



Experimental and modelling approach to the catalytic coproduction of glycerol carbonate and ethylene glycol as a means to valorise glycerol



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ABSTRACT

Due to the current scenario of biodiesel industry facing a challenge in the management of its by-product glycerol, its conversion into value-added products is of the greatest significance. This work presents an experimental and modelling approach to the simultaneous production of glycerol carbonate and ethylene glycol, two highly valuable chemicals, under mild operating conditions reaching yields to the products as high as 96% using the inexpensive catalyst K_2CO_3 . Physical (focused beam reflectance measurement) and chemical (HPLC) analyses were employed to monitor the evolution of the chemical reaction between glycerol and ethylene carbonate, finding that the reacting system evolves from liquid–liquid dispersion to single-liquid system at a conversion of glycerol of 0.34. After minimising mass transfer limitations (800 rpm), a study of the reaction kinetics was performed varying temperature, molar ratio of reactant species and catalyst concentration. The model offering the best fit reflected with high accuracy the physical transition of the system, the reversibility of the reaction and the deactivation of the catalyst, with the following parameters: 91.7 ± 2.7 kJ/mol and 93.9 ± 15.9 kJ/mol for the direct and reverse reactions, respectively, with the deactivation constant having a value of 0.36 ± 0.06 s⁻¹.

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1. Introduction

Policies aimed at increasing gradually the share of use of energy based on renewable sources have been promoted all over the world during the early years of the present century, especially in the European Union. Subsequently, a boom of the biodiesel industry has taken place, which has led to an oversaturation of the glycerol (Gly) market and a subsequent price drop [1]. Awareness of this situation has led to multiple efforts being undertaken to employ this by-product of biodiesel as feedstock in order to improve the economics of the process and approach the Green Chemistry principle of preventing waste generation. The chemical features of glycerol have made it subject to very diverse transformations to obtain many interesting products, which have been accounted for in a significant number of thorough reviews [2,3]. Some examples of the synthetic pathways followed to valorise glycerol include esterification of different organic acids [4,5], hydrogenolysis to 1,2-propanediol [6] or dehydration reactions [7].

The synthesis of glycerol carbonate (GC) has been lately pursued through the transesterification of glycerol with organic car-

bonates, for they present the advantages of (i) being an indirect manner of CO₂ fixation and (ii) allowing the use of milder operating conditions [8]. Operation with dimethyl carbonate (DMC) at atmospheric pressure from 60 to 75 °C has been described with quantitative yield to product [9–18]. Likewise, synthesis with diethyl carbonate has been performed with positive results, though the reaction conditions were more severe: large molar excesses of diethyl carbonate to Gly have been used (17:1 to 21:1) and use of temperatures of 130 °C have been described using different types of hydrotalcites as catalysts [19,20]. Finally, ethylene carbonate (EC) has been put to use in this reaction in a procedure in absence of any catalyst at temperatures ranging from 100 to 140 °C [21] and also in catalytic processes with Mg/Al hydrotalcites and MCM41 based materials at temperatures between 50 and 80 °C and molar excess of EC to Gly of 2 to 1 [22,23].

The interest of GC as a biobased product has been notorious in the past few years bearing in mind its broad spectrum of applications in several fields, mainly as a green solvent in analytical applications [24], Li-ion batteries [25] or as reaction media [26,27]. In addition, it has been supported on immobilised liquid membranes for CO₂ separation [28] or as an additive in construction materials [29]. As a building block, it has been used in the synthesis of further products like polymers for adhesives [30] or esters with surfactant features [31].

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Abbreviations

Chemicals

DMC	dimethyl carbonate
EC	ethylene carbonate
EG	ethylene glycol
EO	ethylene oxide
GC	glycerol carbonate
Gly	glycerol

Nomenclature

AIC	Akaike's information criterion
Cat	catalyst in its original and most active form
Cat'	spent catalyst
C	concentration of the components at a given time (mol/L)
<i>d</i>	chord length (μm)
E_{ai}/R	ratio of activation energy and the ideal gas constant (K)
<i>F</i>	Fischer's <i>F</i> statistical parameter
FBRM	focused beam reflectance measurement
HPLC	high-performance liquid chromatography
ISTD	internal standard
k_d	deactivation constant (s^{-1})
k_i	kinetic constant ($\text{L}^2/\text{gcat}\cdot\text{mol}\cdot\text{min}$)
<i>K</i>	number of parameters of a proposed model
<i>M</i>	initial molar ratio of ethylene carbonate to glycerol
<i>n</i>	total number of components
<i>N</i>	total number of data to which a model is fitted
<i>r</i>	reaction rate (mol·L/min)
RMSE	residual mean squared error
SQR	sum of quadratic residues
<i>t</i>	time (min)
<i>T</i>	temperature (K)
TCS	total counts per second, as provided by FBRM
TOF	turnover frequency (mol converted/mol catalyst·min)
<i>X</i>	average conversion, as defined by Eq. (8)

