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# Process Intensification for Tertiary Amine Catalyzed Glycerol Carbonate Production: Translating Microwave Irradiation to Continuous-Flow Process

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**Abstract:** Different products of interest can be produced from glycerol and glycerol carbonate (GC) has received much attention in the recent years because of its physical properties nontoxicity and water solubility. Here in we report a process intensification protocol for glycerol carbonate production mediated by tertiary amine catalysis where a 24kg $L^{-1}$ $d^{-1}$ productivity was obtained with 79% of isolated yield and a 5hours of operation time without losing efficiency.

## 1. Introduction

The biodiesel industry has grown in the recent years and emerged as a leading source of renewable glycerol (~63%) accounting for 2,247 kilo tons in 2013 and an expected market of $2.52 billion by 2020. Personal care, pharmaceutical industry, food and beverage were the largest application segment for glycerol. [1]

Among the different products of interest that can be produced from glycerol, glycerol carbonate (GC) has received much attention in the recent years mainly because of its physical properties (i.e. fp > 240 $^{o}$C, bp 110-115 $^{o}$C at 0.1 mmHg), nontoxicity and water solubility. The applications of glycerol carbonate are wide and can go from solvent to beauty and personal care.

Several strategies can be used to synthesize glycerol carbonate and many of them have already been reported, but just a few can meet the criteria for a industrial manufacturing strategy as pointed out by Ochoa-Gómez and co-workers (Figure 1). [2]

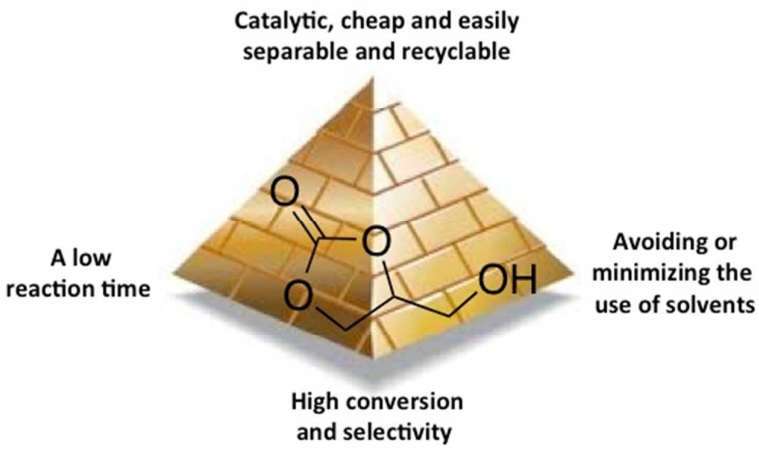



**Figure 1**: Criteria for glycerol carbonate (GC) manufacturing.

As already pointed out in Figure 1, a catalytic process with low reaction time is desirable to achieve an efficient methodology for glycerol carbonate production. Since most of the procedures found over literature reports temperatures above 80$^{o}$C, the use of microwave irradiation can be a good alternative to enhance reaction

kinetics and reduce reaction time. [3-5] Unfortunately, microwave irradiation protocols are not scalable to the extent need for glycerol carbonate production but Kappe and co-workers have shown recently that such procedures can be easily translated to continuous-flow protocols where scalability is not a problem. [6]

Different groups have attempted to use ionic liquids [7-14] and lipases [15-20] as catalysts to produce glycerol carbonate with high yield and selectivity but this strategies are inadequate in terms of high reaction times and prices of the catalysts used, sometimes not commercially available. Other catalysts such as Gold, [21] Palladium, [22, 23] Copper, [24-26] Rhodium, [27] Tungsten, [28, 29] Zinc, [10, 30] Lanthanum, [31-33] Calcium, [34, 35] Magnesium, [36-41] Zeolites, [42, 43] Nafion, [44] Alumina, [45-47] have been used to produce glycerol carbonate by carbonylation of glycerol with alkyl carbonates, [19, 48, 49] $CO_2$ [30] or urea, [50-55] arriving on the desired product with poor (when $CO_2$ is used) to good yields and selectivity (when alkyl carbonates are used). A more convergent approach tends to arrive on the desired glycerol carbonate during the biodiesel process and good results were obtained up to now (Figure 2). [17, 56-61]

