermediate steps, and the atom efficiency could be as high as 87%.

However, up to now all attempts for carrying out this reaction have been unsuccessful due to poor CO₂ reactivity leading to a peak yield of 10%.²⁹ A more promising yield of 32% has been reported by George et al.,³⁰ although their results have not been confirmed by Dibenedetto et al.³¹ who claim that a minimum temperature of 180°C is needed for glycerol conversion. However, at this high temperature and in the presence of the catalysts used, all of them with basic sites, GC would be quickly converted into polyglycerols. Therefore, in our opinion the direct synthesis of GC from glycerol and CO₂ is not possible unless a catalyst able to carry out the reaction at temperatures below 100°C can be found.

According to the results obtained, refluxing temperature was chosen for carrying out the study of the influence of the remaining reaction variables, with the aim of finding experimental conditions for avoiding or reducing GDC formation while keeping a 100% conversion and a 100% GC selectivity.

55 Influence of DMC/glycerol molar ratio

The variation of A_{OH}/A_{C=O} with reaction time at different DMC/glycerol molar ratios (MR1) is depicted in Fig. 2 at refluxing temperature and 0.3 TEA/glycerol molar ratio. Conversions and yields are given in Table 2. Glycidol was not detected. Reaction rate is high in all cases, increasing with MR1 as a result of the equilibrium displacement on the right. However, this increase is slight because the positive influence of equilibrium displacement on reaction rate is partially counteracted by the negative influence of the decrease in both glycerol and TEA concentrations as MR1 increases. Conversions

and yields also increase with MR1 for the same reason.

Table 2. Influence of DMC/glycerol molar ratio (MR1) at refluxing temperature and 0.3 TEA/glycerol molar ratio.

MR1	t_R (h)	C	Y_{GC}	Y_{GDC}
2	1.0	94	92	<1
4	1.1	>99	91	8
6	1.25	100	89	12

5 Symbols as in Table 1

Despite that a very low GDC yield was obtained at a MR1 of 2 we decided to select a MR of 4 as the most suitable for further study because glycerol conversion was not 100% at the lower MR1 studied.

Influence of TEA/glycerol molar ratio

The variation of $A_{OH}/A_{C=O}$ with reaction time at different TEA/glycerol molar ratios (MR2) is depicted in Fig. 3 at refluxing temperature and a DMC/glycerol molar ratio of 4.

15 Conversions and yields are given in Table 3.

As it can be seen in Fig. 3, reaction rate decreases drastically below a MR2 of 0.2 because less catalytic molecules are available for reaction. In addition, reaction rate for GDC formation decreases in a higher degree than that for GC synthesis as it is apparent from results given in Table 3: GDC yield decreases from 8% at 0.3 MR2 to 2% at 0.1 MR2.

From results obtained we can conclude that a TEA/glycerol molar ratio of 0.1 is a good choice for GC synthesis. It allows combining the obtention of a very high glycerol conversion of 99% with a very low GDC yield of 2%, resulting in a process with a GC yield and selectivity of 98% and > 98%, respectively. Additionally, it facilitates the isolation of GC by evaporation avoiding GC conversion into GDC during this step.³² A higher TEA/glycerol molar ratio favours GDC formation while a lower one leads to a too slow reaction.

Separation-purification by liquid-liquid extraction

Results reported in the above section show that there is no need for separating glycerol from GC because conversion is practically 100%. However, another strategy could be stopping the reaction at a lower conversion for precluding GDC formation thereby obtaining a 100% GC selectivity as it could be the case in the process herein reported and in the one reported by M.G. Álvarez et al.²² The penalty is that a step for glycerol and GC separation is needed. Also, such a step is necessary if GC synthesis from glycerol is carried out by means of a process leading to conversions lower than 100%.^{20a} Consequently, we decided to develop a procedure for separating GC from glycerol.

Table 3. Influence of TEA/glycerol molar ratio (MR2) at refluxing temperature and 0.4 DMC/glycerol molar ratio.

