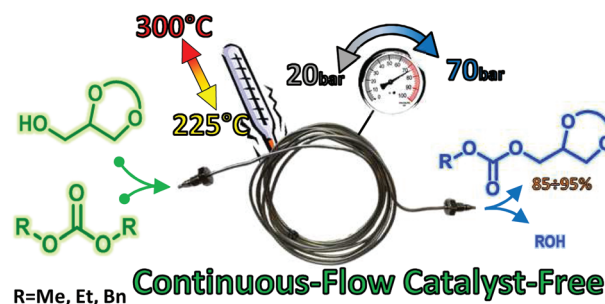# Green Chemistry

1

Upgrading of glycerol acetals by thermal catalyst-free transesterification of dialkyl carbonates under continuous-flow conditions

M. Selva,* S. Guidi and M. Noè

At 225–300 °C and 20–70 bar, glycerol acetals are upgraded by a continuous-flow catalyst-free transesterification of dialkyl and alkylene carbonates.

Please check this proof carefully. **Our staff will not read it in detail after you have returned it.**

Translation errors between word-processor files and typesetting systems can occur so the whole proof needs to be read. Please pay particular attention to: tabulated material; equations; numerical data; figures and graphics; and references. If you have not already indicated the corresponding author(s) please mark their name(s) with an asterisk. Please e-mail a list of corrections or the PDF with electronic notes attached – do not change the text within the PDF file or send a revised manuscript. Corrections at this stage should be minor and not involve extensive changes. All corrections must be sent at the same time.

Please bear in mind that minor layout improvements, e.g. in line breaking, table widths and graphic placement, are routinely applied to the final version.

We will publish articles on the web as soon as possible after receiving your corrections; **no late corrections will be made**.

Please return your **final** corrections, where possible within **48 hours** of receipt, by e-mail to: green@rsc.org

Queries for the attention of the authors

Editor's queries are marked like this [Q1 , Q2 , ...], and for your convenience line numbers are indicated like this [5, 10, 15, ...].

Please ensure that all queries are answered when returning your proof corrections so that publication of your article is not delayed.

Query Reference	Query	Remarks
Q1	For your information: You can cite this article before you receive notification of the page numbers by using the following format: (authors), Green Chem., (year), DOI: 10.1039/ c4gc01750a.	
Q2	Please carefully check the spelling of all author names. This is important for the correct indexing and future citation of your article. No late corrections can be made.	
Q3	As two versions of Scheme 4 and associated caption were supplied, the second version of Scheme 4 has been changed to Scheme 5 and all of the subsequent schemes renumbered accordingly. Please check that the renumbering is correct and that all of the citations within the text correspond to the correct scheme, and indicate any changes required.	
Q4	The meaning of the phrase "the process originated also sizable amounts of" in the sentence beginning "However, in sc-DMC, the nature..." is not clear - please clarify.	
Q5	Ref. 12d is cited within the text but does not appear to be included in the reference list. Do you wish to add this reference to the reference list or would you like the citation to be removed from the text?	
Q6	Ref. 3c: Can this reference be updated?	

Green Chemistry

PAPER

Q1

Q2

Upgrading of glycerol acetals by thermal catalyst-free transesterification of dialkyl carbonates under continuous-flow conditions†

M. Selva,* S. Guidi and M. Noè

At 250–300 °C and 30–50 bar, a continuous-flow (CF) transesterification of different dialkyl and alkylene carbonates (dimethyl-, diethyl-, dibenzyl-, and propylene carbonate, respectively) with two glycerol derived acetals (glycerol formal and solketal) was investigated without any catalyst. An unprecedented result was obtained; not only the desired process occurred, but also the formation of the corresponding mono-transesterification products took place with an excellent selectivity (up to 98%) in all cases. Under isothermal conditions, a study on the effect of pressure allowed us to optimize the conversion of acetals (up to 95%) for the reactions of dimethyl- and diethyl-carbonate (DMC and DEC, respectively). This proved that an abrupt progress of the reaction occurred for very small increments of pressure. For example, at 250 °C, the thermal transesterification of DMC with glycerol formal showed a sharp increase of the conversion from 1–2% at 30 bar to ~85% at 37 bar. The lower the temperature, the lower the pressure interval at which the onset of the reaction is achieved. The absence of catalysts allowed us to run CF-reactions virtually indefinitely and with a very high productivity (up to 68 mg min^{-1}) compared to the capacity (1 mL) of the used CF-reactor. Products of the transesterification of DMC and DEC were isolated in good-to-almost quantitative yields. In the case of heavier carbonates, steric reasons were responsible for the considerably lower reactivity of propylene carbonate (PC) with respect to DMC and DEC, while the transesterification of dibenzyl carbonate (DBnC, solid at room temperature) with glycerol formal required the presence of acetone as an additional solvent/carrier. Although the reactions of both PC and DBnC were not optimized, results offered a proof-of-concept on the extension of thermal transesterification processes to higher homologues of linear and alkylene carbonates.

Introduction

The upgrade of biomass-derived glycerol generally encompasses two classes of reactions: (a) oxidations or reductions to prepare mostly three-carbon atom derivatives, and (b) conversion of glycerol into higher homologues.[1,2] Only to cite a few examples, class (a) often includes metal (Pd, Pt, Bi and Au)-catalysed oxidation[3] and hydrogenation/hydrogenolysis processes,[4] as well as fermentative pathways to produce 1,2- and 1,3-PDO (1,x-propanediol), dihydroxyacetone, glyceric and tartronic acids, biosurfactants (glycolipids), and other organic acids (pyruvic and citric acids),[5] while class (b) is mainly oriented to the chemical conversion of glycerol into (i) esters (especially di- and tri-acetylglycerols) and ethers for pharma-

ceuticals, cosmetics, fuel and food additives, and polymers,[1a,6] (ii) epichlorohydrin (epicerol™) for epoxyresins,[7] (iii) glycerol carbonate and acetals for polymer, surfactant and solvent/antifreezing applications.[8] This massive activity also fuels another area of investigation dealing with the upgrading of major glycerol derivatives. In this context, some years ago, we focused our attention on acetals of glycerol, particularly the most commonly used glycerol formal [GlyF: a mixture of 5-hydroxy-1,3-dioxane (**1a**) and (1,3-dioxolan-4-yl)methanol (**1a′**) in ~3 : 2 ratio, respectively] and solketal [**2a**: 2,2-dimethyl-(1,3-dioxolan-4-yl)methanol] (Scheme 1).

Department of Molecular Sciences and Nanosystems, Centre for Sustainable Technologies, Università Ca' Foscari Venezia, Calle Larga S. Marta, 2137-30123 Venezia, Italy. E-mail: selva@unive.it
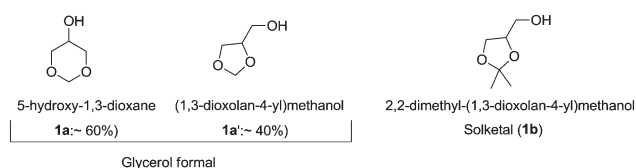
Scheme 1 Most used acetals of glycerol.
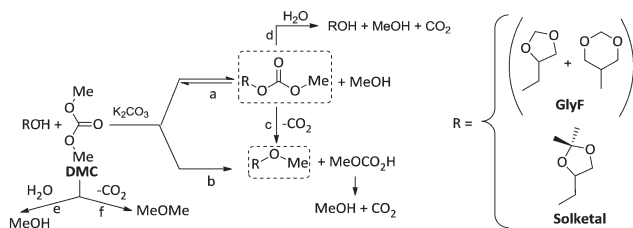
Scheme 2 The mechanism for the methylation of GlyF and Solketal with DMC.[10]

Scheme 3 Selective mono-transesterification of dialkyl carbonates with glycerol acetals.

Both these compounds display attractive physicochemical and reactivity properties; they are high-boiling thermally stable products, miscible with common organic solvents, and they possess a short OH-capped tether (hydroxymethylene group) which allows a synthetic access to a number of other functionalities. Moreover, GlyF and **1b** are safe compounds; they are classified as non-toxic species.[9]
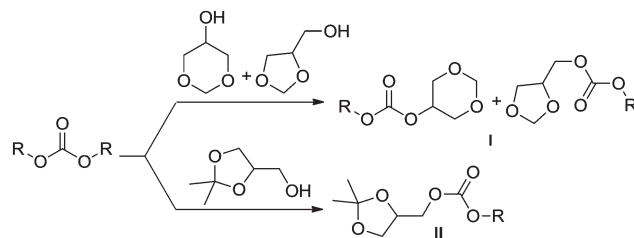
These features stimulated us to explore innovative protocols for the conversion of glycerol acetals into high added-value derivatives. Recently, we succeeded in the reaction of glycerol formal and solketal with different dialkyl carbonates (dimethyl, diethyl-, and dibenzyl-carbonates); under batch conditions (≥ 200 °C), we were able to demonstrate that a highly selective (up to 99%) and high-yielding (80–99%) O-alkylation reaction of acetals occurred at $T \geq 200$ °C and in the presence of K_2CO_3 as a catalyst.[10] Scheme 2 shows the model reaction with dimethyl carbonate (DMC).

The overall transformation could be explained by a combined sequence of alkylation, carboxyalkylation, decarboxylation and hydrolysis processes. Both methyl and carboxymethyl derivatives of acetals were initially formed (ROMe and $ROCO_2Me$, respectively; paths a and b). However, as the methylation proceeded, the reversible transesterification backtracked; $ROCO_2Me$ gradually decreased to zero, while ROMe became the final product. The disappearance of the carboxymethyl product was further assisted by competitive decarboxylation and hydrolysis reactions [paths (c) and (d)][11] that also took place for DMC [paths (e) and (f)].

Besides the synthetic value, the procedure also exemplified a genuine green model since it coupled innocuous renewables (glycerol acetals) to non-toxic alkylating agents such as DAlCs in a catalytic reaction.

In continuation of this investigation we decided to explore the same reaction with a different objective, *i.e.* the selective mono-transesterification of dialkyl carbonates with glycerol acetals (Scheme 3).

No previous studies were available in the literature for such a transformation. Among the possibilities to envisage a synthetic protocol, organocatalysis offered an attractive perspective. As recently reported by us,[12] new weakly basic carboxylate and methylcarbonate phosphonium salts may act as very efficient ionic liquid catalysts for the mono-transesterification of organic carbonates with primary and secondary alcohols, and diols as well. However, other very preliminary results of our group suggested that the reaction (mono-transesterification) could take place also under catalyst-free batch conditions provided that a reasonably high temperature (≥ 200 °C) and pressure were used.[10] Of the two (organocatalysis and catalyst-free) options, the second one was more promising since in the absence of catalysts, operative conditions and product separation procedures could be simplified; moreover, an easier implementation of large scale production could be devised. These aspects have inspired the present work in which we demonstrate that the catalyst-free transesterification in Scheme 3 can be optimized under continuous-flow (CF) conditions. In the CF mode, the reaction of linear and cyclic dialkyl carbonates such as dimethyl-, diethyl-, dibenzyl-, and propylene-carbonate with glycerol formal and solketal proceeds towards the formation of the corresponding mono-transesterification products (I and II, Scheme 3) with a selectivity up to 98% even at substantially quantitative conversions of acetals. This excellent result has been achieved by an investigation of the combined effect of temperature, pressure, and flow rate. For example, at 250–300 °C, the reaction of DMC with GlyF shows a sharp increase of the substrate conversion (from 1–2 to ~85%) for small increments of the pressure in the range of 20–50 bar; the lower the temperature, the lower the pressure interval at which the onset of the reaction is achieved. This behaviour, although less pronounced with heavier and less reactive carbonates, indicates that the outcome of the transesterification is affected by the increase of the density (with pressure) of the reactant mixtures, suggesting the occurrence of the transformation under supercritical conditions. The study has taken advantage from the typical benefits of CF-methodologies, not only for the optimization of the process parameters and productivity, but also for the product separation and the minimization of reaction volumes. In short, a process intensification aiming at improvements of synthetic, energetic and economic efficiencies of the reaction has been achieved.