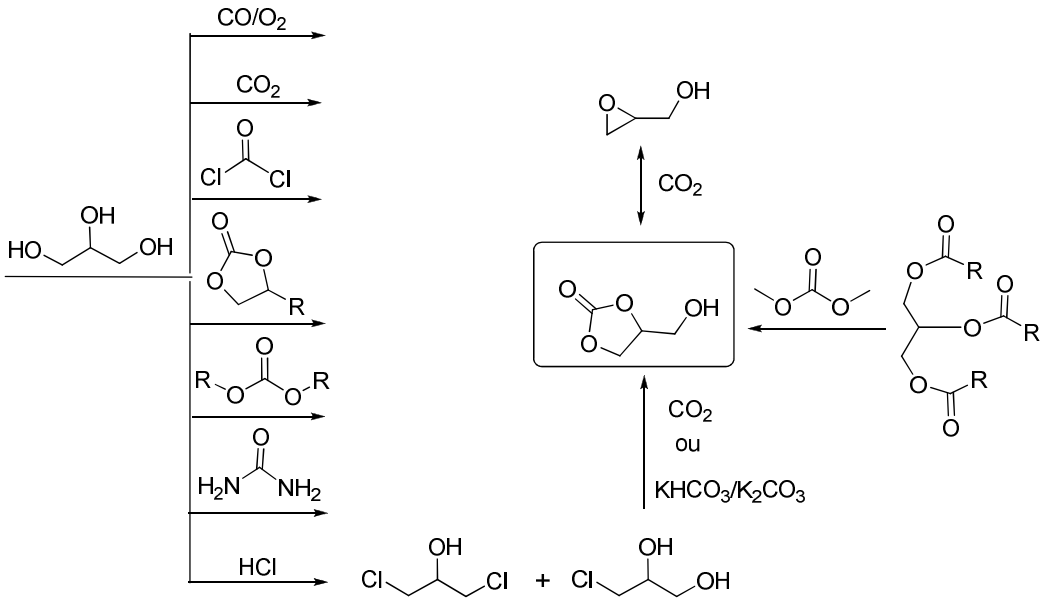



**Figure 2**: Strategies to synthesize glycerol carbonate.

Besides all catalysts already used on the glycerol carbonate production, nucleophilic catalysis performed by tertiary amines seems to be the most reliable procedure since they are safe, easy to separate from reaction media and cheap, where DABCO, [62] DBU, [12, 63] TEA [64] and Imidazole [65] are the most used.

Here in we report our effort on optimizing glycerol carbonate production catalyzed by several tertiary amines, under microwave irradiation and translating the best reaction conditions to continuous-flow protocol aiming to obtain better productivities.

## 2. Materials and Methods

2.1 **Materials**. Glycerol (glycerin), purchased from Vetec Chemistry, dimethyl carbonate (DMC), glyceryl carbonate, the ionic liquid [BMIM][AcO] and all of the amines used: N-methylimidazole, imidazole, DABCO (1,4-diazabicyclo [2,2,2] octane), immobilized DABCO hydrochloride (1.4-diazabicyclo [2,2,2] octane), DMAP (4-dimethylaminopyridine), DBU (1,8-diazibiciclo [5.4.0] undec-7-ene), HMTA (hexamethylenetetramine), triethylamine and pyridine, were purchased from Sigma-Aldrich. All other materials were at least reagent-grade.

2.2 **Batch Reactions**. Glycerol (3 mmol, 1 eq,), DMC (9 mmol, 3 eq.) and a catalyst (sodium acetate, [BMIM][AcO] and N-methylimidazole) (0.23 mmol, 7.7 mol%) were added to 4 ml vials on silicon carbide plates. Reactions were performed at 90°C for 2h. Conversions were analyzed as described in section 2.5.[7]

2.3 **Microwave reactions**. Microwave irradiation experiments were carried out using a Monowave 300 single-mode microwave reactor from Anton Paar GmbH (Graz, Austria). The experiments were performed in a 10 mL Pyrex microwave process vial equipped with a magnetic stirring bar at a rate of 600 rpm. Reaction times

refer to hold times at the temperatures indicated and not to total irradiation times. The reaction conversions were evaluated by GCMS (item 2.5).

2.4 **Continuous-Flow Reactions**. The GC synthesis conditions by microwave irradiation were also performed under continuous flow conditions. For this purpose, the same reactional conditions (molar ratio between glycerol/DMC and temperature) were maintained. Catalyst concentrations of 0.1, 0.5, 1.5 and 2.5 mol% were investigated once it was possible to reduce it under microwave irradiation. Glycerol and DBU were mixed and previously heated to 70°C to turned the mixture able to de pumped by the first pump (solution A). Flows of each pump from Syrris Asia system were carefully adjusted to maintain the proportion of 3:1 between the flows of pump A and B. Pump B (DMC) worked with a flow 3 times higher than pump A (Glycerol + DBU), and for this reason, both solution were pumped together with 1 or 2 mL/min. When pump A worked with 0,234mL/min and pump B with 0,766mL/min, the final solution was mixture in a tubular reactor of 16mL (1/16 i.d.), with a final flow rate of 1mL/min, resulting in a reaction time of 16 min. The isolation of the desired product was performed in a distillation system Buchi B-585 Glass oven (bulb-to-bulb destilation).