MR2	t_R (h)	C	Y_{GC}	Y_{GDC}
0.1	2.5	99	98	2
0.2	1.25	>99	96	5
0.3	1.1	>99	91	8

45 Symbols as in Table 1

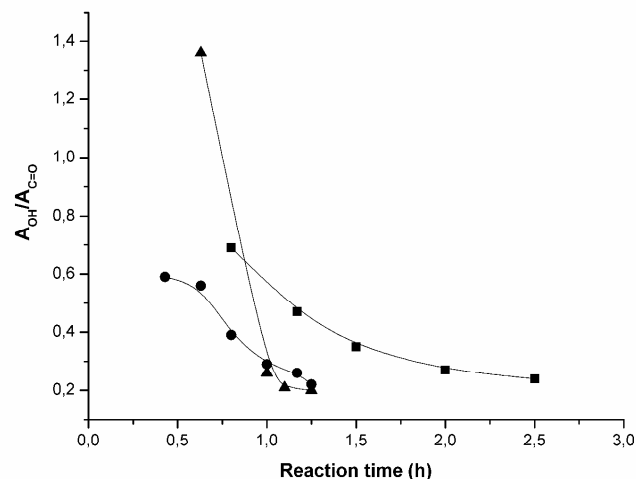


Fig.3. Variation of the OH/C=O peak absorbance ratio with reaction time at different TEA/glycerol molar ratios: 0.1 -■-; 0.2 -●-; 0.3 -▲-. T: reflux; DMC/glycerol molar ratio: 4.

Taking into account the high boiling points of both chemicals distillation was discarded. A good alternative could be liquid-liquid extraction (LLE) if either glycerol or GC were selectively soluble in a moderate (60-120°C) boiling point solvent to facilitate GC isolation from the extract by evaporation and also solvent recycling.

Recently, solubilities of GC and glycerol in 12 organic solvents, nitriles and ketones, have been published by Dubois et al.³³ According to their results, glycerol and GC should be easily separated by LLE with, e.g., acetonitrile (ACN, b.p. 82°C) because GC and glycerol solubilities in the same at room temperature are > 500 g/L and < 0,2 g/l, respectively. After extraction of GC in ACN and phase separation a raffinate of high purity glycerol and an extract consisting of a solution of GC in ACN would be theoretically obtained. Evaporation of ACN from the extract under slight reduced pressure would allow to obtain pure GC and to recover ACN for recycling. However, an experiment carried out with 10 g of a glycerol/GC mixture with a 10 wt% glycerol concentration showed that this is not possible. After adding 20 mL of ACN an homogeneous phase was obtained. It is apparent that GC helps to the dissolution of glycerol in ACN by forming hydrogen bonds.

Phase separation is produced when methyl ethyl ketone (MEK, b.p. 79.6°C), another of the solvents reported by Dubois et al., is used. But MEK is not suitable for extracting selectively GC because although GC solubility is > 500 g/L, glycerol solubility is 43 g/L, not enough low. Thus, when MEK (20 mL) was used to extract 10 g of a glycerol/GC mixture with a 20 wt% glycerol concentration, GC concentration in the extract after solvent removal was 90%, far away from 100%. Diethyl ketone (glycerol solubility = 50 g/L), also reported by Dubois et al., is not either suitable for the same reason.

Consequently, we decided to search for a suitable extraction solvent using the procedure for solvent selection via miscibility number (MN) developed by N.B. Godfrey.³⁴ According to this method, a solvent which has a MN that falls within the miscibility range of another solvent, should be miscible with that solvent.

For instance, glycerol has a MN of 1 and glycerol 1,2-carbonate of 3 while the miscibility range of ACN is 2-26. Consequently, GC should be soluble in ACN but glycerol should not, as occurs when these chemicals are not in admixture but not when they are

as we have stated above. The method is approximate but usually it works quite well and at least facilitates a rapid selection of potentially suitable solvents for liquid-liquid extraction.

All the extraction experiments were carried out using a glycerol/GC mixture with a 80 wt% GC concentration because it corresponds to a glycerol conversion of 80% leading to a 100% GC selectivity for all synthetic procedures based on transesterification of glycerol with an organic carbonate.

Two criteria were used for extraction solvent selection: 1) a boiling point of 60-120°C to facilitate separation of GC and extraction solvent by simple evaporation under slight reduced pressure; and 2) MN of 18-19, that is to say, more distant from the upper limit of the miscibility range of glycerol (16) than 17 (the MN for ACN and MEK, solvents theoretically suitable for our purpose but that did not work experimentally for the above-mentioned reasons) to ensure that glycerol is not miscible with them, but sufficiently close to the upper limit of the miscibility range of GC (18) to provide both phase separation in contact with a mixture of glycerol and GC, and the theoretical possibility of extracting GC selectively. Solvents accomplishing both criteria and leading to phase separation following the qualitative experimental procedure for LLE solvent selection described in the *Experimental section* were finally chosen for quantitative LLE experiments. Results are given in Table 4.

As it can be seen, three solvents accomplish the criteria to be used in GC-glycerol separation by LLE: methyl isobutyl ketone (MIBK), DMC and ethyl acetate. However, phase separation with ethyl acetate was slow and ethyl acetate phase was turbid indicating too much glycerol entrainment. Therefore, it was rejected as extraction solvent. At first, DMC was also rejected because, although phase separation was quick and clear, it has a relatively high 140 g/L solubility in water and the water/solvent mass ratio was, together with temperature, a variable to be studied. Thus, MIBK was chosen for LLE experiments. Both MIBK and DMC are not reported by Dubois et al.