Results

The CF-apparatus

A schematic chart of the experimental setup used for continuous-flow (CF) reactions is depicted in Fig. 1.

The major components of the apparatus included twin HPLC pumps (P_1 and P_2) for the separate delivery of liquid
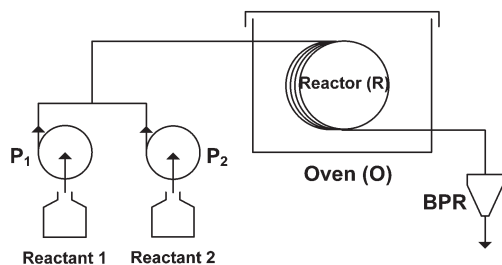
Fig. 1 Experimental setup used for continuous-flow reactions of DMC and GlyF.

reactants (dialkyl carbonates and acetals), a thermostated oven (O) equipped with additional thermocouples for temperature control, a tubular reactor (R) made of an empty spiral-shaped 1/16″ steel tube (L = 1.6 m; V = 1.02 mL), and a back-pressure regulator (BPR) for pressure control.

Dialkyl carbonates including dimethyl-, diethyl-, and propylene-carbonate, and acetals such as glycerol formal and solketal were commercially available ACS grade compounds. Dibenzyl carbonate was prepared according to a procedure recently reported by us.[12c]

Effects of the pressure and the temperature

The catalyst-free reaction of dimethyl carbonate with glycerol formal was chosen as a model process to begin the investigation.

The conditions for the initial tests, in particular the temperature and the reactant molar ratio, were selected according to our preliminary results obtained for batch reactions;[10] four sets of experiments were carried out isothermally at 225, 250, 275, and 300 °C, respectively, using a constant DMC : GlyF molar ratio (Q) of 20 (the excess DMC served both as a reagent and a carrier/solvent). In each experiment, a mixture of DMC (48.6 mL) and GlyF (2.5 mL) was fed to the reactor at a combined volumetric flow rate of 0.05 mL min^{-1}. The pressure was stepwise increased from the ambient value up to 100 bar; typical increments were of 5–10 bar. At any given pressure, the reaction was allowed to proceed for 90 min. Periodic GC/MS analyses of the mixture, collected at the reactor outlet, showed that both the conversion and the product distribution remained steady after a time interval of 60–80 min. Under conditions when a threshold pressure in the range of 20–50 bar was exceeded, an unprecedented result was obtained; not only the desired process occurred, but also the formation of the mono-transesterification product took place with a very high selectivity, over 95% (Scheme 4).

In particular, two isomeric carbonates **2a** and **2a′** [1,3-dioxan-5-yl methyl carbonate and (1,3-dioxolan-4-yl)methyl
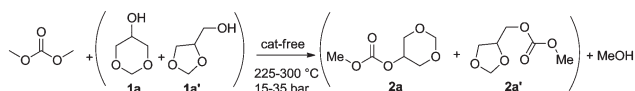
methyl carbonate, respectively] were obtained in the same (3 : 2) relative ratio of the starting acetals **1a** and **1a′**. The structures of **2a/2a′** were assigned by GC/MS and NMR analyses. Other by-products (total ≤5%) derived from the double trans-esterification of DMC with GlyF.

Fig. 2a–d show the trend of reaction conversion and selectivity observed as a function of pressure at each of the investigated temperatures.

In no case did the reaction take place at ambient pressure. However, very small pressure increments could dramatically affect the process. For example, at the lowest investigated temperature (225 °C), a significant enhancement of the conversion from 2 to 48% was achieved between 15 and 20 bar (Fig. 2a). No further improvements of the reaction outcome were appreciated at higher pressures. An analogous behavior was observed as the temperature was increased, though an even more remarkable effect was manifest. At 250 °C, the conversion of GlyF sharply boosted up from 1% to 85% once the applied pressure went from 20 to 27 bar. Then, it (conversion) remained steady throughout the range of 30–60 bar (Fig. 2b). The same held true at 275 °C, where a steep rise of the conversion (up to 87%) was observed between 30 and 37 bar (Fig. 2c). A slightly different trend occurred at 300 °C; the reaction profile followed a gentler sloped sigmoidal curve that reached a stable value of 85–87% only at 50 bar (Fig. 2d).

The comparison of Fig. 2b–d indicated that an equilibrium conversion of ∼85% could be achieved at 250–300 °C. However, as the temperature was increased, the pressure necessary for the reaction to proceed must be progressively augmented from 27 to 37, and to 50 bar, respectively. At 225 °C, although a lower equilibrium conversion (48%) was achieved, a lower operative pressure (20 bar) was required.

An additional test was also devised under batch conditions: a solution (40 mL) of GlyF and DMC in 1 : 20 molar ratio was charged in a glass reactor placed inside a stainless steel autoclave (inner volume 150 mL). Attention was paid to avoid any contact of reagents with inner walls of the autoclave. The overall system was heated at 200 °C for 24 hours. GC/MS analyses of the final reaction mixture showed that the conversion was 84% with a mono-transesterification selectivity of 93% (the only by-product was from the double transesterification of DMC with GlyF). This result definitely proved the thermal nature of the reaction. Since the process occurred in a glass liner, any contribution of catalysis by metal components of stainless steel was ruled out.

Recycle of the mixture, reproducibility, mass balance, and productivity

CF-processes are particularly suited to perform recycling operations aimed at improving the reaction outcome and the final productivity. Accordingly, based on previous results of Fig. 2, two sets (A and B) of experiments were carried out to optimize the conversion of the investigated mono-transesterification. Conditions were those of Fig. 2c. In set A, a continuous reaction of DMC and GlyF (in a 20 : 1 molar ratio, 0.05 mL min^{-1}) was allowed to proceed at 275 °C and 60 bar, for 18 hours.

Scheme 4 The catalyst-free selective transesterification of DMC with glycerol formal.
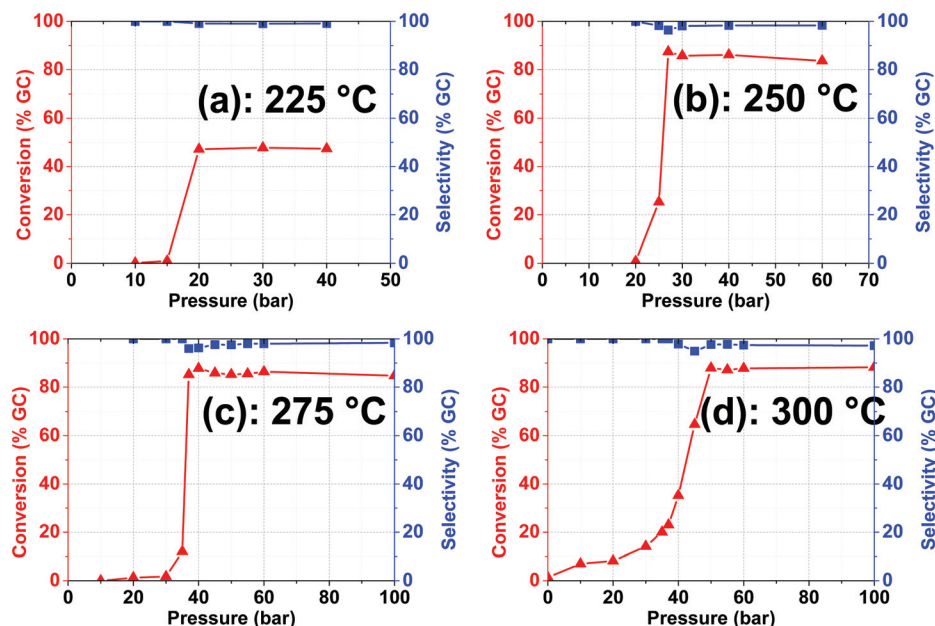
Fig. 2 Effects of temperature and pressure on the non-catalytic (thermal) transesterification of dimethyl carbonate (DMC) with glycerol formal. Four isothermal profiles are shown at: (i) molar ratio Q = DMC : GlyF = 20; (ii) flow rate = 0.05 mL min^{-1}; (iii) sampling time (at any pressure) = 1.5 hours.

Samples of the mixture at the reactor outlet were analyzed at time intervals (by GC/MS, every 1.5 hours). The colourless clear solution (54 mL) recovered at the end of the test was distilled to remove the MeOH–DMC azeotrope (70 : 30 v/v, 2.5 mL; bp = 62–65 °C) formed during the reaction,[13] and the initial volume was restored by addition of fresh DMC. The solution was then recycled by feeding it to the CF-reactor where another reaction was allowed to occur under the above described conditions (275 °C, 60 bar, 0.05 mL min^{-1}). Also in this case, the composition of the mixture at the reactor outlet was periodically monitored by GC/MS.

In set B, two subsequent CF-reactions of DMC and GlyF were performed using the same procedure of set A, except for the fact that no fresh DMC was added between the first and the second reaction. The results are reported in Fig. 3 where the conversion of GlyF and the mono-transesterification selectivity are reported for the two sequential sets of experiments.

Three major aspects emerged: (i) an equilibrium position was readily achieved in all cases. GC/MS analyses showed that mixtures recovered at the reactor outlet preserved the same composition throughout the experiment, from 1 to 18 hours. On average, before the recycle, mixtures were composed of unreacted acetal (**1a/1a′**, 12–13% in total), transesterification product (**2a/2a′**, 84–86% in total), and minor by-products (≤2–3%) (Fig. 3: bars 1, 2 and 5, 6, respectively); while, recycled mixtures (after the second pass through the CF-reactor) contained less than 5% of GlyF and by-products, the remainder being the desired compound (**2a/2a′**) (bars 3, 4 and 7, 8, respectively). This proved that the recycle could improve the conversion of GlyF from ~85% up to a substantially quantitat-
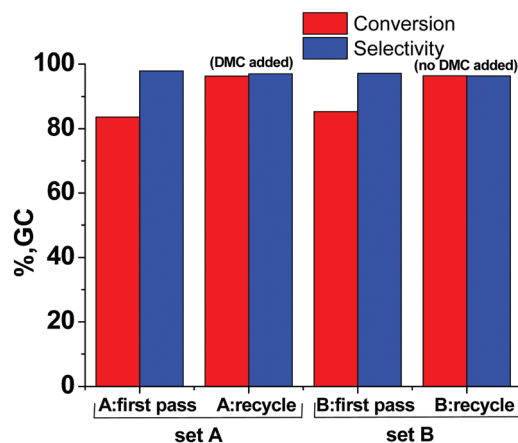

Fig. 3 Recycling tests carried out at 275 °C and 60 bar. Initial runs (fresh) of both sets A and B were performed using a mixture DMC/GLyF in 20 : 1 molar ratio. The volumetric rate (F) was always 0.05 mL min^{-1}. Values of conversions and selectivities were those after 1.5 hours.

ive value (95–97%, second pass), without any appreciable alteration of the selectivity that remained constant at 96–98%; (ii) the addition of fresh DMC before the recycle did not affect the reaction outcome (compare A and B recycle, bars 3, 4 and 7, 8). This suggested that the overall process could be further intensified by decreasing the volume of DMC; (iii) the comparison of Fig. 2c and 3 as well as the consistent composition of reaction mixtures sampled and analyzed during long-running tests (up to 18 hours) indicated that a robust procedure with highly reproducible results was thus achieved. This was substantiated also by the validation of the reaction

mass balance; after the recycle tests, the transesterification product was isolated in 92% yield (total of **2a/2a′**). Isomeric carbonates **2a** and **2a′** were obtained in the same (3 : 2) relative ratio of the starting acetals **1a** and **1a′**. Worth noting was the extremely easy separation procedure that took place through a one-step distillation of the final mixtures (54 mL) without additional purifications or need for extra solvents.