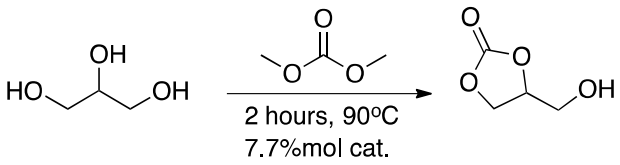
2.5 **GC analysis**. The GC-MS analysis was performed by using a modified method from.[20] Glyceryl carbonate and derived from the reactions were transformed into more volatile silylated derivatives in the presence of N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA). All GC-MS measurements were carried out in triplicate using a DB 5 (Agilent, J&W. Scientific®, USA) capillary column (30 m × 0.25 mm × 0.25 μm). The GC-MS samples were prepared by dissolving 10 μl of the final product in 1 mL of chloroform. 1 μL of this sample

was then injected into Shimadzu CG2010 equipment. The injector and detector temperatures were 250°C, and the oven temperature was constant at 60°C for 1 min, and then increased by 10 °C/min to 250°C, where it was held constant for 3 min. The percentages of conversion and selectivity were analyzed by the area of the chromatograms. GC-FID: HP-5MS capillary column (5% phenyl methyl polysiloxane capillary, 30.0m×250μm×250 μm). Helium was used as carrier gas. 1 μl samples were injected at 100ºC. The oven was heated at 15ºC/min to 150 ºC, at 8ºC/min to 200ºC, at 2ºC/min to 240ºC, and then maintained for 4min. After this, the oven was heated at 15ºC/min to 300ºC.

## 3. Results and Discussion

In the beginning of our studies, our group was first curious (intrigued) about the use of ionic liquids as catalyst for glycerol carbonate production, already reported by several authors over literature. [7, 8, 10-14, 62, 66] Some authors have already proposed that the catalytic activity of some ionic liquids in this reaction can be related to the basicity of the counter anion however we postulated that ionic liquids contaminated with small amounts of methyl imidazole could also catalyze this reaction as suggested above. If it was true it could be further questioned: Why use an expensive catalyst, like ionic liquids, to produce glycerol carbonate?

To evaluate the use of ionic liquids in catalyzing the synthesis of glycerol carbonate, we used standard conditions establish in literature. After screening different ionic liquids, [BMIM][AcO] appeared as the most promising and was further evaluated. Glycerol and DMC (1:3) were mixed together and reacted for 2 hours at 90°C using 7.7% mol of [BMIM][AcO]. Besides ionic liquid, we also decided to evaluate the methylimidole percursor, once it is reported that it is a known contaminant in different IL. The results are shown in Table 1.



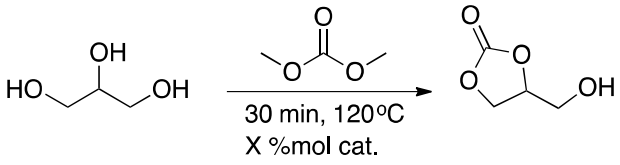

| Entry | Catalyst | Conv. (%) | Selectivity (%) |
|---|---|---|---|
| 1 | [BMIM][AcO] | 81 | 81 |
| 2 | Methyl Imidazol | 85 | 85 |

Reaction conditions: catalystic (7,7 mol%), glycerol and DMC (3:9 mmol), 90° C, 2 h. conventional heating.

**Table 1**: Glycerol carbonate production under basic catalysis.

As shown in Table 1, results obtained with [BMIM][AcO] ionic liquid are similar to those obtained when methyl imidazole.

