Optimization of the production of glycerol carbonate from glycerol using a Mg/Al/Zr catalyst

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Resumen

Se sintetizaron y evaluaron catalizadores con estructura tipo hidrotalcita HDL-Mg/Al y óxidos mixtos en la transesterificación de glicerol para producir carbonato de glicerol. La síntesis involucró glicerol, carbonato de dimetilo y un catalizador seleccionado para la transesterificación. La optimización de las condiciones de reacción se realizó para determinar un proceso de reacción a un bajo costo operativo, i.e., presión atmosférica y temperatura moderada. Los catalizadores se caracterizaron por difracción de rayos X y área superficial BET. Se encontró que el mejor catalizador era el óxido mixto Mg/Al/Zr. Este catalizador mostró una mayor basicidad y requirió considerablemente menos tiempo de reacción que el requerido por otros catalizadores para alcanzar la misma conversión de glicerol. El objetivo fue analizar el efecto de cada factor (temperatura de calcinación, relación molar Mg/Al/Zr, temperatura de reacción, relación molar de glicerol/carbonato de dimetilo y relación glicerol/peso del catalizador) sobre el rendimiento de carbonato de glicerol en el catalizador Mg/Al/Zr. Estos factores se optimizaron con un diseño experimental para obtener el máximo rendimiento de carbonato de glicerol. Se encontró que el rendimiento de carbonato de glicerol depende de la temperatura de reacción, la proporción de glicerol a carbonato de dimetilo y la cantidad de catalizador. Las condiciones óptimas de reacción para maximizar el rendimiento de carbonato de glicerol fueron 90°C, relación molar de glicerol a carbonato de dimetilo de 1:5 mol/mol y una relación másica de glicerol a catalizador de 1:0.15 g/g.

Palabras clave— Carbonato, glicerol, hidrotalcita, biodiesel, optimización.

Abstract

Hydrotalcite-type HDL-Mg/Al and mixed oxide catalysts were synthesized and evaluated for the transesterification of glycerol to produce glycerol carbonate. The synthesis involved glycerol, dimethyl carbonate and a selected catalyst for the transesterification reaction. The optimization of the reaction conditions was performed to determine a reaction process at a low operative cost, i.e.*, atmospheric pressure and a moderate reaction temperature. The catalysts were characterized by X-ray diffraction and BET surface area measurements. The best catalyst was the mixed oxide Mg/Al/Zr. This catalyst showed a higher basicity than the other catalysts tested and required considerably less reaction time than the other catalysts required to reach the same conversion of glycerol. The objective was then to analyze the effects of each factor (calcination temperature, Mg/Al/Zr molar ratio, reaction temperature, glycerol-to-dimethyl carbonate molar ratio and glycerol-to-catalyst weight ratio) on the yield of glycerol carbonate on the Mg/Al/Zr catalyst. These factors were optimized with an experimental design to obtain the maximum glycerol carbonate yield. The glycerol carbonate yield was found to be dependent on the reaction temperature, glycerol-to-dimethyl carbonate ratio and catalyst amount. The optimal reaction conditions to maximize the glycerol carbonate yield were 90°C, a glycerol to dimethyl carbonate molar ratio of 1:5 mol/mol and a glycerol to catalyst weight ratio of 1:0.15 g/g.*

Keywords*— Carbonate, glycerol, hydrotalcite, biodiesel, optimization.*

1. INTRODUCCIÓN

Biodiesel production, achieved through transesterification of triglycerides from vegetable oils or animal fats, has gained significant attention as a renewable and environmentally friendly alternative fuel [1]. Biodiesel can be used in blends with diesel from 5 to 20 vol.%, reducing diesel consumption, improving its lubricity and increasing its cetane number. Biodiesel use represents an alternative for mitigating the impacts of global warming and fossil resource depletion [2].

Biodiesel is produced mainly by the transesterification of triglycerides with methanol. The main product (ca. 90% yield) is a mixture of fatty acid methyl esters (FAME), which can be designated biodiesel if it meets the specifications of the standard ASTM D6751. The remaining 10 weight percent (wt.%) is crude glycerol, which is initially contaminated with water, methanol and soap, so it cannot be used as such and requires subsequent treatment.