To further explore the potential of the investigated procedure, the effect of the DMC amount was analyzed. The protocol in Fig. 2 was changed by decreasing the volume of DMC; in particular, three CF-reactions were performed using reactant molar ratios Q (DMC : GlyF) of 20, 10 and 5, respectively. Experiments were carried out at 250 °C since this temperature offered a good compromise between high conversions and low pressures (20–40 bar; Fig. 2b). In each test, the combined flow rate was set to 0.05 mL min^{-1} and the pressure was gradually increased from the ambient value up to 50 bar.

Results are reported in Fig. 4 which details the trend of the conversion of GlyF with the increase of the pressure at the different Q ratios used.

As Q was decreased from 20 to 10, the shape of reaction profiles was similar, but two differences were manifest: (i) the onset of the reaction took place in the proximity of 15 bar (Q = 10) and 25 bar (Q = 20), respectively; (ii) a slight drop of the equilibrium conversion, from ~85 to ~80%, was observed (black and red curves). The last aspect was far more evident when the Q ratio was further reduced to 5: the maximum allowed conversion declined from ~77% at 15–20 bar, to level off at a value of 70% at higher pressures (≥40 bar, blue profiles).

Also the reaction selectivity (not shown in the figure) towards the product **2a/2a′** slightly decreased from 96–98% at Q = 10–20 to 88–93% at Q = 5, respectively; the lower DMC : GlyF ratio favored the double transesterification of DMC with GlyF. In conclusion, the reaction was most conveniently carried out using an excess DMC of 10 molar equiv. with res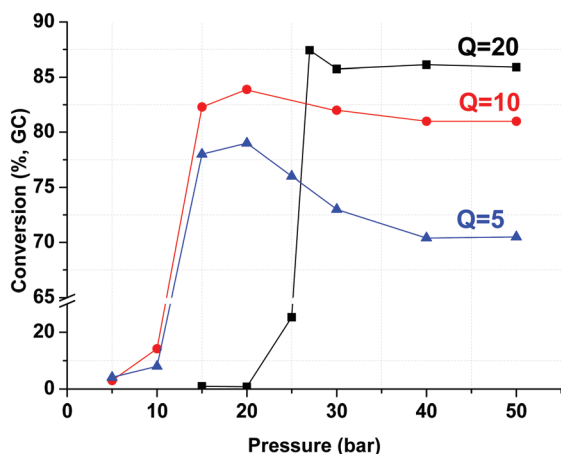pect to GlyF. This allowed us to operate at a moderate pressure (≤30 bar) with only a minor drop of the equilibrium conversion.

Under such conditions, a recycling experiment was analogous to that described in Fig. 3; a continuous reaction of DMC and GlyF (Q = 10; F = 0.05 mL min^{-1}) was allowed to proceed at 250 °C and 30 bar, for 18 hours. Then, the solution (54 mL) recovered at the reactor outlet was distilled to remove the MeOH–DMC azeotrope, and recycled for a second pass through the CF-reactor. The results confirmed those of Fig. 3. The recycle of the mixture enhanced the GlyF conversion from 81 to 94% with no alteration of the mono-transesterification selectivity (≥96%). A final distillation gave isomers **2a/2a′** in a substantially quantitative yield (purity ≥98%, by GC). The relative ratio **2a/2a′** (3 : 2) corresponds to that of the starting acetals **1a/1a′**.

Additional tests were carried out to evaluate and possibly optimize the system productivity (P) as well. This was calculated by the mass of the desired product obtained per time unit (mg min^{-1} of **2a/2a′**). In the CF-mode, a DMC/GlyF mixture (Q = 10) was set to react at 250 °C and 30 bar, by progressively increasing the total volumetric flow rate (F) from 0.05 mL min^{-1} to 0.6 mL min^{-1}. Typical increments were of 0.05–0.1 mL min^{-1}. At any chosen F rate, the same volume (10 mL) of the reaction mixture was used; the corresponding reaction times were varied from 17 to 180 min.[14] The solutions collected from the reactor were analyzed by GC/MS to determine both the conversion of GlyF and the product distribution. Results are reported in Fig. 5.

A 4-fold increase of the flow rate from 0.05 to 0.2 mL min^{-1} had no effects on the conversion that remained substantially constant at 80–83%. The progress of the reaction was apparently disfavored by further increments of F; the conversion dropped from ~80 to 35% as the residence time (τ) was gradually reduced from 300 to 100 s (red profile, in the range of 0.2–0.6 mL min^{-1}). Notwithstanding this, the mono-transesterification selectivity always remained very high (>95%), and even most importantly, the reaction productivity (P) showed an almost linear increase from 7 mg min^{-1} up to a maximum of

Fig. 4 The conversion GlyF at different pressures and DMC : GlyF (Q) molar ratios. T = 250 °C, volumetric rate F = 0.05 mL min^{-1}. Values were determined after 1.5 hours.
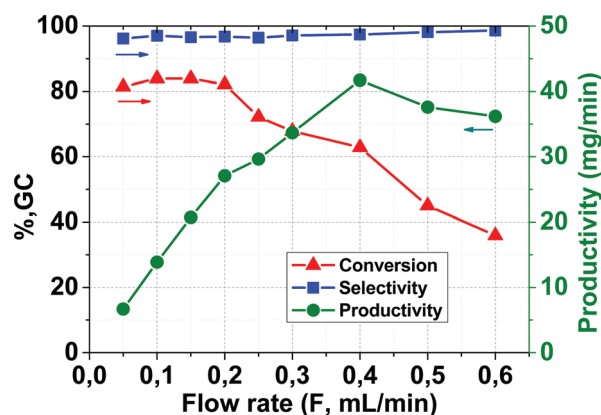

Fig. 5 The effect of the flow rate (F) on conversion (red), selectivity (blue), and productivity (green) of the transesterification of DMC with GlyF. Conditions: 250 °C, 30 bar, Q = 10.

42 mg min^{-1} when F was changed from 0.05 to 0.4 mL min^{-1} (green profile). It (P) then slightly decreased to 35 mg min^{-1} at higher flow rates ($\geq$0.5 mL min^{-1}). Compared to the limited capacity (1 mL) of the used CF-reactor, this result not only highlighted an excellent performance of the reaction, but also opened a perspective for larger scale applications and further process intensification.

Overall, the study described in Fig. 2–5 proved the feasibility of the model catalyst-free thermal transesterification of DMC with glycerol formal, and offered a strategy to optimize the process under CF-conditions. To continue exploring its potential, the investigation was then focused on the scope and limitations of the synthesis using other dialkyl carbonates and glycerol-derived acetals.

Different carbonates: the reaction of diethyl carbonate with glycerol formal

Diethyl carbonate (DEC), the simplest linear C5-homologue of dimethyl carbonate, was initially used. CF-reactions of DEC with GlyF were carried out based on the results, the method, and the apparatus above described for DMC. A mixture of DEC and GlyF (in a 10:1 molar ratio, respectively) was continuously fed through a CF-reactor thermostated at a temperature between 250 and 300 °C. The flow rate was 0.05 mL min^{-1}. In analogy with experiments of Fig. 2 and 4, the pressure was gradually increased from the ambient value up to 100 bar. Conversion and product distribution were determined by GC/MS analyses of the mixtures that were periodically sampled at the reactor outlet.[15] Three isothermal reaction profiles were obtained at 250, 275, and 300 °C, respectively; in all cases, a highly selective (>95%) mono-transesterification reaction occurred provided that an operating pressure above 20 bar was applied (Scheme 5).

As for DMC, this result was never previously reported under catalyst-free conditions, particularly in the CF-mode. The structures of isomeric carbonates **3a** and **3a′** [1,3-dioxan-5-yl ethyl carbonate and (1,3-dioxolan-4-yl)methyl ethyl carbonate, respectively] were assigned by GC/MS and NMR analyses. The relative ratio **3a/3a′** was the same (3:2) observed for starting acetals **1a** and **1a′**. Other by-products (total ≤5%) derived from the double transesterification of DEC with GlyF. Fig. 6 shows the trend of the reaction conversion as a function of pressure, at each of the investigated temperatures.

Isothermal profiles of the transesterification of DEC with GlyF showed both analogies and differences with respect to the corresponding reaction of DMC (Fig. 2). Analogies were as follows: (i) the reaction did not take place at ambient pressure, but only over 20 bar, and (ii) an equilibrium conversion (up to 80%) was reached with increasing pressure (green and orange
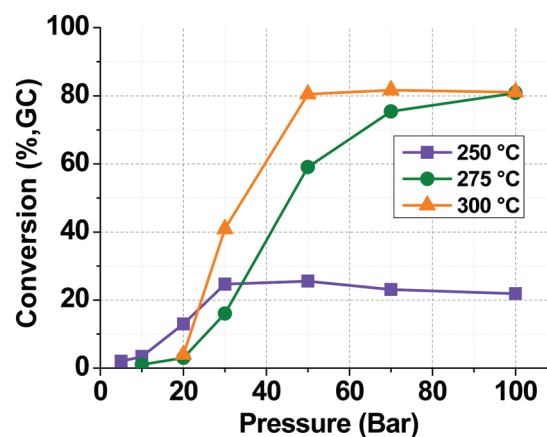

Fig. 6 Effects of temperature and pressure on the non-catalytic trans-esterification of diethyl carbonate (DEC) with glycerol formal. Three iso-thermal profiles are shown at 250, 275, and 300 °C in the range of 10−100 bar. Other conditions: (i) molar ratio Q = DEC : GlyF = 10; (ii) flow rate (F) = 0.05 mL min^{-1}; (iii) sampling time (at any pressure) = 1.5 hours. In all cases the selectivity was greater than 95%.

curves). Differences were as follows: (i) conversion profiles did not show steep abrupt changes, but followed sigmoid-like curves extended over relatively large pressure intervals from 20 up to 50 bar (compare violet, orange, and green profiles); (ii) a higher temperature was required for the reaction. For example, at 250 °C, (equilibrium) conversions of GlyF were 85% and 23% in the transesterification of DMC and DEC, respectively (Fig. 2c and 6); (iii) less evident temperature/pressure relationships were observed. At 250–275 °C, the behavior paralleled that of DMC; as the temperature increased, the pressure interval for the onset of the reaction should also increase. However, at 300 °C, the threshold pressure (25–30 bar) for the transesterification process was similar, if not lower, to that at 275 °C.

The results in Fig. 6 allowed us to conclude that DEC was less reactive than DMC and the formation of products **3a/3a′** could be conveniently carried out at 300 °C and 50 bar. Under such conditions, an additional test was carried out to evaluate the reaction productivity. The same procedure described for DMC (Fig. 5) was used; a DEC/GlyF mixture (Q = 10, 10 mL) was set to react in the CF-mode by progressively increasing the total volumetric flow rate (F) from 0.05 mL min^{-1} to 1 mL min^{-1}. The corresponding reaction times were varied from 10 to 180 min (see note 14). The conversion and the product distribution of mixtures collected at the reactor outlet were determined by GC/MS. Results are reported in Fig. 7.