We decided to look more carefully to the reaction catalyzed by methyl imidazole (MIM) and further evaluate different reaction parameters in order to optimize the reaction conditions, particularly the use of continuous-flow. Now, microwave irradiation was used as a standard heating technique in order to have reaction conditions that could be easily translated to continuous-flow process. [6] Temperature, glycerol:DMC molar ratio and reaction time were screened (see supporting information for further details) and it was found that 120ºC, 1:3 and 30 minutes lead to the best conversions and selectivity's towards the desired product. The amount of catalyst was also investigated and the results are shown in Table 2.




| Entry | X % mol MIM | Conv. (%) | Selectivity (%) |
|---|---|---|---|
| 1 | 0 | 0 | 0 |
| 2 | 0.5 | 37 | 90 |

| | | | |
|---|---|---|---|
| 3 | 1 | 57 | 84 |
| 4 | 2.5 | 83 | 83 |
| 5 | 5 | 85 | 79 |
| 6 | 7.7 | 85 | 85 |

Reaction conditions: glycerol and DMC (3:9 mmol), 120° C, 30 min, MW.

**Table 2**: Glycerol carbonate production under methyl imidazole catalysis at different concentrations.

Table 2 presents the results obtained for different methyl imidazole percentage on glycerol carbonate production under microwave irradiation. It is possible to note that from 2.5 to 7.7 mol % of catalyst (Entries 4 to 6, Table 2) just a small increase on conversion is obtained and do not justify the use of higher amounts of catalyst.

With these results in hands we decided to explore the potential of the developed methodology to other amines such as DMAP, DBU, DABCO, HMTA, TEA and Pyridine. The results are presented on Table 3.

| Catalysts | Conv. (%) | Sel. (%) |
|---|---|---|
| N-methylimidazole | 83 | 85 |
| DMAP | 86 | 76 |
| DBU | 85 | 78 |
| DABCO | 86 | 75 |
| HTMA | 80 | 76 |
| TEA | 88 | 75 |
| Pyridine | 88 | 78 |

Reaction conditions: Catalysts (2,5 Mol%), glycerol and DMC (3:9 mmol), 120° C, 30 min.

**Table 3**: Different nucleophilic catalysts on glycerol carbonate production under microwave irradiation.

A first look at table 3 shows that all catalysts present similar behavior achieving comparable conversion for glycerol carbonate after 30 minutes of reaction, without loss of selectivity. But the evolution of glycerol carbonate formation during the 30 minutes is totally different depending on the catalyst chosen. Figure 1 shows the values of conversion at different reaction times for the catalysts mentioned above.

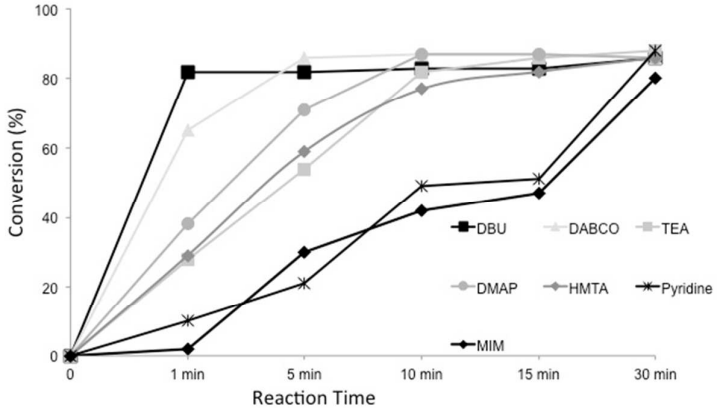



**Figure 3**: Typical conversion time profile. Reaction conditions: glycerol (0.92 g, 10 mmol), DMC (2.67 g, 30 mmol), Temp: 120◦C (MW), Catalyst: 0.025 mmol% (w.r.t glycerol).

As presented here, very good conversion could be obtained for DBU after just one minute of reaction under microwave irradiation. DABCO was also good and lead to high conversions after 5 minutes. The other nucleophilic catalysts have shown also good performance but just after 10 minutes of reaction. When we turn the results obtained in Figure 1 into productivity of each catalyst, DBU pop-ups from the others, presenting high productivities due to the very fast reaction (Table 4). On the other hand, methyl imidazole (MIM) presented very low productivity when compared to the other nucleophilic catalysts.

| Catalyst | Productivity* | USD/mmol |
|---|---|---|
| DMAP | 14.42 | 1.00 |
| MIM | 5.23 | 0.053 |

| | | |
|---|---|---|
| DBU | 153.88 | 0.38 |
| DABCO | 31.90 | 0.19 |
| HTMA | 8.94 | 0.05 |
| TEA | 10.63 | 0.026 |
| Pyridine | 5.04 | 0.09 |

* Productivity: (g of product / h / mmol of catalyst)