Table 4. Solvent selection for glycerol 1,2-carbonate from glycerol by LLE

Solvent	MN	b.p. (°C)	PS	Suitable
Acetophenone	18	201	NT	No: High b.p.
Diethylene glycol monoethyl ether acetate	18	218	NT	No: High b.p.
Isophorone	18	215	NT	No: High b.p.
Tributyl phosphate	18	289	NT	No: High b.p.
1-Decanol	18	233	NT	No: High b.p.
Methyl isobutyl ketone	19	117	Yes	Yes
Ethyl acetate	19	77	Yes	Yes
DMC	19	90	Yes	Yes
Methyl amyl ketone	19	151	Yes	No: High b.p.
Ethylene glycol diacetate	19	187	NT	No: High b.p.
Ethylene glycol monoethyl ether acetate	19	156	NT	No: High b.p.
Methyl formate	19	32	NT	No: Low b.p.

MN: miscibility number; PS: phase separation; NT: not tested.

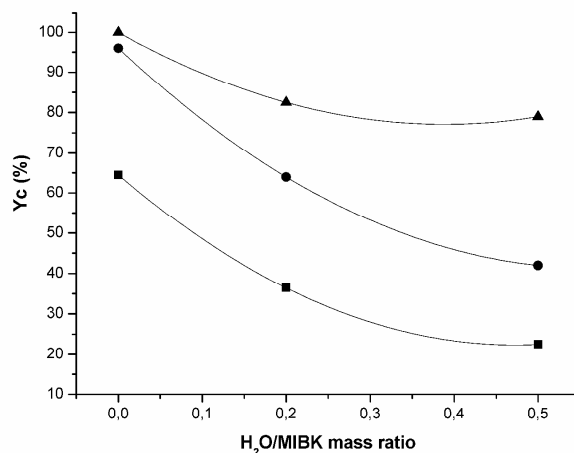


Fig. 4. Separation of glycerol 1,2-carbonate and glycerol by LLE with MIBK. GC cumulative yield (Y_c) as a function of water/MIBK mass ratio at 20°C. Number of extraction steps: 1 ■; 2 ●; 3 ▲.

The influence of $H_2O/MIBK$ mass ratio on the GC cumulative extraction yield (Y_c) at room temperature (20°C) for 1, 2 and 3 extraction steps is depicted in Fig. 4. The use of water as a solvent for the raffinate had two objectives: a) diminishing the viscosity of the glycerol-containing phase in order to favour phase separation, and b) decreasing the glycerol solubility in the extraction phase, due to the formation of hydrogen bonds with the extracted GC, by introducing in the raffinate a solvent with a strong hydrogen bonding capacity such as water. As it can be seen, Y_c increases as $H_2O/MIBK$ mass ratio decreases and also as the number of extraction steps increase, in such a way that a Y_c of 100% is achieved in three extraction steps when a $H_2O/MIBK$ mass ratio of 0 is used. In all experiments, GC purity after solvent removal in the extraction phase was > 98% indicating that glycerol 1,2-carbonate is selectively extracted independently of experimental conditions.

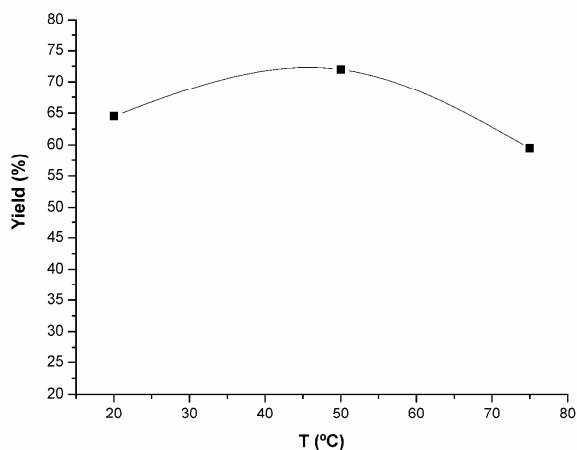
It is apparent that Y_c decreases as $H_2O/MIBK$ mass ratio increases because GC is freely soluble in water thanks to the interactions by hydrogen bonds between both molecules. Therefore, the more water in the feed the less GC amount in the extraction phase. This also means that a higher number of extraction steps are needed to achieve a 100% extraction yield when water is used as a solvent for the raffinate: three steps if $H_2O/MIBK$ mass ratio is 0, and 4 or more if it is ≥ 0.2 .