The productivity was linearly enhanced from 8 to 68 mg of **3a/3a′** per min, when F was increased by a factor of 10 from 0.05 to 0.5 mL min^{-1}. A drop to 48 mg min^{-1} was then observed at greater flow rates. With respect to DMC, the higher reaction temperature (300 vs. 250 °C: Fig. 7 and 5, respectively) was the plausible reason for the better productivity achieved with DEC. The result confirmed that not only the CF-transesterification of DEC with GlyF was practicable under catalyst-free conditions, but also a robust and reproducible procedure was used.
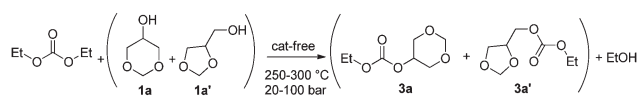
Scheme 5 The catalyst-free mono-transesterification of DEC with glycerol formal.
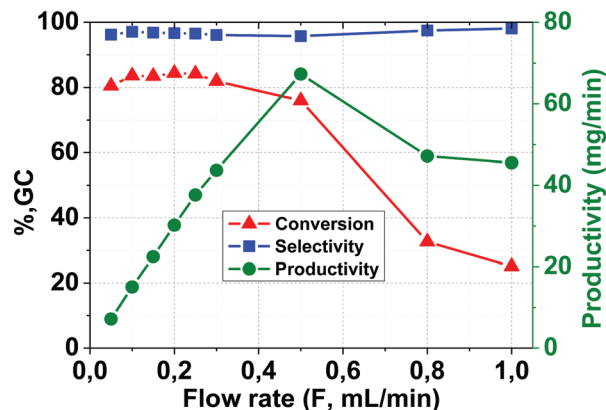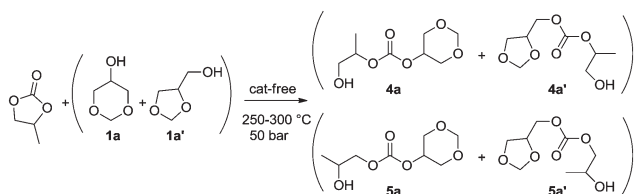
Fig. 7 The effect of the flow rate (F) on conversion (red), selectivity (blue), and productivity (green) of the transesterification of DEC with GlyF. Conditions: 300 °C, 50 bar, Q = 10.

Products **3a**/**3a′** were isolated by distillation of the mixture (total volume 54 mL) recovered after a reaction carried out for 18 hours at 300 °C and 50 bar. However, the separation was tricky; due to the close boiling points of the unconverted GlyF (~15%) and the products, the yield of compounds **3a**/**3a′** did not exceed 73% (further details are in the Experimental section).

Different carbonates: the reaction of propylene- and dibenzyl-carbonate with glycerol formal

Liquid propylene carbonate (PC, bp = 242 °C) was a good model compound to investigate the behavior of cyclic alkylene carbonates in the reaction with GlyF. CF-conditions used for this study were based on the results described for DEC (Fig. 6); a mixture of PC and GlyF (in 10 : 1 molar ratio, respectively; F = 0.05 mL min⁻¹) was set to react continuously at a temperature of 250, 275 and 300 °C, respectively, under a constant pressure of 50 bar. No changes of the operative pressure were considered. GC/MS analyses of solutions recovered at the reactor outlet proved that a highly selective (>95%) mono-transesterification reaction occurred with the formation of four isomeric products (**4a**/**4a′** and **5a**/**5a′**) (Scheme 6).

The structures of such carbonates were assigned by GC/MS analyses. The relative ratios **4a**/**4a′** and **5a**/**5a′** correspond to that of the starting acetals **1a**/**1a′** (3 : 2). Due to the complexity of the reaction mixtures, the NMR characterization was not practicable.[16] Experiments showed that the rise of the temperature from 250 to 275 and 300 °C brought about a corres-

ponding increase of the conversion of GlyF from 7 to 23 and 53%, respectively. These results were not further optimized, nor was the isolation of products accomplished. Any attempt to separate (by distillation) the unreacted GlyF and the excess PC from derivatives **4–5** was not successful because of the close boiling points of the involved compounds. However, tests for the CF-transesterification of PC with GlyF were repeated under the same conditions in Scheme 6 and with the additional validation of GC-analyses using an external standard (n-tetradecane). Results were in very good agreement with those of previous experiments: (calibrated) conversions of 7, 27, and 48% were achieved at 250, 275 and 300 °C, respectively. The overall study confirmed that propylene carbonate could be used for the investigated CF-protocol, though it was less active than diethyl carbonate, and even less than DMC.

Dibenzyl carbonate (DBnC) was finally considered for the transesterification with GlyF. DBnC is a low melting solid (mp: 34 °C) which, upon heating, forms a highly viscous liquid (bp: 180–190 °C 2 mmHg⁻¹). A solvent/carrier was therefore necessary to perform CF-reactions. Two different solvents such as acetone and 1,2-dimethoxyethane (DME) were considered for their physicochemical properties (particularly, low-mid boiling points and polarity[17]), and acceptable toxicological profiles.[18] A preliminary screening was carried out using a solution of GlyF, DBnC and the solvent in a 1 : 5 : 12 molar ratio, respectively. This mixture was set to react in the CF-mode at 250 °C and 50 bar, at a flow rate of 0.05 mL min⁻¹. Experiments demonstrated that after 1.5 hours, the mono-transesterification reaction of DBnC with GlyF was achieved with excellent selectivity (>98%) (Scheme 7 and Fig. 8).

The solvent greatly affected the (equilibrium) conversion of GlyF that improved from 11% in the presence of DME to 94% in acetone (Fig. 8: red bars on left). The result was substantiated by two other tests carried out under the same conditions (50 bar, molar ratio GlyF : DBnC : solvent = 1 : 5 : 12; F = 0.05 mL min⁻¹, 1.5 hours), but at a lower temperature of 225 °C; no reaction took place in DME, while an almost quantitative mono-transesterification was observed in acetone (Fig. 8: red bars on right). Of note, the outcome of such a reaction was even better than that in DMC (compare Fig. 2a). At 225 °C, the acetone-mediated process was allowed to proceed up to 4 hours; the volume (~12 mL) collected at the reactor outlet proved a substantially quantitative recovery of the reaction mixture. The GC/MS analysis of this solution confirmed that GlyF was converted into the corresponding carbonates **6a**/**6a′** with negligible amounts (1%) of double transesterification by-products. At the same time, also a partial decarboxylation of DBnC to dibenzyl ether [(PhCH₂)₂O, DBE] was noted in

Scheme 6 The catalyst-free mono-transesterification of propylene carbonate with glycerol formal.
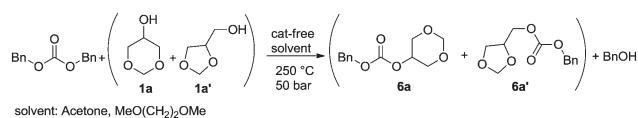
Scheme 7 The catalyst-free mono-transesterification of dibenzyl carbonate with glycerol formal.
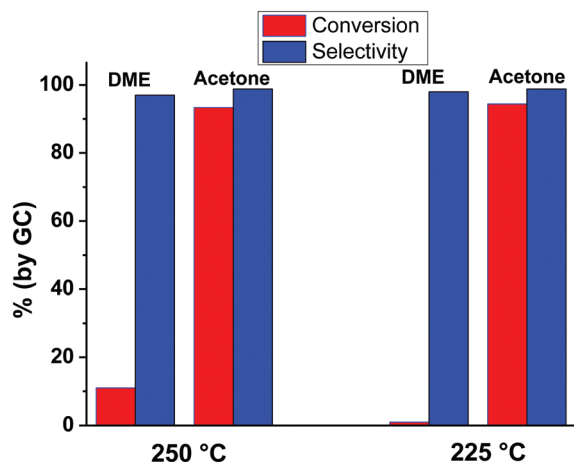
Fig. 8 The transesterification of DBnC with GlyF: the effect of the solvent and temperature on conversion (red), and selectivity (blue). Conditions: 50 bar, molar ratio GlyF : DBnC : solvent = 1 : 5 : 12; F = 0.05 mL min^{-1}, 1.5 hours; left (first four bars): 250 °C; right: (second four bars): 225 °C.

accordance with our previous results on the high-temperature behavior of dialkyl carbonates.[11,12,19]

Products **6a**/**6a′** were new compounds. They were obtained in the same (3 : 2) relative ratio of starting acetals **1a**/**1a′**. Of the different techniques attempted for their isolation, FCC on silica gel (eluent: petroleum ether (PE)–diethyl ether (Et$_2$O), 1 : 1 v/v) was successful to separate even the single isomers in a highly pure form (>95%, by GC). Full structural details of compounds **6a** and **6a′** were achieved by an in-depth NMR characterization study (the description is reported in the Experimental section).

Fig. 8 also indicates that in the range of 225–250 °C, the temperature had a minor effect on both the conversion and selectivity. Although this suggested that there was room for improvement, the optimization of such a reaction was beyond the scope of the work. Overall, the reaction of DBnC not only confirmed that the CF-protocol was feasible for higher carbonates, but also offered new perspectives on benefits of the use of light solvents of low-to-mid polarity.

Different acetals: the reaction of dimethyl- and diethyl-carbonate with solketal

Solketal (**1b**) is the product of the condensation of glycerol with acetone (Scheme 1). This compound was used as a different liquid acetal to study the CF-transesterification of both DMC and DEC. Reaction conditions were those of previous experiments: a mixture of solketal and the chosen dialkyl carbonate (in a 1 : 20 molar ratio, respectively) was set to react in the CF-mode at different temperatures of 250 and 275 °C, and at a total flow rate of 0.05 mL min^{-1}. Tests demonstrated that under a pressure ≥30 bar, highly selective (>98%) mono-transesterifications could be achieved also with solketal (Scheme 8).

In the case of DMC, the reaction was monitored by changing the operating pressure from the ambient value up to 100
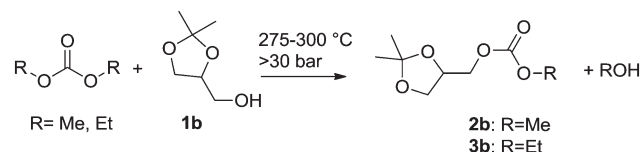
Scheme 8 The catalyst-free mono-transesterification of dimethyl- and diethyl-carbonate with solketal.

bar. Periodic GC/MS analyses of mixtures collected at the reactor outlet showed that both the conversion of solketal and the selectivity were steady after a sampling time of 60 min (at any given pressure). Fig. 9 shows the results.

The behavior was similar to that observed for the reaction of DMC with GlyF (compare Fig. 2b and c). This was especially true at 275 °C where an increment of the pressure from 35 to 40 bar allowed a steep enhancement of the conversion from 4 to 96%, respectively (orange curve). A broader profile was observed at 250 °C; although the onset of the reaction was at 30 bar, the process was almost quantitative only at 50 bar (green curve). The two trends indicated that the lower the temperature, the lower the pressure at which the reaction initiated. Of note, the equilibrium conversion of solketal (>95%) was higher than that achieved for glycerol formal (~85%) in the same transesterification of DMC.

The reaction carried out at 275 °C was allowed to proceed for 18 hours. Then, the mixture collected at the reactor outlet (54 mL) was vacuum distilled. An almost quantitative recovery of crude product **2b** (5.1 g; purity 96% by GC) was achieved. The structure of such a compound was assigned using GC/MS and NMR spectra.