Glycerol has been identified as a valuable commodity, with a wide range of applications in personal care products, gas separation processes, and organic synthesis, as well as a wetting agent in cosmetics, owing to its nontoxic nature, water solubility, and low evaporation rate [3,4]

The large amount of glycerol generated during biodiesel production represents an opportunity for the development of important chemical products, such as acrolein, glyceric acid, esters of glycerol and glycerol carbonate [5].

Glycerol carbonate (GC) is one of the most versatile derivatives of glycerol. Owing to its chemical reactivity, it can be applied as a solvent, as a novel component in gas separation membranes and in the synthesis of polycarbonates used in transparent and translucent roofs, domes and skylights for industrial machinery guards [6].

Glycerol can be converted into GC via four main synthetic routes, which were recently reviewed by Procopio and Di Gioia [7]. The earliest reported route was that of phosgene [8], which has the advantage that GC can be produced at low reaction temperatures with high yield; however, the raw materials are highly toxic [7].

A second chemical route is the alcoholysis of urea with glycerol with hydrotalcite, ionic liquids, and several metal salts and metal oxides (CaO, La_2O_3, MgO, ZrO_2, and Al_2O_3) as catalysts [9]; this method has the advantages that the raw materials are easy to obtain and the yield and selectivity are both high; however, it generates NH_3 and requires decompression [7].

A third chemical route is CO/CO_2 oxidative carbonylation, in which the most studied catalyst is $PdCl_2$ [10]. Although this reaction is complex, it has the advantages that GC can be generated under relatively mild conditions, product separation is easy, and both the selectivity and product yield are high; however, owing to the toxicity and explosiveness of CO, it has limited industrial application [7].

A fourth chemical route is the transesterification of glycerol with dimethyl carbonate (DMC), exemplified by the reaction shown in Figure 1, in which an Al/Ca hydrotalcite-like compound can be used as a catalyst [11]. Hydrotalcite-type materials offer advantages over Pd/Cl_2 catalysts, including improved activity, selectivity, metal dispersion, reduced waste, and enhanced catalyst recuperation [12]. A disadvantage is that catalysts may be easy to deactivate [7].

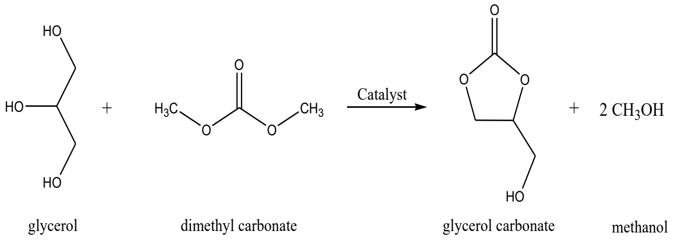


Figure 1. Synthesis of glycerol carbonate from glycerol and DMC.

This work proposes the use of a mixed oxide Mg/Al/Zr catalyst for the synthesis of GC by transesterification of glycerol with dimethyl carbonate since it possesses higher basicity than other Mg/Al-type HDL catalysts do [11,13], which can favor the alkaline transesterification reaction.

2. MATERIALS AND METHODS

2.1. Materials

All the reactants used in this work were purchased from Sigma–Aldrich (Mexico), and no further purification was conducted. The analytical grade salts $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and $ZrO(NO_3)_2 \cdot H_2O$, which are precursors of the catalyst, were purchased from Sigma Aldrich. The 2 M sodium hydroxide solution used to control the pH during catalyst preparation was prepared by performing the necessary calculations to determine the amount of sodium hydroxide needed for a given volume of water.

2.2. Methods

To perform a statistical analysis of the variables to be optimized and thus obtain a mathematical model to predict the maximum yield of glycerol carbonate in a small number of experiments, a 2^k factorial experimental design was formulated via Design Expert V.23 software. In the design of the experiments (DOE), 5 factors were considered with two levels each, that is, a 2^5-level design. Hence, 32 experiments were required to complete the analysis. Table 1 shows the conditions of the experiments formulated with the 2-factorial design, including the factors and levels used.