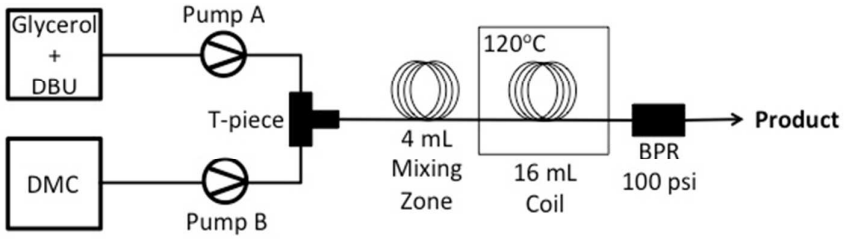
Reaction conditions: glycerol (0.92 g, 10 mmol), DMC (2.67 g, 30 mmol), Temp: 120◦C (MW), Catalyst: 0.025 mmol%(w.r.t glycerol), * Productivity: (g of product / h / mmol of catalyst).

**Table 4**: Productivity of several nucleophilic catalysts on the production of glycerol carbonate under microwave irradiation at 120$^{o}$C.

The same heating profile cannot be properly performed under batch conditions using reflux condenser since dimethyl carbonate boiling point is around 90$^{o}$C, which drops the conversion of the reaction to 50% when catalyzed by DBU.

The use of microwave irradiation can take chemistry to new process windows but scaling up the conditions already optimized is still a challenge. As proposed by Kappe and co-workers this conditions can be easily translated to continuous-flow protocols where conventional heating can take place as fast as inside the microwave reactor due to the high surface to volume ratio.

With these results in hands we start to develop our continuous-flow process. For this purpose we have used to syringe pumps connected through a T-piece (4 mL mixing zone) into a 16mL coil (heated at 120$^{o}$C) and 100 psi back pressure regulator, as shown in Figure 3. A solution of DBU in Glycerol was pumped through pump A (0.234 mL/min) and mixed with neat DMC from pump B (0.766 mL/min) at a total flow rate of 1 mL/min, respecting the stoichiometry optimized under microwave irradiation, leading to a residence time of 16 minutes.




Reaction conditions: 1:3 glycerol (37.84g, 0.41 mol and DMC (32.1 g , 30 mL, 1.23 mol), DBU (0.010 mol, 2.5 mol%) , 120° C, pump A: 0.234 mL/min, pump B: 0.766 mL/min, flow rate: 1 mL/min.

**Figure 3**: Continuous-flow approach to glycerol carbonate production catalyzed by DBU at 120°C.

The set up presented on Figure 4 lead to 84% of conversion and 86% of selectivity to the desired glycerol carbonate. Further optimization was also performed trying to reduce residence time and the amount of DBU used as catalyst. Under a total flow rate of 2mL/min (0.468 mL/min – pump A and 1.532 mL/min pump B) and using 1.5% mol of DBU, 80% of conversion could be obtained with 82% of selectivity with chemical yield isolated 79% to glycerol carbonate. The system was stable for 5 hours of operation where now change on conversion and selectivity was observed.

As already reported by other authors [61, 67] glycerol carbonate can be obtained direct from vegetable oils through a cascade reaction where glycerol from triacylglycerol hydrolysis is used *in situ* for the reaction with DMC and glycerol carbonate formation. We were also interested in this approach and decided to test the protocol optimized with DBU under continuous-flow conditions. The results suggest that catalysis by DBU promotes coproduction of biodiesel and glycerol carbonate under continuous-flow conditions (Table 5).

| Entry | Flow rate (mL/min) | Residence time (min) | Glycerol carbonate (%) | Biodiesel (%) |
|---|---|---|---|---|
| 1 | 1 | 16 | 90 | 80 |
| 2 | 2 | 8 | 70 | 62 |

**Table5:** Coproduction of biodiesel and glycerol carbonate in continuous-flow conditions catalyzed by DBU.

## Conclusion

In conclusion we were able to develop a protocol for a tertiary amine catalyzed glycerol carbonate production using microwave irradiation and its translation into continuous-flow system. With all the catalysts tested, low catalyst loading, high yields and selectivity were observed in only 30 minutes under microwave irradiation. In addition, among the catalysts tested DBU presented higher productivity and its reaction translated into continuous-flow. Under solventless continuos-flow, 80% yield and 82% selectivity was observed in 16 minutes residence time. These conditions lead to a space-time yield of 24k g. $L^{-1}$. $day^{-1}$ for the production of glycerol carbonate. The same continuous-flow system was also used to obtain glycerol carbonate direct from vegetable oil with 80.0% biodiesel production and 90.0% production of glycerol carbonate was reached.

## 4. Acknowledgments

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