As the best results are achieved with a $H_2O/MIBK$ mass ratio of 0, DMC could also be an extraction solvent which it would be advantageous because it could be used as reagent, reaction solvent and also extraction solvent, thereby decreasing the chemicals inventory in an hypothetical manufacturing facility. An experiment carried out in a single extraction step at 20°C resulted in a 54% GC extraction yield with a 98% purity after solvent removal, i.e. similar results than those for MIBK ($Y_c = 59.5\%$, 98% pure).

The influence of temperature was studied for a single extraction step in order to determine whether an increase of the same allows a high increase in GC extraction yield or not, because this would lead to a remarkable decrease in the number of extraction steps needed for obtaining a GC extraction yield of

View Online

100%. Results are depicted in Fig. 5. Yc yield increases from ~64% to ~72% when temperature rises from 20 to 50°C and then decreases to ~60% at 75°C.



5 **Fig. 5.** Separation of glycerol 1,2-carbonate and glycerol by LLE with MIBK. GC extraction yield as a function of temperature for a single extraction step at a water/MIBK mass ratio of 0.

A plausible explanation of this behaviour may be related to a balance between glycerol-glycerol and GC-glycerol interactions on one hand, and GC-MIBK interactions on the other hand, both by hydrogen bonding. Below a critical temperature, glycerol-glycerol interactions predominate over GC-glycerol interactions and consequently GC can form hydrogen bonds with MIBK in a relatively easy way resulting in an increase of GC extraction yield with temperature. However, the energy input provided by the increase in temperature promotes the rupture of glycerol-glycerol hydrogen bonds in such a way that above such a critical temperature there are a high enough number of free glycerol molecules to interact preferentially with GC by hydrogen bonding resulting in a decrease in the extraction yield.

The eight point increment in the extraction yield from room temperature to 50°C is not enough so as to compensate neither the highest energetic expenditure nor the more expensive equipment and safety measurements needed at high temperatures. Therefore, room temperature is preferred for LLE of GC with MIBK from glycerol-GC mixtures.

Experimental

Materials

GC was supplied by Tokyo Chemical Industries (> 90% pure, it contains minor amounts of glycerol and GDC as shown by gas chromatography and FTIR (band at 1277 cm⁻¹ from GDC)). Glycerol dicarbonate was obtained as described below. All other chemicals were synthetic grade and were purchased from Sigma-Aldrich (Madrid, Spain).

35 Synthesis of glycerol dicarbonate (methyl (1,3-dioxolan-2-one-4-yl)methyl carbonate)

Glycerol (99.9%) (7.2 g, 77.5 mmol), dimethyl carbonate (69.8 g, 775 mmol) were placed into a 100 mL round bottom, 3-neck, glass reactor fitted with a magnetic stirrer, a 18-plates Vigreux

rectifying column, a reflux condenser and a thermometer. The reaction mixture was heated up to the reflux temperature under stirring in a glycerol bath kept at 100°C. Then K₂CO₃ (1.07 g, 7.75 mmol) was added as catalyst. The reaction was carried out by continuously removing methanol from the reaction mixture.

45 Reflux temperature decreased to 76°C in 7 min. Then, it was continuously increasing as a consequence of methanol removal by distillation and after 90 min (21 mL of DMC/methanol mixture distilled) it was 88°C, the boiling temperature of DMC at the pressure of our lab). The OH band was negligible as shown by FTIR. The reaction mixture was cooled, filtered and the filtrate was evaporated at vacuum on a rotatory evaporator at 80°C to remove DMC. The yellow liquid residue solidifies on cooling (12 g, 87.5% crude yield). After crystallization in 25 mL of ethanol, a crystalline yellowish white solid was obtained (10.5 g, 74%, m.p. 79-80°C).³⁵ The procedure herein described improves remarkably the 34% isolated yield reported by Rokicki et al.¹¹

Elemental analysis: Found: C, 41.0; H, 4.5. Calc. for C₆H₈O₆: C, 40.9; H, 4.6%.

60 FTIR $\nu_{\max}/\text{cm}^{-1}$ (film on a NaCl dish after melting at 110°C and spreading the solid): 1797 (C=O cyclic), 1755 (C=O linear), 1445 (OCH₃), 1397 (CH₂), 1277 (C(=O)-O-C linear), 1171 (C(=O)-O-C cyclic).

¹H NMR (400 MHz, DMSO-6_d; Me₄Si) δ (ppm) 5.05–5.07 (m, 1H, CH-O), 4.59 (t, 1H, OCH₂CHCH₂O-C(=O)OCH₃), 4.33–4.42 (m, 3H, -OCH₂CHCH₂O-C(=O)OCH₃, OCH₂CHCH₂O-C(=O)OCH₃), 3.74 (s, 3H, OCH₃).