Table 1. Experimental design

Factors		Levels	
		-1	+1
A	Catalyst calcination temperature, °C	550	650
B	Mg/Al/Zr molar ratio, mol/mol/mol	2/1/1	3/1/1
C	Reaction temperature, °C	60	90
D	Glycerol:DMC molar ratio, mol/mol	1:5	1:8
E	Glycerol:catalyst weight ratio, wt/wt	1:0.1	1:0.15

These factors and their levels were selected on the basis of previous studies[11,13]. The calcination temperature of the catalyst has a great influence on the activity of the catalyst and therefore on transesterification. The Mg/Al/Zr molar ratio is also an important variable since it is directly related to the basicity of the catalyst. The reaction temperature is relevant because it significantly affects the glycerol carbonate yield, and the glycerol:DMC and glycerol:catalyst ratios are important for elucidating the effects of their variation on the glycerol carbonate yield and reducing reactant or catalyst consumption, respectively.

The response studied was the glycerol carbonate yield (Y_{GC}, in wt%), which was measured experimentally. A mathematical model was then developed that allowed the yield to be predicted under different input conditions, as well as the maximum glycerol carbonate yield to be determined. Finally, the model was evaluated under three different experimental conditions, and the deviation was determined, thereby evaluating its accuracy and predictive capability.

3. EXPERIMENTAL

3.1. Catalyst Preparation

Catalytic materials with different Mg/Al/Zr molar ratios (3:1:1 and 2:1:1 molar ratios) were prepared by coprecipitation at a constant pH of 10. The calculated amounts of $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$ and $ZrO(NO_3)_2 \cdot 1H_2O$ were dissolved in distilled water using an aqueous solution of NaOH at a constant pH of 10. After aging overnight at 80°C, the solid was washed with excess water to remove alkali ions. The obtained solid was then dried at

120°C overnight. Finally, the solid was calcined in air at 550 to 650°C for 4 h to obtain the Mg/Al/Zr catalyst.

3.2. Catalyst characterization

X-ray powder diffraction (XRD) patterns of the catalysts were recorded on a Bruker D8 Advance diffractometer. The measurements were obtained in the 2θ range of 10–80°. The surface area of the catalysts was obtained via the BET method via a Quantachrome Nova 2000 instrument. The catalyst sample was pretreated by degassing at 300°C for 3 h. Nitrogen adsorption–desorption was then performed at -196.15°C, which is the boiling point of liquid nitrogen.

3.3. Catalytic evaluation test

GC was synthesized in the liquid phase at atmospheric pressure and at the conditions given by the DOE. In a typical experiment, 1 g of glycerol and 4.8913 g of dimethyl carbonate were fed into a 20 mL tube reactor along with 0.1 g of catalyst. The reaction was carried out at the desired temperature, e.g., 60°C. The products were identified via gas chromatography on a 30 × 32 mm Elite HT5 column.

4. RESULTS AND DISCUSSION

4.1. Catalyst characterization

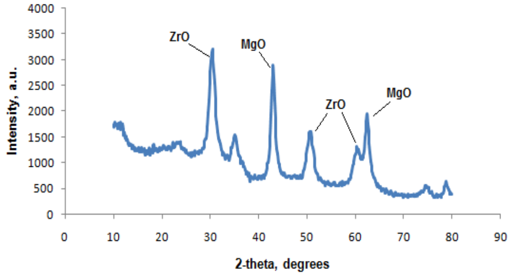
The surface area of each catalyst studied is shown in Table 2. The results show that the surface area of the Mg/Al/Zr (3/1/1) catalyst calcined at 650°C is larger than those of the other catalysts and that this catalyst likely has the largest Mg, Al and Zr ratios and calcination temperatures. The catalyst also presented a larger surface area for chemical species to be adsorbed.

Table 2. Surface area of each catalyst studied in this work.

