

Synthesis and Optimization of Glycerol Carbonate from Crude Glycerol Using Sodium Carbonate (Na_2CO_3) as a Heterogeneous Catalyst

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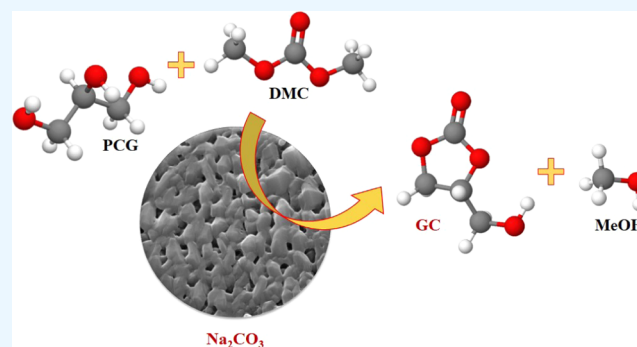
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ABSTRACT: The essential need for sustainable energy sources to replace fossil fuels has fueled interest in renewable energy and biorefinery processes. Biodiesel production generates a considerable amount of crude glycerol (CG), which poses a challenge for the industry. This study aims to address this challenge by purifying CG through acidification. The acidification process successfully purified crude glycerol (PCG), resulting in a purity of 98.4 wt %. Subsequently, synthesizing glycerol carbonate (GC) from PCG and dimethyl carbonate (DMC) was undertaken by using heterogeneous catalysts. Sodium carbonate (Na_2CO_3) emerges as the most promising catalyst, considering its suitability in the presence of impurities such as 0.72 wt % of water and 0.57 wt % of matter organic nonglycerol (MONG) in PCG. The optimum catalyst dosage of Na_2CO_3 was determined as 2.1% mol of PCG. The experiments were carried out using a central composite design (CCD) methodology. By employing the response surface method (RSM), the optimal reaction conditions were determined to be a PCG/DMC molar ratio of 1:2.37 and a reaction time of 1.83 h. Under these conditions, an observed GC yield of 72.13% and PCG conversion of 78.39% were achieved. Despite the purification process, PCG still contains residual water, making Na_2CO_3 a suitable catalyst capable of tolerating a water content up to 3 wt %. This study not only enhances the effective utilization of CG within the biodiesel industry but also offers valuable insights for further exploration of sustainable chemical processes in future research.



1. INTRODUCTION

Fossil fuels such as oil, coal, and natural gas have been the primary energy sources for human machinery for centuries. Unfortunately, their use has an impact on the global climate. Human activities, including burning fossil fuels and deforestation, have led to a gradual rise in average global temperatures in both the Earth's atmosphere and oceans.¹ Greenhouse gas emissions primarily consist of carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O) released through combustion.² These greenhouse gases accumulate in the atmosphere of the Earth, resulting in a continued increase in global temperatures. There has already been a significant increase in global surface temperature, with a recorded rise of 1.09 °C above preindustrial levels observed between 2011 and 2020.³ Projections indicate that by the end of this century, the world may experience a general temperature increase of 1 to 3.7 °C.²

In the present era, there is a global emphasis on renewable energy, driven by several factors such as environmental degradation, innovation in clean energy technologies, the shortage problem in fossil fuel reserves,⁴ and the high price volatility of petroleum-based fuels. These factors contribute to

the growing recognition of renewable energy as a viable alternative worldwide.

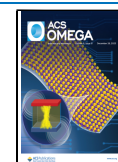
In the current context, the pursuit of green and sustainable energy sources to replace fossil fuels has become increasingly vital. The biorefinery market is projected to experience significant growth in the next 5 years, with an estimated rise of USD 68.5 billion in the forecast period of 2022–2027, accompanied by an 8.2% compound annual growth rate.⁵ Biodiesel, known for its renewable and biodegradable characteristics,⁶ has attracted attention as an environmentally friendly biomass fuel that exhibits low levels of pollution and nontoxic properties. Produced through the transesterification of renewable resources such as vegetable oils or animal fats,⁷ biodiesel has become a subject of interest for researchers in recent decades. During biodiesel production, a substantial quantity of crude glycerol (CG) is generated,⁸ presenting a

