



Phenomenological kinetic model of the synthesis of glycerol carbonate assisted by focused beam reflectance measurements



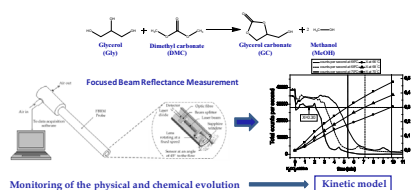
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HIGHLIGHTS

- Synthesis of glycerol carbonate using inexpensive catalysts was studied.
- The reacting system is a liquid–liquid mixture evolving into a monophasic system.
- The evolution of the dispersion was observed by FBRM.
- The change in the phase regime affects the catalytic behaviour.
- Phenomenological kinetic models were proposed, fitted and verified.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, the synthesis of glycerol carbonate from glycerol and dimethyl carbonate is studied. First, operating conditions and a catalyst were selected after screening of different alkali metal salts, resulting K_2CO_3 the most active species. Afterwards, given the low degree of miscibility between the reactants, a study of the phase change from a liquid–liquid emulsion to a monophasic sample throughout the reaction was successfully performed with the aid of a focused beam reflectance probe. This change took place at a conversion of approximately 0.30. With the findings of this study, distinct kinetic models were proposed and fitted to the experimental data obtained after the completion of a series of kinetic runs varying temperature (66–70 °C), molar ratio of dimethyl carbonate to glycerol (1.5–3) and catalyst load (0.75–1.25% w/w). A model composed of two potential equations was proposed with activation energy of $179.2 \pm 3.7 \text{ kJ mol}^{-1}$. The model was capable of describing the initial biphasic stage and the monophasic regime correlated best to the experimental data, with errors below 6.8%.

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1. Introduction

The saturation of the market of glycerol (Gly) following the significant development of the biodiesel industry has led to a marked price drop of this formerly valuable by-product,

considered as a building block from biomass [1]. Thus, research on the synthesis of valuable products derived from glycerol has been a blooming issue as a means of its valorisation. Examples of the processes studied are selective oxidation to dihydroxyacetone, hydrogenation to 1,2-propanediol, ketalization to solketal or even microbiological transformations to 1,3-propanediol and 2,3-butanediol [2,3]. However, currently the synthesis of glycerol carbonate (GC) by carboxylation and transesterification is on the focus of research due to its numerous applications as a multipurpose green solvent as well as a component of gas separation membranes, coating materials and pozzolanic-based building materials. In addition, it has been reported to be a synthon for many different

Abbreviations: DMC, dimethyl carbonate; GC, glycerol carbonate; Gly, glycerol; MeOH, methanol.

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Nomenclature

AIC	Akaike's information criterion		
C	concentration of the components at a given time (mol L ⁻¹)		
E_{ai}/R	ratio of activation energy and the ideal gas constant (K)		
F	Fischer's F statistical parameter		
FBRM	focused beam reflectance measurement		
HPLC	high-performance liquid chromatography		
K	number of parameters of a proposed model		
M	initial molar ratio of dimethyl carbonate to glycerol		
n	total number of components		
N	total number of data to which a model is fitted		
r	reaction rate (mol L min ⁻¹)		
RMSE	residual mean squared error		
SQR	sum of quadratic residues		
T	temperature (K)		
TOF	turnover frequency (mol converted·mol catalyst ⁻¹ min ⁻¹)		
X	conversion, as defined by Eq. (8)		
		<i>Greek letters</i>	
		γ	heteroscedasticity parameter
		ν	stoichiometric coefficient of the component i
		ω	agitation rate (rpm)
		<i>Subscripts</i>	
		0	relative to the start of the reaction, time equals zero
		i	relative to component i
		cat	relative to the catalyst
		crit	relative to the critical conversion at which the phase regime changes
		DMCsol	relative to concentration of DMC dissolved in the glycerol-rich phase

end products, especially polymers used for adhesives and protective coatings or esters obtained by acylation, with good surfactant and oxidation stability features [4].