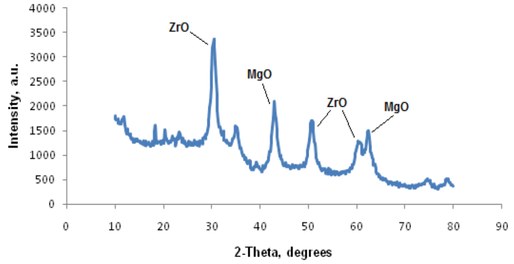
Catalyst	Surface Area (m^2/g)
Mg/Al/Zr (3/1/1) calcined at 650°C	267
Mg/Al/Zr (2/1/1) calcined at 650°C	244
Mg/Al/Zr (3/1/1) calcined at 550°C	210
Mg/Al/Zr (2/1/1) calcined at 550°C	198

The XRD patterns of the catalysts are shown in Figs. 2 (a-d). The X-ray diffraction patterns of the MgAlZr hydrotalcite samples exhibited three distinct diffraction peaks at 2θ values of 35.6°, 43.2°, and 62.5°. These peaks could be reliably assigned to the periclase MgO-like structure (PDF No. 45--946) [13], suggesting that an increase in the ratio of Mg to Al and Zr leads to an increase in the crystallite sizes of the Mg and Zr oxides.

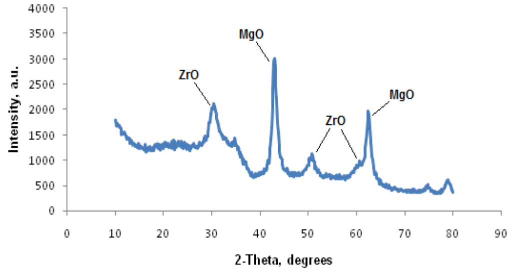
The peak at 35.6° disappeared, and only a broad diffraction peak corresponding to tetragonal ZrO_2 (t-ZrO_2, PDF No. 49--1642) appeared at 30.8°. Furthermore, no diffraction peak due to Al_2O_3 was observed for any of the samples. This observation suggests that Al_2O_3 may exist in an amorphous state [14]. Furthermore, the lattice parameters obtained at a 2θ of 43.2° for the MgO-like material were all less than those of pure MgO (4.21 Å) [15]. This finding indicates that the incorporation of Al and Zr cations into the MgO lattice may have resulted in the formation of a solid solution, which could increase the stability of the catalyst during the reactions.



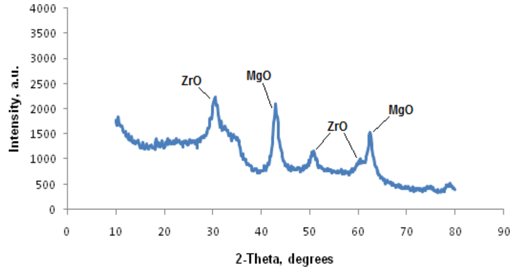
a) Mg/Al/Zr (3/1/1) catalyst calcined at 650°C



b) Mg/Al/Zr (2/1/1) catalyst calcined at 650°C



c) Mg/Al/Zr (3/1/1) catalyst calcined at 550°C



d) Mg/Al/Zr (2/1/1) catalyst calcined at 550°C

Figures 2 (a-d). X-ray diffraction patterns of the catalysts

4.2. Catalytic evaluation for glycerol carbonate synthesis

The Mg/Al/Zr catalysts were evaluated for the transesterification of glycerol with dimethyl carbonate to yield GC, and the results are shown in Fig. 3. The GC yield according to the activity of each catalyst is shown. The formation of GC increased with increasing Mg to Al or Zr ratios and calcination temperatures. Among these catalysts, the catalyst with a high Mg to Al or Zr ratio (Mg/Al/Zr (3/1/1) catalyst) and a calcination temperature of 650°C presented the highest transesterification activity.

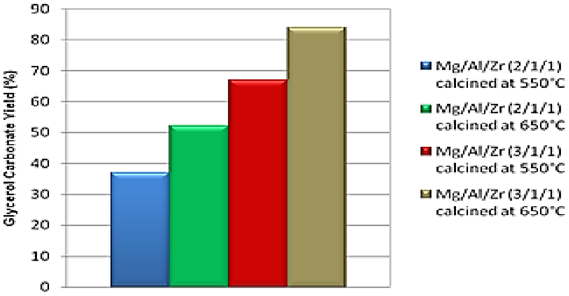


Figure 3. Transesterification of glycerol activity over the catalysts

These results suggest that the activity of the catalyst can be enhanced by using a greater number of mixed oxides and a higher calcination temperature.