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challenge for the industry due to its status as a byproduct. Approximately 10 wt % of biodiesel production results in the generation of CG.⁹

According to the findings reported, glycerol has garnered significant industrial interest due to its remarkable growth as a valuable industrial molecule.¹⁰ The current market value of pure glycerol is estimated to be around USD 540–820/ton. However, due to its lower purity level of 80%, CG is valued much lower, ranging from USD 80–180/ton.¹¹ Consequently, the utilization of CG for value-added products has become a concern within the biodiesel industry. The molecules derived from glycerol, glycerol carbonate (GC), as shown in Figure 1

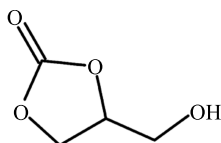


Figure 1. Molecular structure of glycerol carbonate (GC).

(4-hydroxymethyl-1,3-dioxolan-2-one, CAS no. #931–40–8), a five-membered cyclic carbonate, are one of the high-value-added glycerol derivatives because of its remarkable properties, i.e., biodegradability,¹⁰ high boiling point, low flammability (flash point >204 °C), and low-toxicity (no hazardous R-phrases listed in the material safety data sheet (MSDS) for this substance).¹² GC is a high-value-added product with a market price greater than USD 8141/ton.¹³ It can be applied in a wide variety of fields, i.e., polymers as plasticizers, electrolyte liquid carriers in the semiconductor industry,¹⁴ cosmetics as emulsifiers, pretreatment agents for lignocellulosic biomass,¹⁵ and chemical intermediates.^{16,17}

Glycerol can be used to synthesize GC through either direct or indirect synthetic routes. One commonly studied route is the transesterification of glycerol with dialkyl carbonate, which is an environmentally friendly method.¹⁴ As shown in Figure 2, the transesterification reaction is a process that involves the exchange of carbonates between alcohols and carbonate sources facilitated by a catalyst,¹⁷ which plays a vital role in the process. Transesterification, particularly the trans-carbonation reaction, emerges as a highly advantageous approach for producing GC. This method harnesses green reagents such as DMC and glycerol, resulting in elevated yields and selectivity, all while maintaining mild reaction conditions and minimizing energy requirements. However, some reported methods use hazardous substances like phosgene,¹³ making them less suitable due to safety concerns. Alternatively, the transesterification of glycerol with DMC has emerged as a promising and safer option.¹⁸

The catalyst promotes the conversion of glycerol and DMC into GC as the desired product, while methanol (MeOH) is produced as a byproduct. In the process of catalyst selection, it

is important to consider several factors beyond the catalytic performance. These factors encompass considerations such as separation efficiency and environmental impact. In previous studies,^{13,19,20} several homogeneous catalysts, such as potassium carbonate (K₂CO₃), potassium hydroxide (KOH), sodium hydroxide (NaOH), and sulfuric acid (H₂SO₄), were investigated for their effectiveness in facilitating the transesterification reaction. However, it has been reported that homogeneous catalysts pose significant challenges in terms of reusability²¹ and separation from the reaction products.²² To overcome these limitations, heterogeneous catalysts have emerged as a promising alternative to homogeneous catalysts. Unlike their homogeneous counterparts, heterogeneous catalysts can be easily separated from the reaction mixture, as they do not dissolve in the reaction medium. This characteristic leads to products with reduced impurities, requiring less purification.²³ Consequently, the investigation of heterogeneous base catalysts has gained significant importance in research. Nonetheless, these catalysts demonstrate certain drawbacks during the transesterification process of DMC with glycerol.²⁴

The choice of calcium oxide (CaO) as a catalyst stems from its well-known robust basicity and cost-effectiveness. CaO can be readily sourced from materials such as calcium carbonate and calcium hydroxide, making it a practical choice for both industrial and research applications. Notably, previous research has highlighted the remarkable catalytic performance of CaO in synthesizing glycerol carbonate via transesterification reactions, achieving an impressive yield of 98%.¹⁹ However, it is essential to acknowledge a significant limitation of CaO, namely, its susceptibility to deactivation when exposed to moisture. This vulnerability to moisture-induced deactivation has been documented in earlier studies, including those by de Caro et al.¹⁰ and Lu et al.²⁵ The turbidity observed in the solution further supports the potential impact of water on the dissolution of CaO when exposed to ambient conditions.²⁶