In the case of diethyl carbonate, two CF-experiments were carried out at 275 °C under a constant pressure of 30 and 50 bar. The conversion of solketal was 70 and 72%, respectively. This indicated that an equilibrium position was plausibly
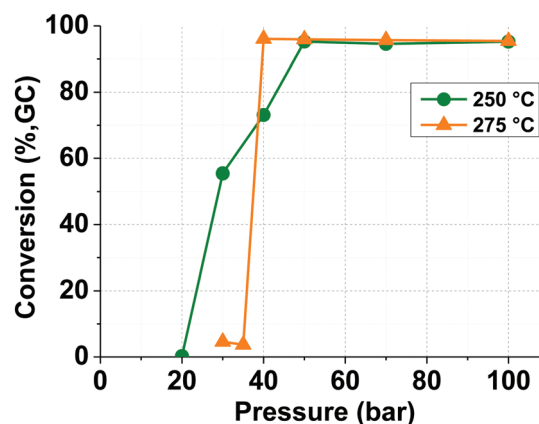

Fig. 9 Effects of temperature and pressure on the non-catalytic transesterification of dimethyl carbonate (DMC) with solketal. Isothermal profiles at 275 and 300 °C were obtained under the following conditions: (i) molar ratio Q = DMC:**1b** = 20; (ii) flow rate = 0.05 mL min^{-1}; (iii) sampling time (at any pressure) = 1 hours.

reached, though at a lower conversion than that achieved with dimethyl carbonate (>95%, Fig. 9). As for the transesterifications with GlyF, reactions of solketal confirmed that DEC was less active than DMC.

The vacuum distillation of the mixtures (54 mL) recovered after these experiments allowed us to isolate the crude product **3b** in 73% yield (3.2 g; purity 98% by GC), whose structure was assigned using GC/MS and NMR spectra.

Discussion

The non-catalytic nature of the reaction

The present study provides evidence that the investigated CF-transesterification of dialkyl carbonates with glycerol acetals is triggered by a combined effect of temperature and pressure. Isothermal reaction profiles at $T \geq 250$ °C show that the conversion of acetals can be tuned and improved by increasing the operative pressure over a threshold value in the range of 20–50 bar. Then, as expected for reversible processes, the transesterification reaches an equilibrium position with excellent conversions (85–95%) that remain steady for higher pressures (70–100 bar).

This is a general outcome that, although with some variations, is observed when both different carbonates react with the same acetal (Fig. 2 and 6), and alternatively, different acetals react with the same carbonate (Fig. 2 and 9).

The behavior of CF-reactions and the results of batch (autoclave) experiments on the transesterification of DMC with GlyF offer a convincing support for the occurrence of thermal (non-catalytic) processes. Such (thermal) transesterifications are not new reactions, but literature examples are almost exclusively referred to the production of biodiesel. Among the first reported cases, in 1998, an investigation proposed a kinetic model for batch reactions of soybean oil with methanol performed at 220–235 °C and 55–60 bar.[20] Thereafter, different fundamental and applied studies demonstrated that the non-catalytic transesterification of vegetable oils conveniently proceeded in both batch and continuous-flow modes in the presence of supercritical light alcohols (sc-methanol and ethanol).[21] Reaction kinetics took great advantage of the supercritical state; according to some authors, this was possibly due to a decrease of the dielectric constant of sc-alcohols which favored the oil-in-alcohol miscibility and the formation of a single reacting phase.[21a,22] Other benefits were further emphasized by the absence of any catalysts which allowed easy and cheap separation of products (fatty acid methyl/ethyl esters, FAME and FAEE, respectively).

In the synthesis of biodiesel, also the potential of supercritical dimethyl carbonate (sc-DMC: T_c = 284 °C; P_c = 48 bar; ρ_c = 3.97 g mL^{-1},[23]) was explored for batch transesterifications of rapeseed and Jatropha oils.[24] These studies showed that at 350 °C and 20 MPa, yields of transesterification products (FAME) obtained in sc-DMC were substantially equivalent to those in sc-MeOH. However, in sc-DMC, the nature (thermal, catalytic or both) of the reaction was unclear since the process

originated also sizable amounts of citramalic acid that was suspected to act as a catalyst.[25] Q4

The reaction of GlyF and DMC

Notwithstanding the conceptual similarity, the thermal transformations investigated in this work differ from those cited in the case of biodiesel production, for the important fact that GlyF, solketal and carbonate products (**1a–6a/1a′–6a′** and **2b–3b**) form perfectly homogeneous solutions with dialkyl carbonates. Miscibility is therefore not an issue. However, since thermal processes may have substantial activation barriers, they require high reaction temperatures;[26] the relative vapor tension of reactants becomes a crucial factor. Consider, for example, the model case of the CF-transesterification of DMC (bp = 90 °C) with GlyF (bp = 192–193 °C) (Fig. 2 and 4). At $T \geq 200$ °C and ambient pressure, reactants are in the vapor state even though dynamic flow conditions may allow some mixing of gases. As the pressure is increased, the vaporization is more difficult: the high boiling GlyF becomes mostly liquid, while the more volatile DMC initiates to partition between the gas and the GlyF liquid phases. The contact of the reactants starts to be effective as is highlighted by all further increments of the pressure, to the point that intimate interactions between GlyF and DMC allow the reaction to take place. In particular, the sigmoidal-like curves of Fig. 2 and 4 indicate that transesterification starts once the optimal pressure (and the density of the reacting mixture) is reached, which corresponds to an abrupt improvement of the conversion. A hypothesis for this behavior stands on the occurrence of near-critical or supercritical solutions able to favor the contact of reactants and the process kinetics. Although a detailed investigation of this aspect is beyond the scope of the present work, it should be noted that (i) in Fig. 2, P and T (225–300 °C, 20–50 bar) are not far from the supercritical state of DMC which shows a density four times higher than its liquid state.[25] The presence of GlyF in the reacting solutions may possibly alter the supercritical parameters with respect to pure sc-DMC. However, minor changes are expected due to the large excess (up to 20 molar equiv.) of the carbonate;[27] (ii) conversion profiles are consistent with the effect of the temperature and of the DMC : GlyF molar ratio (Q). In Fig. 2, the increase of the temperature plausibly reduces the density of the reacting mixtures so that a higher pressure is necessary to trigger the process. In Fig. 4, the decrease of the Q ratio originates in solutions richer in the denser and less volatile component (under ambient conditions, densities of GlyF and DMC are 1.20 and 1.07 g mL^{-1}, respectively[18]). This favors the contact between reagents and lowers the pressure interval at which the onset of the reaction is achieved; (iii) in general, conversion profiles parallel the isothermal trend of density with pressure displayed by several mixtures and pure compounds during the transition to their supercritical states.[28]

Recycle and productivity

The reversible nature of the transesterification offers an explanation for results in Fig. 3 and 4. In the model case of the

reaction of DMC with GlyF, the success of the recycling procedure proves that the transesterification equilibrium may be shifted to the right by increasing the residence time of the reactant mixture in the CF-reactor. This helps to improve the conversion from 85 to 95% (Fig. 3). On the other hand, the excess of the dialkyl carbonate also exerts control on the reaction equilibrium; if the Q molar ratio (DMC : GlyF) is decreased, the reduced availability of DMC not only disfavors the conversion, but also the reaction selectivity, and the onset of a double transesterification process is observed (Fig. 4).

As far as the productivity of both the reactions of DMC and DEC with GlyF is concerned, the optimization of the reactant flow rate allows quite satisfactory results, especially if one considers the limited capacity (1 mL) of the CF-reactor used in our study (Fig. 5 and 7). An issue however may concern the overall convenience of the procedure in terms of energy consumption and safety. In a perspective of a larger scale application, it should be noted that technologies for the integrated heat and energy recovery of modern chemical plants often allow a very cheap access to high temperature (over 200 °C) and mid-to-low pressure (40–50 bar) conditions. Detailed analyses of these aspects are available in the literature. Consider, for example, sc-transesterification reactions of oils. Although conditions for such processes may be rather severe (270–400 °C and 10–65 MPa), a recent simulation of a biodiesel production carried out for the reaction of triglycerides with methanol at 400 °C and 200 bar, has proven that the total energy consumption and the output PEI (potential environmental impact) per mass of product of a plant capacity of 10 000 tons per year are even lower than that of a conventional base-catalyzed transesterification process.[29] Similar conclusions have been reported by other comparative studies on energy requirements of sc- and catalytic-reactions.[30]

Different carbonates and acetals

Isothermal trends of conversion *vs.* pressure show a sigmoidal shape also for the transesterification of DEC with GlyF (Fig. 6). However, with respect to DMC, not only conversion profiles display smoother increases, but also the reaction is more energy demanding; both higher temperatures and pressures are necessary (275–300 °C and 30–70 bar, respectively). Among the factors that may account for such a difference, one of the most relevant is the intrinsic lower reactivity of DEC compared to DMC. This behavior, plausibly due to steric reasons, has been confirmed by a number of catalytic processes which include transesterifications and decarboxylations,[10,11] etherifications,[12] and alkylations.[31] A very recent study has further substantiated such a trend also for thermal reactions; higher activation energies have been measured for transesterifications of vegetable oils carried out in supercritical DEC with respect to analogous transformations in sc-DMC.[32] In analogy with the above discussion, another contribution to the results of Fig. 6 is possibly given by the variation of the density of the reacting mixture with pressure. This aspect however, can be hardly analyzed because of the lack of thermodynamic data; experiments in Fig. 6 take place under conditions very close to the super-

critical state of DEC (T_c = 302 °C; P_c = 3.4 MPa[32]), but any information on the density of sc-DEC is unknown.

The relative reactivity of the two GlyF isomers (**1a** and **1a′**) should also be considered. Irrespective of the dialkyl carbonate (and of temperature and pressure) used, isomeric products **2a/2a′** and **3a/3a′** are always obtained in the same relative ratio (3 : 2) of the starting acetals **1a/1a′**. In contrast to our previous findings on base-catalyzed alkylations of GlyF with DMC,[10] thermal (non-catalytic) conditions level off the relative transesterification rate of 5- and 6-membered ring acetals with both DMC and DEC. This holds true for higher carbonates. At present, no clear explanations can be offered for this behaviour.

Propylene carbonate (PC) is considerably less reactive than DEC; at 300 °C and 50 bar, the conversion of the reaction of PC with GlyF does not exceed 53% (Scheme 6). Also in this case, steric reasons may be invoked to account for the result. A support from the literature comes for example from studies on the synthesis of DMC *via* the transesterification of cyclic carbonates with methanol; these investigations have demonstrated that slower reactions as well as poorer (even three times lower) equilibrium yields are achieved when the bulkier propylene carbonate is used instead of ethylene carbonate.[33] Notwithstanding the moderate reactivity, other properties of PC (mostly the boiling point and the viscosity) make this compound a preferred choice over other cyclic carbonates.

The CF-transesterification of dibenzyl carbonate (DBnC) with GlyF takes place in the presence of acetone as a solvent/carrier. Although this does not allow a direct comparison with the reactivity of other carbonates, the study of DBnC-mediated reactions provides two pieces of evidence: (i) the nature of additional solvents may critically affect the thermal process; (ii) a non-toxic, cheap, moderately polar and aprotic solvent such as acetone is not only compatible with the CF-setup, but remarkably, it also allows quantitative transformations under less demanding conditions with respect to DMC (Fig. 8, right). These aspects suggest the potential of eco-friendly solvents for fundamental investigations and innovative preparative protocols in the arena of transesterifications.

To sum up, one should note that further studies are necessary to optimize and implement the CF-reactions of both PC and DBnC with GlyF, especially to improve the conversion and the product separation. The results of this work however offer a convincing proof-of-concept on the extension of thermal transesterification processes to higher homologues of linear and alkylene carbonates.

A comment should be finally made on the comparison between the two investigated acetals. Both the reactions of GlyF and solketal confirm the lower reactivity of DEC with respect to DMC. However, solketal may offer better results than GlyF. This is well exemplified by the transesterification of DMC carried out at 275 °C and 40 bar; under these conditions, the equilibrium conversions were 85% for GlyF and 96% for solketal (Fig. 2c and 9). Such a difference can be hardly explained, though the higher density of GlyF (1.21 g mL^{-1}) with respect to solketal (1.07 g mL^{-1}) might play a role.