The strong basicity of the Mg/Al/Zr (3/1/1)-material was responsible for the high transesterification activity, as this reaction is facilitated by the presence of basic sites. Other catalysts also showed reasonable activity due to the presence of moderately basic sites. On the basis of these results, we can claim that the basicity of the catalyst is the main factor in obtaining a higher glycerol carbonate yield.

4.3. Influence of the reaction temperature on glycerol carbonate synthesis

The effect of the reaction temperature on the GC yield was studied for each catalyst, and the results are shown in Fig. 4 for both calcination temperatures, i.e., 550 and 650°C. The reaction temperatures used in this work were 60 and 90°C. The glycerol carbonate yield increased in all cases at a reaction temperature of 90°C, which is the reaction temperature at which the catalysts showed maximum catalytic activity, i.e., at a calcination temperature of 650°C.

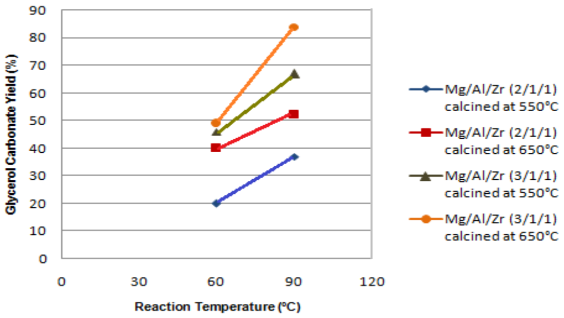


Figure 4. Influence of the reaction temperature on the yield of glycerol carbonate.

4.4. Effect of the molar ratio of glycerol to dimethyl carbonate

The glycerol to dimethyl carbonate molar ratio is another factor that affects the conversion of glycerol and, therefore, the yield of glycerol carbonate. The effect of the molar ratio of glycerol-to-dimethyl carbonate was evaluated using the four catalysts and a reaction temperature of 90°C because, at this temperature, the glycerol carbonate yield was greater. The results are shown in Fig. 5.

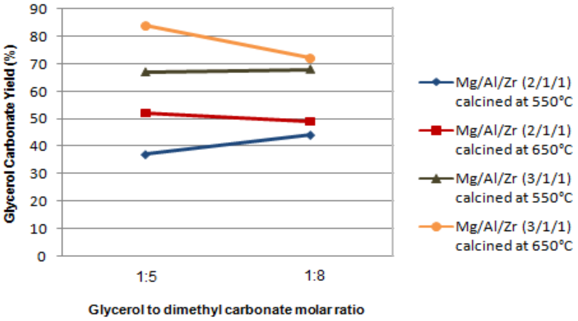


Figure 5. Effect of the glycerol-to-dimethyl carbonate molar ratio on the yield of glycerol carbonate.

These results suggest that when molar ratios of 1:5 and 1:8 are used, the variation in the glycerol carbonate yield is not high, but when the Mg/Al/Zr (3/1/1) catalyst is calcined at 650°C, the yield is increased by 12% at a corresponding ratio of 1:5. Consequently, a glycerol-to-dimethyl carbonate molar ratio of 1:5, or lower can be considered an appropriate molar ratio.

4.5. Effect of catalyst amount

The influence of the catalyst amount on the synthesis of glycerol carbonate is not significant because the glycerol carbonate yield does not vary considerably. The results are shown in Fig. 6. These results suggest that the conversion of glycerol at the two calcination temperatures increased with increasing glycerol-to-catalyst ratio, up to 7%. The highest yield of glycerol carbonate was achieved at a glycerol-to-catalyst weight ratio of 0.15 wt./wt.