¹³C NMR (100 MHz, DMSO-6_d; Me₄Si) δ (ppm) 56.1 (OCH₃); 66.9 (CH₂-O, ring); 67.9 (CH); 75.3 (CH₂-O, linear); 155.8 (C=O, cyclic); 155.9 (C=O, linear).

Experimental set up and reaction procedure

Glycerol (about 30 g, 0.325 mol) and DMC were mixed (in the specified molar ratios given in *Results and discussion* section) in a 0,25 L flat bottom, 4-neck, glass jacketed reactor fitted with a magnetic stirrer, a reflux condenser and a thermometer. The mixture was heated with stirring to the desired temperature by recirculating water through the jacket and then TEA was added to start the reaction. The degree of progression of the reaction was monitored by FTIR by following the variation of the OH/C=O peak absorbance ratio with time after automatic baseline correction and spectrum normalization at an absorbance of 1.0. The wave number of the OH peak shifts from 3368 cm⁻¹ (pure glycerol) to 3410–3435 cm⁻¹ (pure GC, with the wave number depending on the purity degree) as the reaction proceeds. 85 Carbonyl peak of GC appears at 1785–1790 cm⁻¹. For this purpose, some droplets were periodically withdrawn from the reaction mixture by means of a Pasteur pipette and placed on a NaCl dish, solvent was quickly evaporated at 110°C, the residue was spread with an adsorbent paper to form a thin film and the 90 FTIR spectrum was recorded using a Perkin Elmer Spectrum 2000 spectrometer. When OH/C=O absorbance ratio was constant or equal to the one of pure GC (0.20–0.22, depending on purity degree), reaction was stopped by cooling quickly the reaction mixture in an ice/water bath.³⁶ As an example, in Fig. 6 are 95 depicted the spectra obtained at different reaction times for the reaction carried out at reflux, a DMC/glycerol molar ratio of 2 and a TEA/glycerol molar ratio of 0.3. The peak at 921 cm⁻¹ is

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

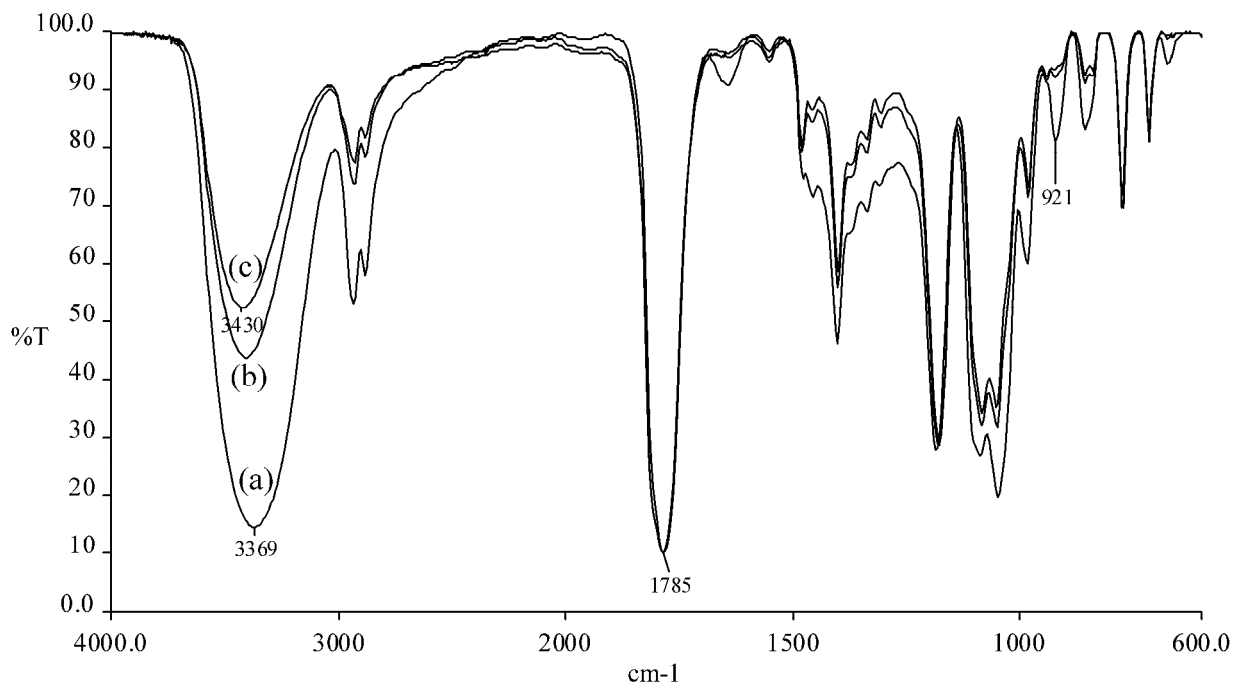


Fig. 6. Spectra obtained at different reaction times for the reaction carried out at reflux, a DMC/glycerol molar ratio of 2 and a TEA/glycerol molar ratio of 0.3: (a) 30 min, (b) 60 min, (c) 75 min.

characteristic of glycerol. The spectrum obtained at 75 min coincides with that of glycerol 1,2-carbonate.