Conclusions

This investigation proposes the first reported procedure for the continuous-flow thermal mono-transesterification of dialkyl carbonates (DAlCs) with glycerol formal and solketal. The method not only offers a clean synthetic route for the reaction, but also identifies a strategy – potentially valuable for large scale preparations and transferable to intensified process equipment – for the selective upgrading of glycerol acetals to the corresponding carbonates.

Besides the synthetic scope, the reaction exemplifies a genuine green archetype since it couples innocuous reactants of renewable origin (glycerol acetals) to non-toxic compounds such as DAlCs.

The process is triggered by a combined effect of temperature and pressure. Under isothermal conditions at 250–300 °C, the increase of the pressure in the range of 20–50 bar favors the contact/mixing of the reactants (by reducing the vaporization of liquids) at the point that the conversion of acetals can be improved up to 95%. On the other hand, the product distribution is tuned by the reactant molar ratio; a 10-molar excess of the dialkyl carbonate conveniently shifts to the right of the equilibrium to reach a mono-transesterification selectivity as high as 98%.

Both the recycling operations and the productivity take advantage of CF-conditions; the first (recycle) can be simply implemented through the reuse of mixtures collected from the CF-reactor, without additional purification steps; the second (productivity) can be optimized up to ~70 mg min^{-1} according to the design and the capacity of the CF-apparatus. Moreover, the absence of any catalysts allows one to run reactions virtually indefinitely with easy and cheap separation of products.

Two further aspects should be commented on: (i) the investigation carried out so far discloses the potential of a catalyst-free CF-method for the transesterification of a family of linear and alkylene dialkyl carbonates with glycerol acetals, though a case-by-case optimization is necessary and future studies will be required for a practical implementation of the reactions of heavier carbonates (propylene- and dibenzyl-carbonate) by the use of additional solvents; (ii) one could be concerned about the energy consumption due to the demanding conditions for non-catalytic transesterification processes. This problem may be considerably mitigated by modern technologies for heat and energy recovery. Recent examples of such engineering solutions (rather beyond the scope of this work) have been reported for the case of supercritical transesterification of oils. These prove that sc-processes may be even economically advantageous over conventional base-catalyzed transesterification methods (see details in the Discussion section).

Experimental

General

Glycerol formal (GlyF, **1a** + **1a′**), solketal (**1b**), acetone, 1,2-dimethoxyethane (DME), *n*-tetradecane, dimethyl carbonate (DMC), diethyl carbonate (DEC), propylene carbonate (PC), benzyl alcohol, ethyl acetate (EA), ethyl ether (Et$_2$O), petroleum ether (PE) and dichloromethane (CH$_2$Cl$_2$) were of ACS grade. They were all from Aldrich and were used as received. Dibenzyl carbonate (DBnC) was prepared *via* the transesterification of benzyl alcohol with DMC using a method recently reported by us.[12d] GC/MS (EI, 70 eV) analyses were carried out using a HP5-MS capillary column (L = 30 m, $\varnothing$ = 0.32 mm, film = 0.25 μm). The following conditions were used. Carrier gas: He; flow rate: 1.2 mL min^{-1}; split ratio: 10; initial T: 50 °C (3 min), ramp rate: 15 °C min^{-1}; final T: 250 °C (3 min). ^{1}H NMR spectra were recorded at 400 MHz, ^{13}C spectra at 100 MHz and chemical shifts were reported in δ values downfield from TMS; CDCl$_3$ was used as the solvent.

CF-apparatus

The apparatus used for the investigation was assembled in-house according to the chart in Fig. 1. Two twin Shimazdu LC-10AS HPLC pumps were used to deliver liquid reactants to a stainless steel tubular reactor (1/16″ inner diameter, L = 1.6 m, 1.0 mL inner volume). The reactor was placed in a GC oven by which the desired reaction temperature was reached. The outlet of the reactor was connected to a back pressure regulator (JASCO BP-2080) to set and control the operative pressure throughout the process.

SAFETY WARNING. Operators of high pressure equipment should take proper precautions to minimize the risk of personal injury.[34]

General procedure for the CF non-catalytic transesterification

In a typical CF, non-catalytic transesterification reaction, the following operations were performed. At ambient temperature and pressure, a preliminary conditioning of the apparatus was carried out by delivering a mixture of reactants (5 mL; the molar ratio of dialkyl carbonate : glycerol acetal was set to 20, 10, and 5 respectively) to the CF-reactor. Afterwards, the back pressure regulator (BPR) was set to the operating pressure (10–100 bar) and the flow rate of the mixture was adjusted to the desired value (0.05–1.00 mL min^{-1}). The reactor was then heated at a temperature between 225 and 300 °C. At any given temperature and pressure, the reaction mixture was collected out of the BPR at time intervals of approximately 90 min. Samples were analyzed by GC/MS. Once the experiment was complete, the oven was set to 100 °C and the pumping of reagents was stopped. The overall apparatus was then cleaned by a flow of acetone (50 mL). The reactor was allowed to cool at room temperature and the pressure was gradually decreased to the ambient value.

Reaction of glycerol formal (1a–1a′) with DMC

Three reactants' solutions (51 mL each) were prepared by adjusting the DMC : GlyF molar ratio at 20, 10, and 5, respectively. They were obtained by dissolving the same amount of GlyF (3 g, 28.8 mmol) in 48.6, 24.3, and 12.1 mL of DMC. The corresponding molar concentrations were 0.56, 1.08, and 1.97.

Effect of the pressure and the temperature (Fig. 2)

According to the above described general procedure, a 0.56 M solution of GlyF in DMC (51 mL; DMC : GlyF molar ratio = 20) was sent to the CF-reactor at a constant volumetric flow rate of 0.05 mL min^{-1}. Four isothermal tests were performed by heating the reactor at 225, 250, 275, and 300 °C, respectively. In each test, the pressure was stepwise increased from the ambient value up to 100 bar. Typical increments were of 5–10 bar. At any given pressure, the reaction was allowed to proceed for 90 min to achieve steady conditions. Then, samples of the mixture were collected at the reactor outlet and analyzed by GC/MS.

Recycling tests (Fig. 3)

According to the above described general procedure, two sets (A and B) of experiments were carried out. In the set A (Fig. 3, left), a 0.56 M solution of GlyF in DMC (molar ratio DMC : GlyF = 20) was delivered to the CF-reactor at a flow rate of 0.05 mL min^{-1}. The temperature and pressure were kept constant at 275 °C and 60 bar, respectively. The reaction was allowed to proceed for 18 hours. The mixture collected at the reactor outlet (54 mL) was then analyzed by GC/MS, and subjected to a partial distillation at ambient pressure. A total of 5 mL were distilled; they were composed of a MeOH–DMC azeotrope (2.5 mL, 70 : 30 v/v, bp = 62–65 °C) and pure DMC (2.5 mL, bp = 90 °C). The residual solution (49 mL) was added with fresh DMC (5 mL) to restore the initial volume. This mixture was recycled. Under the above described conditions (0.05 mL min^{-1}, 275 °C and 60 bar), it (mixture) was allowed to flow once again through the reactor for 18 hours. Samples were collected at the reactor outlet every 90 min and analyzed by GC/MS. In the set B (Fig. 3, right), two subsequent reactions were performed using the same procedure of set A except for the fact that no fresh DMC was added after the distillation carried out between the first and the second reaction.

A third recycling test was also run using a 1.08 M solution of GlyF in DMC (molar ratio DMC : GlyF = 10). This mixture was set to react at 250 °C and 30 bar for 18 hours. Then, the solution recovered at the reactor outlet (54 mL) was topped by distillation and recycled using the same procedure described for the above described set A. This test was commented on in the Results section.

Effect of the DMC : (1a–1a′) molar ratio (Fig. 4)

The available reactants' solutions (51 mL each) of GlyF in DMC (0.56 M, 1.08 M, and 1.97 M, respectively; see above) were used in three separate tests. According to the above described general procedure, each mixture was set to react at a constant temperature of 250 °C. The flow rate was 0.05 mL min^{-1}. The operating pressure was gradually increased from the ambient value up to 100 bar, with typical increments of 5–10 bar. At any given pressure, the reaction was allowed to proceed for 90 min to ensure steady conditions. Then, samples of the mixture were collected at the reactor outlet and analyzed by GC/MS.

Effect of the flow rate and estimation of productivity (Fig. 5)

According to the above described general procedure, a 1.08 M solution of GlyF in DMC (molar ratio DMC : GlyF = 10) was set to react at 250 °C and 30 bar. The initial flow rate (0.05 mL min^{-1}) was stepwise increased up to 0.6 mL min^{-1}. Typical increments were of 0.1 mL min^{-1}. At any given flow rate, the same volume (10 mL) of the reactants' mixture was delivered to the CF-reactor in order to achieve steady conditions with an homogeneous composition of the stream recovered out of the BPR. Samples collected at the end of each test were analyzed by GC/MS. Data of conversion and selectivity were used to evaluate the reaction productivity.

Reaction of glycerol formal (1a–1a′) with different carbonates

In the case of diethyl carbonate (DEC) and propylene carbonate (PC), reactants' solutions (51 mL each) were prepared to achieve a molar ratio of dialkyl carbonate : GlyF = 10. They were obtained by dissolving 4.1 g of GlyF (39.4 mmol) in 47.7 mL of DEC and 5.7 g of GlyF (54.6 mmol) in 46.3 mL of PC, respectively. The corresponding molar concentrations were 0.77 (DEC) and 1.07 (PC).

DEC (Fig. 6 and 7)

According to the above described general procedure, a 0.77 M solution of GlyF in DEC was sent to the CF-reactor at a constant volumetric flow rate of 0.05 mL min^{-1}. Three isothermal tests were performed by heating the reactor at 250, 275, and 300 °C, respectively. In each test, the pressure was stepwise increased from the ambient value up to 100 bar. Typical increments were of 5–10 bar. At any given pressure, the reaction was allowed to proceed for 90 min to ensure steady conditions. Then, samples of the mixture were collected at the reactor outlet and analyzed by GC/MS (Fig. 6).

Another experiment based on the transesterification of DEC with GlyF was carried out to investigate the effect of the flow rate and evaluate the reaction productivity (Fig. 7). The test was performed in analogy with that described for DMC (Fig. 5). A 0.77 M solution of GlyF in DEC was set to react at 300 °C and 50 bar. The initial flow rate (0.05 mL min^{-1}) was stepwise increased up to 1 mL min^{-1}. Typical increments were of 0.1 mL min^{-1}. At any given flow rate, the same volume (10 mL) of the reactants' mixture was delivered to the CF-reactor in order to achieve steady conditions with an homogeneous composition of the stream recovered out of the BPR. Samples collected at the end of each test were analyzed by GC/MS. Data of conversion and selectivity were used to evaluate the reaction productivity.

PC

CF-transesterifications of PC with GlyF were carried out by the same procedure described for DEC. A 1.07 M solution of GlyF in PC was used. The conversion of GlyF was evaluated by a calibration method using *n*-tetradecane (C$_{14}$) as an external standard (further details are described in ESI†).

Dibenzyl carbonate (DBnC, Fig. 8)

CF-transesterifications of DBnC (low melting point solid, mp: 34 °C) with GlyF were investigated in the presence of DME and acetone as solvents/carriers. Two mixtures of GlyF, DBnC and the solvent in a 1 : 5 : 12 molar ratio, respectively, were prepared. They were obtained by dissolving GlyF (0.69 g, 6.61 mmol) and DBnC (8 g, 33.0 mmol) in DME (8.2 mL) or acetone (5.8 mL). According to the above described general procedure, both the solutions were set to react at 225 and 250 °C, under a constant pressure of 50 bar. The flow rate was 0.05 mL min^{-1}. Each reaction was allowed to proceed for 90 min. Then, samples of the mixture were collected at the reactor outlet and analyzed by GC/MS.