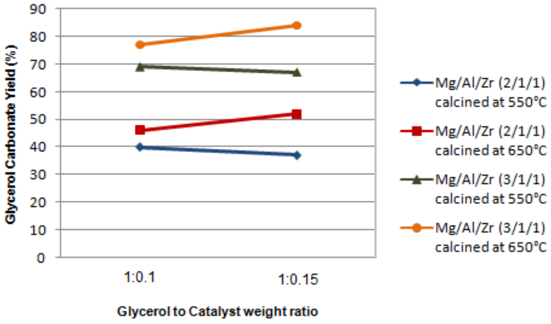


Figure 6. Effect of catalyst weight on the yield of glycerol carbonate.

4.6. Statistical analysis and optimization

The Shapiro–Wilk test along the half-normal plot of effects and the Pareto chart were used to select the significant factors (t-value > 2.05954). An analysis of variance was then performed, yielding the mathematical models represented in Equation (1) for actual values or in Equation (2) for coded values:

$$Y_{\mathrm{GC}} = -61.24302 + 0.082056A - 7.76021B - 0.499167C + 5.76167D + 88.8375E + 0.578625BC - 2.71708BD \quad (1)$$

$$Y_{\mathrm{GC}} = 44.05 + 4.1A + 8.99B + 14.21C - 1.55D + 2.22E + 4.34BC - 2.04BD \quad (2)$$

where: Y_{GC} = yield of GC, wt.%; A = catalyst calcination temperature,°C; B = Mg/Al/Zr molar ratio, mol/mol; C = reaction temperature, °C; D = glycerol:dimethyl carbonate molar ratio, mol/mol; and E = glycerol:catalyst weight ratio.

The R^2 was 0.9592. The F–value was 80.7; therefore the model can be considered statistically significant. The p–value for all factors in the model was lower than 0.05, except for the D factor, which was 0.0543, although slightly better predictions were obtained with the inclusion of D. As shown by the parity plot in Figure 7, the model can predict the experimental values with a high-level of precision.

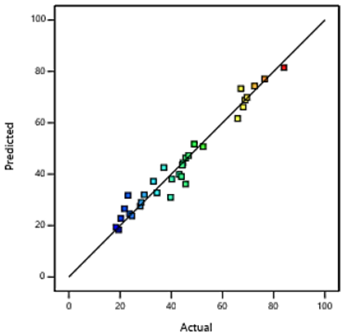


Figure 7. Parity plot: Predicted vs actual values

An optimization was then performed to predict the optimal experimental conditions at which the maximum Y_{GC} can be obtained. The best solution was obtained at the following conditions: A = 650°C, B = 3 mol/mol, C = 90°C, C = 1:5 mol/mol and E = 1:0.15 g/g. The maximum Y_{GC} as shown in Figures 8 and 9 was equal to 81.494 wt%. The observed trends were as follows: a higher reaction temperature, a higher calcination temperature, a larger Mg/Al/Zr molar ratio and a larger glycerol-to-catalyst weight ratio favor the production of carbonate glycerol.

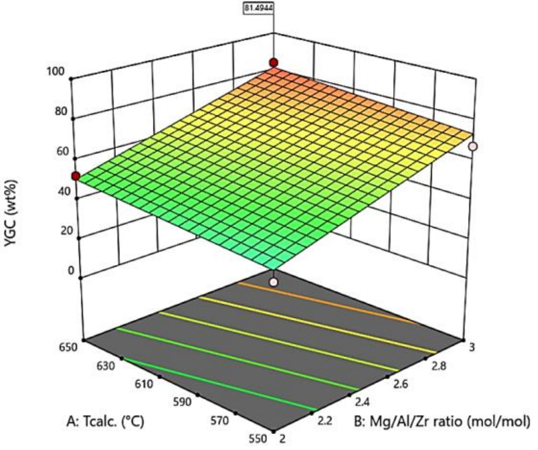


Figure 8. Effect of the calcination temperature and Mg/Al/Zr molar ratio on the glycerol carbonate yield.