Then, volatile chemicals were evaporated at vacuum on a rotatory evaporator at $\leq 40^\circ\text{C}$.³² The residue was analysed for glycerol conversion and glycerol 1,2-carbonate, glycidol and glycerol dicarbonate yields according to the analytical method given below. According to the stoichiometry of the reactions, yields of GC and GDC were calculated by dividing the number of moles of each product by the number of moles of the limiting reactant, with glycerol being always the limiting reactant under the experimental conditions used.

Reactions carried out at temperatures higher than the boiling point of the reaction mixture were performed in closed vessels under autogeneous pressure using an Autoclave Engineers model MagneDrive II equipped with 5 stainless steel vessels of 100 mL which can be operated simultaneously under different reaction conditions. In this case, reactions were not monitored by FTIR but carried out at a specified time after which reaction mixtures were worked-up and analyzed as before.

Liquid-liquid extraction procedure

Selection of suitable solvents for LLE was carried out according to the following qualitative procedure: in a test tube, GC (about 0.5 g) was mixed with 1 mL of the solvent to be tested and the mixture was shaken. If GC was not soluble, more solvent (1 mL) was added and it was rejected if insolubility went on. If soluble,

glycerol (about 0.1 g) was added to the mixture which was shook, and the solvent was chosen if phase separation occurred after halting shaking; if not, another 1 mL of solvent was added, the mixture was shaken again, shaking was halted and the solvent was selected if phase separation occurred and rejected if not.

Extraction experiments with the selected solvents (MIBK and DMC) were carried out as follow: 25 g of a mixture consisting of 80 wt % GC and 20 wt % glycerol was placed into a 100 mL beaker together with the necessary amount of water to give the desired H₂O/MIBK mass ratio, and the resulting solution was extracted with 50 mL of solvent under magnetic stirring for 5 min at the desired temperature. Then, the mixture was transferred to a separatory funnel for phase separation. The solvent of the upper phase (extract) was removed at vacuum in a rotatory evaporator and the concentration of GC in the residue was determined by measuring its refractive index using a Digital Abbe Refractometer Model way-1S. The GC percentage in the mixture was determined from a calibration curve obtained from mixtures of glycerol and GC standards of known concentrations.

This extraction procedure was repeated with the bottom phase (raffinate: glycerol plus unextracted GC plus water if present) to study the influence of the number of extraction steps on the extraction performance.

Analytical

Conversions, yields and GC purity were analyzed by gas

View Online

chromatography using a Varian 450-GC apparatus equipped with a split/splitless injection mode and a flame ionization detector according to the procedure previously reported.²⁷ Retention times (min): glycidol, 6,67; ethylene glycol (internal standard), 7,96; glycerol, 12,59; GDC, 15,15; GC, 15,77.

Elemental analysis were carried out by the *Servicios Técnicos de Investigación* of the University of Alicante (Alicante, Spain) in a Thermo Finnigan 1112 Series Flash Elemental Analyzer (ThermoFisher Scientific).

NMR spectra were carried out by Dr. Carmen Sanmartín of the Pharmaceutical and Organic Chemistry Department of the University of Navarra (Navarra, Spain) in a 400 MHz BRUKER AC NMR spectrometer using tetramethylsilane as internal reference and deuterated dimethyl sulfoxide as solvent.

Conclusions

The synthesis of glycerol 1,2-carbonate (GC) by transesterification of glycerol with dimethyl carbonate (DMC) can be carried out by using triethylamine (TEA) as a facile separable homogeneous catalyst. Reaction rate increases dramatically with temperature. At a TEA/glycerol molar ratio of 0.3 reaction is fast at refluxing temperature: a > 99% glycerol conversion and a 91% GC yield are achieved in about 1 h with a DMC/glycerol molar ratio of 4. However, at this high TEA/glycerol molar ratio is difficult to stop the reaction in the target molecule and glycerol dicarbonate (GDC) is also formed in a 8% yield. GDC yield increases both with TEA/glycerol and with DMC/glycerol molar ratios.

A good reaction control can be achieved by decreasing the TEA/glycerol molar ratio but at the expense of a longer reaction time. Thus, a 99% glycerol conversion and a 98% GC yield are obtained in 2.5 h with a TEA/glycerol molar ratio of 0.1 and a DMC/glycerol molar ratio of 4 at refluxing temperature. This low TEA/glycerol molar ratio also prevents the evolution of GC to GDC during GC isolation by evaporation under reduced pressure, which in any case must be carried out at $\leq 40^\circ\text{C}$.