Reaction of solketal (1b) with different carbonates

Two reactants' solutions (51 mL each) were prepared to achieve a molar ratio of dialkyl carbonate : solketal = 20. They were obtained by dissolving 3.72 g of solketal (28.15 mmol) in 47.4 mL DMC and 2.64 g of solketal (19.98 mmol) in 48.4 mL DEC, respectively. The corresponding molar concentrations were 0.55 (DMC) and 0.39 (DEC).

DMC (Fig. 9)

A study on the effect of the pressure and temperature on the thermal transesterification of DMC with solketal was carried out in analogy with that described for the same reaction of GlyF (Fig. 2). According to the above described general procedure, a 0.55 M solution of solketal in DMC was set to react at 250 and 275 °C, respectively. The volumetric flow rate was 0.05 mL min^{-1}. In each test, the pressure was stepwise increased from the ambient value up to 100 bar, with increments of 5–10 bar. At any given pressure, the reaction was allowed to proceed for 90 min to achieve steady conditions. Then, samples of the mixture were collected at the reactor outlet and analyzed by GC/MS.

DEC

The transesterification of DEC with solketal was performed by a procedure similar to that used for DMC (Fig. 9). A 0.39 M solution of solketal in DEC was set to react at 275 °C. The flow rate was 0.05 mL min^{-1}. Two reactions were allowed to proceed for 90 min under a pressure of 30 and 50 bar, respectively. Then, mixtures collected at the reactor outlet were analyzed by GC/MS.

Isolation and characterization of products

1,3-Dioxan-5-yl methyl carbonate (2a) and (1,3-dioxolan-4-yl)methyl methyl carbonate (2a′). A CF-reaction was carried out under the conditions shown in Fig. 2b (0.56 M solution of GlyF in DMC; 250 °C, 40 bar, 18 hours; F = 0.05 mL min^{-1}). The mixture (54 mL) collected at the reactor outlet was topped at atmospheric pressure to remove the co-product methanol (as a 70 : 30 MeOH–DMC azeotrope, bp = 62–65 °C). The residual solution (49 mL) was subjected to a second CF-transesterification at 250 °C and 40 bar. A GlyF conversion of 94%

was achieved. The final reaction mixture was concentrated by rotary evaporation (50 °C, 40 mbar) and distilled (94 °C, 40 mbar). Title products were obtained as a liquid colorless mixture of isomers in 92% yield (4.5 g, purity 96% by GC/MS). They were characterized by ^{1}H NMR, ^{13}C NMR and GC/MS (see ESI†). The ratio **2a** : **2a′** was approximately the same for the starting isomers of GlyF.

^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 5.04 (s, 1H), 4.89 (m, 2H), 4.81 (d, J = 6.2 Hz, 1H), 4.59 (m, 1H), 4.30 (qnt, 1H), 4.25–4.13 (m, 2H), 4.07–3.92 (m, 5H), 3.80 (s, 3H), 3.79 (s, 3H), 3.73 (dd, J = 8.5, 5.4 Hz, 1H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm): 155.5, 155.1, 95.4, 93.5, 72.8, 68.8, 68.1, 67.2, 66.6, 54.9. Signals in the ^{13}C spectrum of **2a/2a′** were all singlets. GC/MS (relative intensity, 70 eV) m/z: **2a** 162 (M$^+$, <1%), 161 ([M − H]$^+$, 6), 132 (10), 102 (100), 86 (63), 59 (38), 58 (60), 57 (30), 55 (15), 45 (44), 44 (12), 43 (42); **2a′** 162 (M$^+$, <1%), 161 ([M − H]$^+$, 8), 103 (32), 86 (61), 77 (25), 73 (100), 59 (38), 58 (23), 57 (40), 45 (92), 44 (35), 43 (23).

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl methyl carbonate (2b). A CF-reaction was carried out under the conditions shown in Fig. 9 (0.55 M solution of solketal in DMC; 275 °C, 40 bar, 18 hours; F = 0.05 mL min^{-1}). The final conversion was 95%. The mixture collected at the reactor outlet (54 mL) was concentrated by rotary evaporation (50 °C, 40 mbar) and distilled (99 °C, 40 mbar). The title product was obtained as a colorless liquid in 93% yield (5.3 g, purity 95% by GC/MS). Compound **2b** was characterized by ^{1}H NMR, ^{13}C NMR and GC/MS (see ESI†).

^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 4.38–4.29 (m, 1H), 4.19–4.15 (m, 2H), 4.08 (dd, J = 8.6, 6.4 Hz, 1H), 3.81–3.75 (m, 4H), 1.43 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm): 155.5, 109.8, 73.2, 67.9, 66.2, 54.9, 26.6, 25.2. Signals in the ^{13}C spectrum of **2b** were all singlets. GC/MS (relative intensity, 70 eV) m/z: 190 (M$^+$, <1%), 175 (50), 101 (17), 73 (10), 72 (11), 71 (19), 59 (31), 57 (14), 43 (100), 42 (12), 41 (19).

1,3-Dioxan-5-yl ethyl carbonate (3a) and (1,3-dioxolan-4-yl)-methyl ethyl carbonate (3a′). A CF-reaction was carried out under the conditions shown in Fig. 6 (0.77 M solution of GlyF in DEC; 300 °C, 50 bar, 18 hours; F = 0.05 mL min^{-1}). The final conversion was 81%. The mixture collected at the reactor outlet (54 mL) was concentrated by rotary evaporation (65 °C, 40 mbar) and distilled (116 °C, 40 mbar). Due to the close boiling points of the unconverted GlyF (~20%) and the products, the distillation was tricky; title products were obtained as a liquid colorless mixture of isomers in 73% yield (5.27 g, purity 98% by GC/MS). They were characterized by ^{1}H NMR, ^{13}C NMR and GC/MS (see ESI†). The ratio **3a/3a′** was approximately the same for the starting isomers of GlyF.

^{1}H NMR (CDCl$_3$, 400 MHz) δ (ppm): 5.0 (s, 1H), 4.9–4.9 (m, 2H), 4.8 (d, J = 6.2 Hz, 1H), 4.6 (m, 1H), 4.3 (qnt, 1H), 4.3–4.1 (m, 6H), 4.1–3.9 (m, 5H), 3.7 (dd, J = 8.5, 5.4 Hz, 1H), 1.3 (dt, J = 7.1, 3.3 Hz, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ (ppm): 154.7, 154.3, 95.2, 93.3, 72.7, 68.4, 68.0, 66.8, 66.4, 64.1, 14.0, 13.9. Signals in the ^{13}C spectrum of **3a/3a′** were all singlets. GC/MS (relative intensity, 70 eV) m/z: **3a** 176 (M$^+$, <1%), 175 ([M − H]$^+$, 1), 116 (14), 86 (34), 57 (28), 55 (12), 45 (32),

44 (100), 43 (31); **3a′** 176 (M⁺, <1%), 175 ([M − H]⁺, 2), 91 (10), 89 (11), 86 (38), 73 (57), 58 (21), 57 (42), 45 (100), 44 (42), 43 (29).

(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl ethyl carbonate (3b). A 0.39 M solution of solketal in DEC was set to react in the CF-mode at 275 °C and 50 bar, for 18 hours ($F = 0.05$ mL min⁻¹). The final conversion was 72%. The mixture collected at the reactor outlet (54 mL) was concentrated by rotary evaporation (65 °C, 40 mbar) and distilled (102 °C, 40 mbar). The title product was obtained as a liquid colorless in 76% yield (3.28 g, purity 98% by GC/MS). Compound **3b** was characterized by ¹H NMR, ¹³C NMR and GC/MS (see ESI†).

¹H NMR (CDCl₃, 400 MHz) δ (ppm): 4.33 (m, 1H), 4.24–4.13 (m, 4H), 4.08 (dd, $J = 8.5$, 6.4 Hz, 1H), 3.78 (dd, $J = 8.5$, 5.8 Hz, 1H), 1.42 (s, 3H), 1.35 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 3H). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): 154.7, 109.6, 73.1, 67.5, 66.0, 64.0, 26.4, 25.1, 14.0. Signals in the ¹³C spectrum of **3b** were all singlets. GC/MS (relative intensity, 70 eV) m/z: 204 (M⁺, <1%), 189 (39), 161 (31), 101 (27), 72 (12), 61 (10), 59 (18), 57 (25), 43 (100), 42 (10).

Benzyl 1,3-dioxan-5-yl carbonate (6a) (1,3-dioxolan-4-yl)-methyl benzyl carbonate (6a′). A mixture of GlyF–DBnC–acetone in 1 : 5 : 12 molar ratio, respectively, was allowed to react for 4 hours at 250 °C and 50 bar ($F = 0.05$ mL min⁻¹). The final conversion of GlyF was 94%. The reaction mixture was concentrated by rotary evaporation (50 °C, 40 mbar), but the title product could not be isolated by further distillation under vacuum. The oily residue (2 g, after rotary evaporation) was subjected to flash column chromatography (FCC) over silica gel, using a petroleum ether (PE)–diethyl ether (Et₂O) 1 : 1 v/v solution (column $L = 8$ cm, Ø = 2.5 cm) as the eluent. Under such conditions, isomers **6a** and **6a′** were both isolated in a pure form (98% by GC/MS); the first product (**6a**) was a colorless liquid, while the second compound (**6a′**) slowly crystallized on standing. They were characterized by GC/MS, ¹H NMR and ¹³C NMR (2D-NMR spectra were also available for compound **6a′**; see ESI†).

¹H NMR (CDCl₃, 400 MHz) δ (ppm): **6a** 7.5–7.3 (m, 5H), 5.2 (s, 1H), 4.9 (d, $J = 6.2$ Hz, 1H), 4.8 (d, $J = 6.3$ Hz, 1H), 4.7–4.6 (m, 1H), 4.0 (dd, $J = 12.1$, 2.8 Hz, 1H), 4.0 (dd, $J = 12.1$, 4.3 Hz, 1H); **6a′** 7.5–7.3 (m, 5H), 5.2 (s, 2H), 5.0 (s, 1H), 4.9 (s, 1H), 4.3 (m, 1H), 4.3–4.2 (m, 2H), 4.0 (dd, $J = 8.5$, 6.7 Hz, 1H), 3.7 (dd, $J = 8.5$, 5.4 Hz, 1H). ¹³C NMR (CDCl₃, 100 MHz) δ (ppm): **6a** 154.3, 140.8, 134.7, 128.4, 128.2, 93.4, 69.8, 68.8, 68.0; **6a′** 155.0, 135.1, 128.7, 128.7, 128.5, 95.6, 73.0, 70.0, 67.4, 66.8. Signals in the ¹³C spectrum of **6a** and **6a′** were all singlets. GC/MS (relative intensity, 70 eV) m/z: **6a** 238 (M⁺, 1%), 107 (15), 92 (10), 91(100), 77 (10), 65 (17), 57(10); **6a′** 238 (M⁺, <1%), 147(17), 107(17), 92 (18), 91(100), 79 (10), 77 (15), 73 (11), 65 (19), 57 (15), 45 (24).