Synthesis of GC has been researched as a means to valorise glycerol as well as to substitute the traditional environmentally unfriendly production via the phosgene route. Carboxylation with CO₂ under high demanding energy conditions has been achieved, with applied pressures ranging from 3.5 to 10 MPa and temperatures between 80 and 180 °C using zeolites and different metal-based catalysts [5–8]. Vacuum conditions and temperatures around 150 °C with metallic oxides and sulphates have been reported for the glycerolysis of urea as an alternative pathway for the production of GC [9–12]. However, transesterification of glycerol with organic carbonates appears as a methodology with less demanding operating conditions, especially when working with dimethyl carbonate (DMC) or ethylene carbonate. Atmospheric pressure and temperatures from 60 to 75 °C have been reported in the former case [13–16] and around 50 °C in the latter [12,17]. Additionally, solventless syntheses are common practice contrary to the procedures described in the paragraph above and even the catalyst used in some cases are inexpensive, like calcium oxide and potassium carbonate [13,18].

The present study follows the line of the transesterification reaction using DMC as the carbonate source. Initially, in the absence of any catalyst, the reactants Gly and DMC have very low miscibility with each other, which results in an emulsion-like liquid–liquid biphasic system. Nevertheless, as the reaction takes place and products generate, the system evolves into a single phase liquid [19,20]. This type of behaviour has previously been reported for certain esterification [21] transesterification reactions [22].

The mechanism through which the transesterification reaction between glycerol and dialkyl carbonates proceeds requires a basic catalyst. This mechanism basically consists of four steps: (a) formation of a glyceroxide anion by extraction of one of the protons from glycerol by the basic catalyst; (b) attack on the carbonate group by the nucleophile glyceroxide anion releasing a non-cycled unstable reaction intermediate as well as an alkoxide ion; (c) regeneration of the catalyst releasing a proton that combines with the alkoxide ion to form a molecule of alcohol; (d) finally, the unstable intermediate species suffers a rapid cyclation to yield glycerol carbonate and a second molecule of alcohol is also released. [14,23].

The selectivity of the reaction of DMC and Gly to yield has been reported to be above 96% and very close to 100% in many cases using assorted catalysts. Examples of these would be Na₂O [24], KF modified hydroxyapatites, selectivity above 98% [15], Mg–Al hydrotalcites [23], calcined and non-calcined CaO [24] as well as supported on Diatomite, Kaolin and Al₂O₃ [13]. Finally, when potassium carbonate was used the selectivity reported has been 100% for a reaction at very similar conditions to those being tested in this work [14].

The behaviour of distinct phases in multiphasic systems can be measured on-line by different optical techniques like spatial filtering velocimetry, photometric stereo imaging, the patented Eyecon® technology (based on flash imaging), endoscopy or focused beam reflectance measurement (FBRM) [25,26].

Among them, the latter technology has been typically used to determine the particle size distribution of suspensions of solid suspensions in liquid phases, such as in flocculation processes [27,28]. However, more recently it has been employed to monitor the evolution and calculate particle size distributions of the phases of liquid–liquid dispersions consisting of mineral oils and water [29–31]. There is also a reference that reports on the measurement of droplet size distributions by means of a microphotographic system known as bubble-cap tray while the transesterification of Gly with methyl oleate takes place [22].

The performance of the reaction between Gly and DMC under different operating conditions and catalysts has been widely addressed, as already mentioned; however, the kinetic aspects of this process have not been given so much attention. Since a change in the phase regime occurs throughout the conversion to products, it is reasonable to suggest a model that addresses this observation and the potential consequences it can produce on the catalytic behaviour of the system.

Thus, as a means to shed more light on these aspects behind the transesterification of Gly with DMC, the evolution of the initially biphasic system was monitored by FBRM and a set of kinetic runs was completed varying temperature, concentration of catalyst and initial molar ratio of the reactant species.

A series of kinetic models was reasoned and proposed to explain the data observed from a phenomenological standpoint. Discrimination and final selection of a definite phenomenological kinetic model was made on the basis of physicochemical and statistical criteria.

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