Greek letters

β	relative catalytic activity of final form of catalyst with respect to the original one (Remaining activity)
γ	heteroskedasticity parameter
ν	stoichiometric coefficient of the component <i>i</i>
ρ	Density (g/mL)
ω	agitation rate (rpm)

Subscripts

0	relative to the start of the reaction, time equals zero
<i>i</i>	relative to component <i>i</i>
calc	relative to a calculated value
cat	relative to the catalyst
crit	relative to the critical conversion value
exp	relative to experimental values or the exponential function
<i>d</i>	relative to deactivation of the catalyst
ECsol	relative to concentration of EC dissolved in the glycerol-rich phase

cess, in which EO is carbonated and subsequently hydrated to yield 99.5% EG, a further effort to reach the most valuable product and the maximum achievable exploitation of feedstock [32–34]. EG has traditionally been widely used in antifreeze and dye inks formulations, though it has recently marked a new trend in the development of fuel cells. Substitution of direct methanol fuel cells for ethylene glycol-based fuel cells has been a recent trend owing to the advantages that the latter compound offers, such as a higher boiling point or a superior capacity in terms of Ah/ml. Additionally, EG is already established in the automobile industry supply chain, while methanol is not [35].

The reaction mechanism of this type of reaction has been covered [10,19], being the key aspect the presence of a basic catalyst to initiate the reaction through a glyceroxide anion. Furthermore, the selectivity of the reaction with several different catalysts has been reported to be almost complete despite the mechanism implying the presence of an intermediate species, which is in turn highly unstable allowing for its immediate cyclation to the final product GC [10,12,19].

Moreover, the reactants of this system, glycerol and EC, initially show very limited miscibility at temperatures between 40 and 50 °C. As the reaction proceeds and products generate, the initial liquid–liquid biphasic system evolves into a single phase liquid [36]. This type of ongoing physical changes can be monitored by means of optical techniques like focused beam reflectance measurement (FBRM) [37,38] and has proven of importance in the determination of a kinetic model for the transesterification of glycerol and DMC [11].

The aim of this work is the study of the transesterification of EC with Gly using inexpensive potassium carbonate as basic catalyst. Considering the very limited information on the kinetics of the catalytic synthesis of GC available in the literature through this route [39], the objective of the present work is to obtain a kinetic model as a necessary stage towards process development and reactor design. An assessment is herein made in physicochemical and statistical terms on whether there is a relationship between the kinetics of the reaction and the evolution of the dispersion-like system.

2. Materials and methods

2.1. Materials

During the course of the experimental work, the next chemicals were utilised: extra pure glycerol (assay grade, 99.88%, Fischer Chemical) and ethylene carbonate (synthesis grade, purity > 99%, Scharlau) as the reactant species; potassium carbonate (purity > 99%, Alfa Aesar) as a catalyst; finally, ethylene glycol (99.8%, anhydrous, Sigma-Aldrich), glycerol carbonate (purity \geq 99.5%, Sigma-Aldrich) and citric acid ACS reagent (purity \geq 99.5%, Sigma-Aldrich) for calibration and as internal standard for HPLC analysis purposes.

2.2. Experimental device

A scheme of the apparatus with all the main components labelled is displayed in Fig. 1. The main piece is a bespoke stainless steel tank reactor (1) featuring deflector baffles wherein the reaction takes place (2). This vessel is provided with a heating resistor surrounding the outer diameter (3) connected to an OMRON E5CN PID temperature controller (4). The reacting mixture is stirred by a six-blade impeller (6) regulated by an IKA RW20 motor (200–2000 rpm) (7). An opening (8) on the bottom of the vessel was made to allow for the introduction of the FBRM probe (9) and avoidance on any interference on the online droplet size distribution measurements. Additionally, a series of ports are located on the upper part of the reactor for insertion of a thermocouple (5)

Transesterification of glycerol with EC offers the additional advantage of producing ethylene glycol (EG) as a supplementary product of the reaction. EG stems from the hydrolysis of ethylene oxide (EO), giving EG and oligoglycols. Currently, the best industrial approach to its synthesis appears to be Shell's OMEGA pro-

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