1,3-Dioxan-5-yl (1-hydroxypropan-2-yl) carbonate (4a), (1,3-dioxolan-4-yl)methyl (1-hydroxypropan-2-yl) carbonate (4a′), 1,3-dioxan-5-yl (2-hydroxypropyl) carbonate (5a) and (1,3-dioxo-lan-4-yl)methyl (2-hydroxypropyl) carbonate (5a′). A 1.07 M solution of GlyF in propylene carbonate was set to react for 4 hours at 300 °C and 50 bar ($F = 0.05$ mL min⁻¹). The final

conversion of GlyF was 48%. The reaction mixture was concentrated by rotary evaporation (50 °C, 40 mbar), but the title product could not be isolated by further distillation under vacuum. Also, any attempt to purify and separate compounds **4–5** by FCC was not successful. The oily residue was analyzed by GC/MS. Structures of products **4–5** were assigned by comparison of their MS spectra with those of starting acetals (**1a/1a′**) (see ESI†).

GC/MS (relative intensity, 70 eV) m/z: **4a** 206 (M⁺, <1%), 131 (45), 102 (18), 87 (41), 85 (44), 71 (11), 59 (84), 58 (38), 57 (65), 55 (11), 45 (100), 44 (68), 43 (56), 42 (11), 41 (38), 39 (17); **4a′** 206 (M⁺, <1%), 131 (46), 87 (52), 85 (69), 73 (19), 71 (12), 59 (87), 58 (18), 57 (100), 45 (86), 44 (31), 43 (56), 42 (12), 41 (38), 39 (22); **5a** 206 (M⁺, <1%), 131 (27), 87 (50), 85 (39), 73 (12), 59 (71), 58 (70), 57 (77), 45 (100), 44 (30), 43 (54), 42 (13), 41 (29), 39 (18); **5a′** 206 (M⁺, <1%), 117 (12), 88 (15), 87 (24), 75 (13), 73 (27), 72 (10), 71 (10), 59 (59), 58 (19), 57 (45), 45 (100), 44 (25), 43 39), 42 (10), 41 (21), 39 (12).

Acknowledgements

Notes and references

1 (a) M. Pagliaro and M. Rossi, in *The Future of Glycerol*, ed. J. H. Clark and G. A. Kraus, The Royal Society of Chemistry, Cambridge, 2nd edn, RSC Green Chemistry Series N°. 8, 2010; (b) C. O. Tuck, E. Pérez, I. T. Horváth, R. A. Sheldon and M. Poliakoff, *Science*, 2012, **337**, 695–699.

2 (a) D. T. Johnson and K. A. Taconi, *Environ. Prog.*, 2007, **262**(4), 338–348; (b) A. Bevilacqua Leoneti, V. Aragão-Leoneti and S. Valle Walter Borges de Oliveira, *Renewable Energy*, 2012, **45**, 138–145.

3 (a) B. Katryniok, H. Kimura, E. Skrzynska, J.-S. Girardon, P. Fongarland, M. Capron, R. Ducoulombier, N. Mimura, S. Paul and F. Dumeignil, *Green Chem.*, 2011, **13**, 1960–1979; (b) J. C. Beltran-Prieto, K. Kolomaznik and J. Pecha, *Aust. J. Chem.*, 2013, **66**, 511–521; (c) S.-S. Liu, K.-Q. Sun and B.-Q. Xu, *ACS Catal.*, 2014, DOI: 10.1021/cs5005568. Q6

4 (a) A. Perosa and P. Tundo, *Ind. Eng. Chem. Res.*, 2005, **44**, 8535–8537; (b) M. Akiyama, S. Sato, R. Takahashi, K. Inui and M. Yokota, *Appl. Catal., A*, 2009, **371**, 60–66; (c) I. Gandarias, P. L. Arias, S. G. Fernández, J. Requies, M. El Doukkali and M. B. Güemez, *Catal. Today*, 2012, **195**, 22–31.

5 (a) P. F. Fonseca Amaral, T. Felix Ferreira, G. Cardoso Fontes and M. A. Zarur Coelho, *Food Bioprod. Process.*, 2009, **87**, 179–186; (b) R. W. Nicol, K. Marchand and W. D. Lubitz, *Appl. Microbiol. Biotechnol.*, 2012, **93**, 1865–1875.

6 (a) G. Morales, M. Paniagua, J. A. Melero, G. Vicente and C. Ochoa, *Ind. Eng. Chem. Res.*, 2011, **50**, 5898–5906; (b) A. Sunder, R. Hanselmann, H. Frey and R. Mulhaupt, *Macromolecules*, 1999, **32**, 4240–4246; (c) N. Rahmat, A. Z. Abdullah and A. R. Mohamed, *Renewable Sustainable Energy Rev.*, 2010, **14**, 987–1000.

7 M. McCoy, *Chem. Eng. News*, 2012, **90**, 15.

8 (a) I. Agirre, M. B. Güemez, A. Ugarte, J. Requies, V. L. Barrio, J. F. Cambra and P. L. Arias, *Fuel Process. Technol.*, 2013, **116**, 182–188; (b) L. Li, T. I. Korányi, B. F. Sels and P. P. Pescarmona, *Green Chem.*, 2012, **14**, 1611–1619; (c) C. Len and R. Luque, *Sustainable Chem. Process.*, 2014, **2**, 1, http://www.sustainablechemical-processes.com/content/2/1/1.

9 (a) A. Behr, J. Eilting, K. Irawadi, J. Leschinski and F. Lindner, *Green Chem.*, 2008, **10**, 13–30; (b) A. E. Dıaz-Alvarez, J. Francos, B. Lastra-Barreira, P. Crochet and V. Cadierno, *Chem. Commun.*, 2011, **47**, 6208–6227; (c) Lambiotte & Cie, http://www.lambiotte.com/Products (accessed August 2014).

10 M. Selva, V. Benedet and M. Fabris, *Green Chem.*, 2012, **14**, 188–200.

11 (a) M. Selva, M. Fabris and A. Perosa, *Green Chem.*, 2011, **13**, 863–872; (b) Hydrolysis reactions were plausibly due to traces of water adsorbed by the highly hygroscopic K_2CO_3 (see J. S. Moya, E. Criado and S. De Aza, *J. Mater. Sci.*, 1982, **17**, 2217–2217).

12 (a) M. Selva, M. Noè, A. Perosa and M. Gottardo, *Org. Biomol. Chem.*, 2012, **10**, 6569–6578; (b) M. Selva, A. Caretto, M. Noè and A. Perosa, *Org. Biomol. Chem.*, 2014, **12**(24), 4143–4155; (c) G. Fiorani and M. Selva, *RSC Adv.*, 2014, **4**, 1929–1937.

13 (a) D. Delledonne, F. Rivetti and U. Romano, *Appl. Catal., A*, 2001, **221**, 241–245; (b) M. Fuming, L. Guangxing, N. Jin and X. Huibi, *J. Mol. Catal. A: Chem.*, 2002, **184**, 465–468.

14 The chosen volume (10 mL) of the reactant mixture was equal to ten times that of the reactor. Under such conditions, the stream spilled from the CF-reactor showed a constant composition with time.

15 As for DMC, no variations of the conversion and the product distribution of the reactant mixtures were appreciated after the initial 60–80 min of reaction.

16 NMR analyses were recorded at 400 MHz. Under such conditions, mixtures derived from the reaction of PC and GlyF showed a plethora of overlapped NMR resonances due to the presence of 4 diastereomers and 8 enantiomers with very similar structures. This made doubtful and unreliable any interpretation of NMR spectra.

17 (a) M. Mohsen-Nia, H. Amiri and B. Jazi, *J. Solution Chem.*, 2010, **39**, 701–708; (b) J.-F. Cotè, D. Brouillette, J. E. Desnoyers, J.-F. Rouleau, J.-M. St. Arnaud and G. Perron, *J. Solution Chem.*, 1996, **25**, 1163–1173.

18 See MSDS on http://www.sigmaaldrich.com.

19 The relative ratio of DBnC/DBE from GC/MS analyses allowed estimation that ~1% of the starting DBnC underwent a decarboxylation reaction. In line with results reported in ref. 11 and 12, DBnC was less thermally stable than other dialkyl carbonates such as DMC and DEC.

20 M. Diasakou, A. Louloudi and N. Papayannakos, *Fuel*, 1998, **77**(12), 1297–1302.

21 (a) S. Saka and D. Kusdiana, *Fuel*, 2001, **80**, 225–231; (b) A. Demirbas, *Energy Convers. Manage.*, 2002, **43**, 2349–2356; (c) K. Bunyakiat, S. Makmee, R. Sawangkeaw and S. Ngamprasertsith, *Energy Fuels*, 2006, **20**, 812–817; (d) M. N. Varma and G. Madras, *Ind. Eng. Chem. Res.*, 2007, **46**, 1–6; (e) S. A. Pasias, N. K. Barakos and N. G. Papayannakos, *Ind. Eng. Chem. Res.*, 2009, **48**, 4266–4273; (f) Y.-T. Tsai, H. M. Lin and M.-J. Lee, *Bioresour. Technol.*, 2013, **145**, 362–369.

22 K. T. Tan and K. T. Lee, *Renewable Sustainable Energy Rev.*, 2011, **15**, 2452–2456.

23 W. V. Steele, R. D. Chirico, S. E. Knipmeyer, A. Nguyen and N. K. Smith, *J. Chem. Eng. Data*, 1997, **42**, 1037–1052.

24 (a) Z. Ilham and S. Saka, *Bioresour. Technol.*, 2009, **100**, 1793–1796; (b) Z. Ilham and S. Saka, *Bioresour. Technol.*, 2010, **101**, 2735–2740.

25 The transesterification of oils in sc-DMC gives glycerol carbonate (GlyC) as a co-product. Citramalic acid is plausibly originated by the reaction of GlyC and DMC in the presence of water and free fatty acids in the feedstock (crude oils).

26 K. N. Houk, R. Wells Gandour, R. W. Strozier, N. G. Rondan and L. A. Paquette, *J. Am. Chem. Soc.*, 1979, **101**, 6797–6802.

27 Unfortunately, very limited studies are available on the thermodynamic properties of DMC; to the best of our knowledge, except for a semi-computational analysis (Y. Zhou, J. Wu and E. W. Lemmon, *J. Phys. Chem. Ref. Data*, 2011, **40**, 043106, no systematic experimental investigations have been ever undertaken on the behaviour of DMC, especially on its density, near and in the sc-state.

28 P. G. Jessop and W. Leitner, in *Chemical Synthesis Using Supercritical Fluids*, Wiley-VCH, 2008.

29 V. F. Marulanda, *J. Cleaner Prod.*, 2012, **33**, 109–116.

30 (a) S. Glisic and D. Skala, *J. Supercrit. Fluids*, 2009, **49**, 293–301; (b) J. M. N. van Kasteren and A. P. Nisworo, *Resour., Conserv. Recycl.*, 2007, **50**, 442–458.

31 (a) A. Perosa, M. Selva, P. Tundo and F. Zordan, *Synlett*, 2000, 272–274; (b) M. Selva, A. Perosa and M. Fabris, *Green Chem.*, 2008, **10**, 1068–1077.

32 V. Rathore, S. Tyagi, B. Newalkar and R. P. Badoni, *Ind. Eng. Chem. Res.*, 2014, **53**, 10525–10533.

33 (a) B. M. Bhanage, S.-I. Fujita, Y. Ikushina and M. Arai, *Appl. Catal., A.*, 2001, **219**, 259–266; (b) C. Murugan, H. C. Bajaj and R. V. Jasra, *Catal. Lett.*, 2010, **137**, 224–231; (c) A. Pyrlik, W. F. Hoelderich, K. Müller, W. Arlt, J. Strautmann and D. Kruse, *Appl. Catal., B*, 2012, **125**, 486–491.

34 P. G. Jessop, T. Ikariya and R. Noyori, *J. Am. Chem. Soc.*, 1996, **118**, 344–355.