Above 90°C glycidol is also obtained. Its synthesis can be justified by means of a mechanism in which TEA abstracts a proton from the hydroxyl moiety of GC resulting in the formation of the strong nucleophile 1,3-dioxolan-2-one-4-methoxide, which evolves to glycidol with CO_2 evolution through an intramolecular nucleophilic attack of the negatively charged oxygen atom to the methyne carbon in the ring.

GDC formation can be avoided working at conversions below 100% but in this case GC is highly impurified with glycerol after solvent removal by evaporation. To separate both chemicals a liquid-liquid extraction method has been developed using both methyl isobutyl ketone (MIBK) and DMC as selective extraction solvents for GC. GC can be extracted selectively at room temperature in a 100% yield from a glycerol/GC mixture consisting of 80 wt% GC by using a MIBK/mixture mass ratio of 1.6 and three extraction steps. GC purity is higher than 98% as shown by gas chromatography.

Acknowledgments

Thanks are due to the Ministerio de Economía y Competitividad of the Spanish Government for financial support (project

CTQ2009-11376 (sub-programme PPQ)). The contribution of Leire Lorenzo-Ibarreta to the experimental work is also gratefully acknowledged.

Notes and references

- ^a *TECNALIA, TECNALIA-Energy, Department of Bioenergy, Parque Tecnológico de Álava, Leonardo Da Vinci, 11, 01510 Miñano, Spain. Fax: +34 945198117; Tel: +34 629087981; E-mail: jramon.choa@tecnalia.com.*
- ^b *Universidad Alfonso X el Sabio, Department of Industrial Technology, Avda de la Universidad 1. 28696 Villanueva de la Cañada, Madrid, Spain. Fax: +34 91 8109781; Tel: +34 629087981; E-mail: jrochoag@telefonica.net*
- F.M. Kerton, in *Alternative Solvents for Green Chemistry*; RSC Green Chemistry Book Series, RSC Publishing, Cambridge, 2009, pp. 103-104.
- J. Kahre, T. Loehl, H. Tesmann, and H. Hensen, *DE Pat.*, 19 756 454, 1999.
- JEFFSOL® GC, *Glycerine Carbonate in Beauty & Personal Care*, Huntsman Technical Bulletin, 2011, http://www.huntsman.com/performance_products/Media/JeffsolGCMar2011.pdf
- D.P. Abraham, *US Pat. Appl.*, 2011/0117445A1, 2011.
- C. Magniont, G. Escadeillas, C. Oms-Multon and P. De Caro, *Cem. Concr. Res.* 2010, **40**, 1072-1080.
- A.T. Brooker, *EP Pat.*, 2 380 958, 2011.
- J.R. Ochoa-Gómez, O. Gómez-Jiménez-Aberasturi, C. Ramírez-López and Mikel Belsué, *Org. Process. Res. Dev.*, 2012, **16**, 389-399.
- M.J. Climent, A. Corma, P. De Frutos, S. Iborra, M. Noy, A. Velty and P. Concepción, *J. Catal.*, 2010, **269**, 140-149.
- Z. Mouloungui, J.W. Yoo, C. Gachen and A. Gaset, *EP Pat.*, 0 739 888, 1996.
- H.-J. Cho, H.-M. Kwon, J. Tharun, and D.-W. Park, *J. Ind. Eng. Chem.*, 2010, **16**, 679-683.
- G. Rokicki, P. Rakoczy, P. Parzuchowski, M. Sobiecki, *Green Chem.*, 2005, **7**, 529-539.
- J.R. Ochoa-Gómez, O. Gómez-Jiménez-Aberasturi, B. Maestro-Madurga, A. Pesquera-Rodríguez, C. Ramírez-López, L. Lorenzo-Ibarreta, J. Torrecilla-Soria and M.C. Villarán-Velasco, *Appl. Catal. A*, 2009, **336**, 315-324;
- J. Li and T. Wang, *J. Chem. Thermodyn.* 2011, **43**, 731-736.
- F.S.H. Simanjuntak, T.K. Kim, S.D. Lee, B.S. Ahn, H.S. Kim and L. Hyunjo, *Appl. Catal. A*, 2011, **401**, 220-225.
- J. Li and T. Wang, *Reac. Kinet. Mech. Cat.*, 2011, **102**, 113-126.
- M. Du, Q. Li, W. Dong, T. Geng and Y. Jiang, *Res. Chem. Intermed.*, 2012, **38**, 1069-1077.
- A. Takagaki, K. Iwatani, S. Nishimura and K. Ebitani, *Green Chem.*, 2010, **12**, 578-581.
- R. Bai, S. Wang, F. Mei, T. Li and G. J. Li, *Ind. Eng. Chem.* 2011, **17**, 777-781.
- M. Malyaadri, K. Jagadeeswaraiyah, P.S. Sai Prasad and N. Lingaiah, *Appl. Catal. A*, 2011, **401**, 153-157.
- (a) M. Tudorache, L. Protesescu, S. Coman and V. I. Parvulescu, *Green Chem.*, 2012, **14**, 478-48219; (b) K.H. Lee, C.H. Park and E.Y. Lee, *Bioprocess Biosyst. Eng.* 2010, **33**, 1059-65; (c) S.C. Kim, Y.H. Kim, H. Lee, D.Y. Yoon and B.K. Song, *J. Mol. Catal. B: Enzym.* 2007, **49**, 75-78.
- C. Chiappe and S. Rajamani, *Pure Appl. Chem.* ASAP article, 2012, **84**, 755-762.
- (a) M.G. Alvarez, A.M. Segarra, S. Contreras, J.E. Sueiras, F. Medina and F. Figueras, *Chem. Eng. J.*, 2010, **161**, 340-345; (b) M.G. Alvarez, M. Plíšková, A.M. Segarra, F. Medina and F. Figueras, *Appl. Catal. B*, 2012, **113-114**, 212-220.
- (a) L. Zhang, W. Guo, D. Liu, J. Yao, L. Ji, N. Xu and E. Min, *Energy Fuels*, 2008, **22**, 1353-1357; (b) L. Wang, Z. Tang, W. Xu and J. Yang, *Catal. Commun.*, 2007, **8**, 1511-1515.