It is important to highlight that this particular catalyst effectively facilitates the conversion of CG, which has a purity of 88 wt %. Meanwhile, the majority of syntheses have been investigated using either pure glycerol or glycerol with water content <2 wt %.²⁰ To address the inherent drawbacks of CaO sensitivity to moisture, the study incorporated a modified CaO-based catalyst, as explored by Tang et al.²⁷ In their research, they screened various CaO catalysts supported with 15 wt % active components, including LiCl, NaCl, and KCl. These catalysts were subjected to a transesterification reaction with a glycerol/DMC of 1:1 at 65 °C. The results of this initial screening revealed that LiCl/CaO exhibited the highest catalytic activity, achieving an impressive 85.3% yield of GC. Notably, this yield was 6.5% higher than that obtained with pure CaO. Following this initial screening, the study delved further into the impact of varying LiCl loadings and calcination temperatures on catalytic activity. The results unveiled the

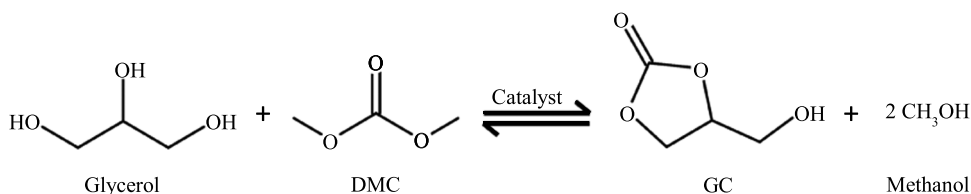


Figure 2. Transesterification reaction of DMC with glycerol to synthesize GC.

remarkable efficacy of CaO loaded with 10% LiCl at 600 °C for 5 h, yielding an impressive 94.19% GC after just 1 h.²⁷

In the review of de Caro et al.,¹⁰ on the synthesis of GC and the evaluation of its plasticizing properties, they explore three types of reactions: glycerolysis of urea, trans-carbonation of DMC, diethyl carbonate (DEC), or cyclic carbonates with glycerol, and reactions using CO₂. The preferred method for synthesizing GC involves utilizing DMC and glycerol as raw materials due to its ability to yield high quantities of GC with excellent selectivity. This process operates under mild conditions, reducing energy consumption during separation processes. Effective catalytic conditions employing Na₂CO₃ as a catalyst in GC synthesis offer numerous benefits: facilitating high GC yields and streamlining the purification process without necessitating GC distillation. The catalytic conditions involving Na₂CO₃ prove to be cost-effective, as it requires mild temperatures (73–78 °C) and generates minimal waste. Moreover, the adoption of Na₂CO₃ as a catalyst aligns with its recognized advantages. The review of Adesina emphasizes the environmental and economic merits of Na₂CO₃ as a sustainable alternative to conventional-like sodium silicate (Na₂SiO₃) and NaOH.²⁸

In this study, the objective was to address the challenge of effectively utilizing abundant waste CG from biodiesel production to maximize the use of CG in the biodiesel industry by transforming it into valuable chemicals. To achieve this objective, the study focused on purifying CG through an acidification process to achieve a high level of purity and identifying the most suitable catalyst for synthesizing GC from purified crude glycerol (PCG) while considering impurities and water content. Additionally, the study involved a comprehensive characterization of the prepared and commercial catalysts using X-ray diffractometry (XRD), scanning electron microscopy (SEM), and Brunauer–Emmett–Teller (BET) analysis techniques. Subsequently, to evaluate the performance of the catalysts, CaO, LiCl/CaO, and Na₂CO₃ were employed to determine the optimal catalyst for GC synthesis via the transesterification of DMC with PCG. The experimental design employed a CCD and utilized the trial version of Design-Expert software, version 13, enabling the optimization of reaction conditions to achieve the highest possible yield of GC and conversion of PCG. Furthermore, the study explored the reusability of the catalyst and investigated the influence of water content in PCG on the transesterification process.