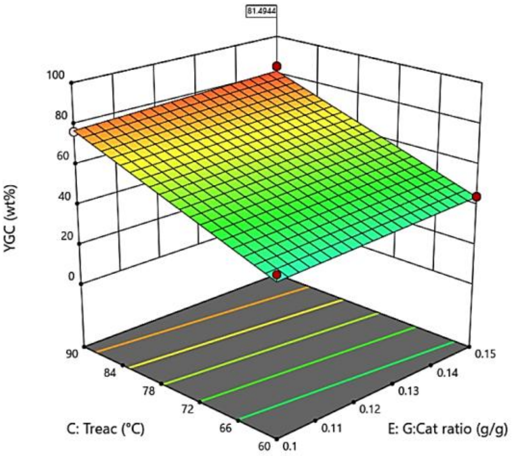


Figure 9. Effect of the reaction temperature and glycerol:catalyst weight ratio on the glycerol carbonate yield

4.7. Model validation

Three experiments were carried out using the factors shown in Table 3. The se values were selected randomly to compare the values obtained with the model and the experimental values and thus determine if the model can predict glycerol carbonate yields (Y_{GC}) with factors other than those used in the design of experiments.

Table 3. Experiments performed for model validation.

Experiment No.	*Calcination temperature (°C)*	*Mg/Al/Zr molar ratio*	*Reaction temperature (°C)*	*Glycerol:DMC molar ratio*	*Glycerol:Cat. weight ratio*
1	650	3:1:1	80	1:7	1:0.18
2	650	2:1:1	95	1:9	1:0.20
3	650	3:1:1	95	1:7	1:0.18

After the three experiments were conducted, the glycerol carbonate yields shown in Table 4 were obtained. To evaluate the model's predictive ability, the experimental Y_{GC} values were compared with the Y_{GC} values predicted by the model. The deviation between the experimental and predicted values was calculated via the relative error (%E), whose calculation is described in Equation (3).

$$\%E = \frac{\left| Y_{GC_{experimental}} - Y_{GC_{predicted}} \right|}{Y_{GC_{experimental}}} \; x\,100 \quad (3)$$

Table 4. Comparison of the predicted and experimental glycerol carbonate yields.

Run	***YGC (wt. %)***		**%E**
	Experimental	Predicted	
1	68.87	67.01	2.70
2	61.12	59.81	2.15
3	83.46	85.56	2.52

The low values of relative errors suggest that the mathematical model is adequate for predicting glycerol carbonate yield because it accurately captures the relationship between the input and output variables.

4.8. Process scale-up

It may be possible to scale up the processing for obtaining GC in a continuous way. For example, the hydrotalcite-like phase can be readily obtained through thermal decomposition. A notable attribute of MgAl hydrotalcite-like materials is their exceptional resistance to leaching, a process that accelerates the dissolution of conventional catalysts. Millimeter-sized extrudates featuring basic properties comparable to those of powder samples and high mechanical stability are obtained using bentonite as a binder, as reported by Lari et al. [16]. Upon testing in a continuous reactor under tuned conditions of temperature and pressure and in the presence of an aprotic solvent, the system attained the same glycerol yield as in the batch tests. During 100 h on stream, its activity decreased by 20% due to fouling but could be fully restored upon burning off carbonaceous deposits. Thus, hydrotalcite-like materials are capable of being scaled up to produce higher amounts of GC.

5. CONCLUSIONS

The Mg/Al/Zr catalyst with a molar ratio of 3/1/1 calcined at 650°C was the best catalyst of the four catalysts studied in this work for the synthesis of GC by transesterification of glycerol with dimethyl carbonate due to the presence of strong basic sites. These synthesis conditions are recommended for achieving a relatively high Y_{GC}. With respect to the reaction conditions, a higher reaction temperature, a higher glycerol to catalyst weight ratio and a lower glycerol to dimethyl carbonate molar ratio increase the Y_{GC}. Experimentally, the highest Y_{GC} was 84.03%, whereas the maximum Y_{GC} predicted with the model was 81.494%, under the same conditions. The relative error of the model is between 2% and 3%. The model can be used to predict the conditions at which Y_{GC} is close to 90%, reducing the experimental time and using the optimal amount of reactants.

6. ACKNOWLEDGEMENT

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