- 24 L. Xing-Quan, J. Zhao-Xia, W. Yu-Tang and Y. Zuo-Long, *J. Nat. Gas Chem.*, 199, **8**, 76-92.
- 25 D. Derouet, G.T.M. Nguyen and J-C. Brosse, *Eur. Polym. J.*, 2002, **38**, 2017-2021.
- 5 26 R.A. Grey, *US Pat.*, 5 091 543, 1992.
- 27 J. R. Ochoa-Gómez, O. Gómez-Jiménez-Aberasturi, C. Ramírez-López, J. Nieto-Mestre, B. Maestro-Madurga and M. Belsué, *Chem. Eng. J.*, 2011, **175**, 505-511.
- 28 S.R. Sandler and F.R. Berg, *J. Polym. Sci. A: Polym. Chem.*, 1996, **4**, 1253-1259.
- 10 29 (a) M. Aresta, A. Dibenedetto, F. Nocito and C. Pastore, *J. Mol. Catal. A: Chem.*, 2006, **257**, 149-153; (b) M. Aresta, A. Dibenedetto, C. Pastore, A. Angelini, B. Aresta and I.J. Pápai, *J. Catal.*, 2010, **269**, 44-52; (c) M. Aresta, A. Dibenedetto, C. Pastore, C. Cuocci, B. Aresta, S. Cometa and E. De Giglio, *Catal. Today*, 2008, **137**, 125-131; (d) A. Dibenedetto, M. Aresta, C. Fragale, M. Distaso, C. Pastore, A.M. Venezia, C.J. Liu and M. Zhang, *Catal. Today* 2008, **137**, 44-51.
- 30 J. George, Y. Patel, S. Muthukumar and P.J. Munshi, *J. Mol. Catal. A: Chem.* 2009, **304**, 1-7.
- 31 A. Dibenedetto, A. Angelini, M. Aresta, J. Ethiraj, C. Fragale and F. Nocito, *Tetrahedron*, 2011, **67**, 1308-1313.
- 32 Keeping evaporation temperature equal or below 40°C is crucial, mainly at the higher TEA concentrations and the higher DMC/glycerol molar ratios. Otherwise, reaction goes on and GC is converted into glycerol dicarbonate by transesterification with DMC as long as TEA is not completely evaporated.
- 25 33 J.-L. Dubois, M. Aresta, A. Dibenedetto, C. Ferragina and F. Nocito, *US Pat. Appl.*, 2011/0245513 A1, 2011.
- 30 34 (a) N.B. Godfrey, *Chem. Technol.*, 1972, **2**, 359-363; (b) www.huntsman.com/performance_products/.../miscibility_predictor.pdf.
- 35 Heating time must be minimized as much as possible. In some batches a transesterification between GDC and ethanol resulting in glycerol 1,2-carbonate was observed with a consequent reduction in yield.
- 35 36 Reaction progression can also be monitored by means of the boiling point of the reaction mixture which decreases with reaction time from 88°C, the boiling point of DMC at the pressure of our lab, to 68-70°C, the boiling point of the DMC-MeOH mixture obtained under reaction conditions.
- 40