2. EXPERIMENTAL SECTION

2.1. Materials. The CG was collected from the Specialized R&D Center for Alternative Energy at the Palm Oil and Oil Crops, Faculty of Engineering, Prince of Songkla University in Thailand. CG was used as a starting material for GC synthesis. All purchased chemicals were analytical grade without further purification. H₂SO₄ (98 wt %), NaOH (98 wt %) pellets, hexane (99 wt %), and lithium chloride (LiCl) (98 wt %) used as the Li precursor were obtained from Loba Chemie, India. DMC (>99 wt %) was purchased from Alfa Aesar and Thermo Fisher Scientific, United Kingdom. The commercial CaO (96 wt %), Na₂CO₃ (>99.5 wt %), glycerol (>99.5 wt %), MeOH (99.8 wt %), and isopropanol (99.5 wt %) were purchased from KemAusTM, Australia. GC (>94 wt %) was purchased from TCI Chemical Co., Ltd., Tokyo.

2.2. Purification of the CG. The process of purifying CG involves several steps. First, the CG was heated at 60 °C for 30

min and then filtered to remove any solid impurities. Next, it was transferred to a 2000 mL Pyrex beaker and stirred at a constant speed of 300 rpm while being heated to 70 °C. Here, it was mixed with 1 M H₂SO₄ that had been initially acidified to achieve the desired pH value (pH 2–4) and stirred for 1 h. The mixture was then left to settle at room temperature for 24 h. The process leads to the separation of a top layer rich in free fatty acids (FFA) through decantation.²⁹ The inorganic salt bottom layer was filtered out using a 1.2 μm paper filter. The glycerol-rich intermediate layer was neutralized by adding 5 M NaOH to achieve a pH of 7. The inorganic salt and FFA that formed during neutralization were filtered again using a 1.2 μm paper filter.

Next, the soluble impurities, including glycerides, FFA, and methyl ester, were removed from the PCG by extracting it with hexane at a 1:1 weight ratio of PCG. The mixture was stirred at 300 rpm for 30 min and left to settle in a separatory funnel for 2 h. The residue of hexane in the CG was removed by heating it for approximately an hour at 70 °C. Activated carbon was then added to the mixture at a ratio of 0.05:1 by weight of PCG and stirred at 300 rpm for 3 h. It plays a crucial role in the purification process by effectively absorbing unwanted odor and color components present in the PCG. Finally, the activated carbon was filtered using a 1.2 μm paper filter. To address the issue of reducing the water content in PCG, we employed a method involving heating the PCG in an oil bath at a carefully controlled temperature of 105 °C and stirring at 300 rpm until the desired amount (<2 wt %) was achieved.

2.3. Characterization of CG and PCG. The pH measurements of CG and PCG were conducted using a pH meter (Sartorius, Japan). The water content was determined using a Coulometer Karl Fisher Titrator (Mettler Toledo DL39) following the standardized method described in ISO 2097–1972 for sample preparation. The ash content analysis was performed by burning 1 g of PCG in a furnace at 750 °C for 3 h, following the method outlined in ISO 2098–1972. The MONG of PCG was calculated using the standard method described in ISO 2464–1973 by subtracting the sum of the glycerol, ash, and water content.

2.4. Catalyst Preparation. The commercial CaO support was first dried in an oven at 105 °C overnight to eliminate any adsorbed water. Next, the support was calcined in a furnace at 900 °C for 3 h. The calcined CaO was then impregnated with a LiCl solution containing the metal precursor for 24 h. The resulting catalyst was subsequently dried in an oven at 105 °C overnight, followed by calcination at 600 °C for 5 h; the catalyst was named 10% LiCl/CaO.^{24,26} Additionally, Na₂CO₃ was dried in a hot air oven at 105 °C for 24 h. All catalysts were stored in vials with caps and kept in a desiccator to prevent exposure to atmospheric moisture.

2.5. Characterization of the Catalyst. The phase structure of the catalyst was analyzed by XRD (X-ray, Epyrean Panalytical, The Netherlands) with a copper target tube, releasing K α radiation, accelerated at 30 mA and 40 kV, 3°/min of scanning speed (arranged 5–90°).

The surface morphology of catalysts was analyzed using SEM (Quanta 400, Czech Republic) with 10.0–20.0 kV of an accelerating voltage.

The surface area and pore volumes were determined using a surface area and micropore analyzer (ASAP2460 Micro-meritics) using low-temperature nitrogen (N₂) adsorption–desorption; the specific surface areas and pore volumes were

calculated by the BET equation and the Barrett–Joyner–Halenda method.

2.6. Transesterification Reaction. The transesterification reaction was carried out under the following conditions: a PCG/DMC molar ratio of 1:3 for 2 h, with a catalyst dosage of 3% mol % PCG. Heterogeneous catalysts, CaO, 10% LiCl/CaO, and Na₂CO₃, were utilized to determine the most suitable catalyst. The reaction was performed in a 100 mL three-necked round-bottom flask equipped with a condenser to separate MeOH, which was produced as a byproduct during the reaction. The flask was placed in an oil bath on a magnetic stirrer. Prior to the reaction, PCG and DMC were heated to the desired temperature (*T*) of 75 °C. Then, the catalyst was added to the mixture and stirred at 300 rpm. Once the reaction time (*t*) was reached, the catalyst was separated from the mixture via centrifugation, and the liquid phase was collected for analysis. After analyzing the suitable catalyst, the next step in the study involved determining the optimal dosage of the catalyst for synthesizing GC from PCG within a range of 0.3–3.0% mol of PCG. The same reaction conditions were applied: a PCG/DMC molar ratio of 1:3 for 2 h at 75 °C.

2.7. Experimental Design. Once the most suitable catalyst and optimal dosage for synthesizing GC from PCG via transesterification were determined, the experiments proceeded with a design based on a CCD using the trial version of Design-Expert software version 13 (Stat-Ease, Inc.). The CCD aimed to statistically evaluate two independent variables: the PCG/DMC molar ratio (*x*₁) and reaction time (*x*₂), with five levels (−2, −1, 0, +1, +2), in order to optimize the dependent variables of yield and conversion using RSM, as presented in Table 1.

Table 1. CCD Independent Variables for The Transesterification Reaction of DMC with PCG

factors	units	coded factor level				
		−2	−1	0	+1	+2
<i>x</i> ₁ : molar ratio ^a	mol	1	2	3	4	5
<i>x</i> ₂ : reaction time	h	0.5	1.0	1.5	2.0	2.5

^aPCG/DMC molar ratio.

According to the runs of the reaction eq 1, there are four factorial points, four axial points, and five replicated center points. As shown in Table 7, 13 experiments were carried out in a random sequence.

$$R = 2^n + 2n + m \quad (1)$$

where *R* represents the number of experiments, *n* represents the number of independent variables as factors, and *m* represents the number of center points.

The analysis of variance (ANOVA) was used to determine the coefficients of the resultant polynomial model from the experimental data. The accuracy of the output of the polynomial model was measured using the coefficient of determination (R-square, *R*²), while its statistical significance was evaluated through *p*-value.

$$y = b_0 + b_1x_1 + b_2x_2 + b_{11}x_1^2 + b_{22}x_2^2 + b_{12}x_1x_2 + e \quad (2)$$

Based on Table 5, the quadratic polynomial model was chosen, and eq 2 was employed to evaluate the experimental data, where *y* represents the response factor, *b*₀ represents the intercept value, *b*₁ and *b*₂ represent the first-order coefficient, *x*₁ and *x*₂ represent the independent factors, *b*₁₁ and *b*₂₂ represent the quadratic coefficient of *x*₁ and *x*₂, respectively, *b*₁₂ represents the linear coefficient for the effect of interaction between factors, *k* represents the number of factors studied as well as optimized, and *e* represents the experimental error ascribed to *y*.

2.8. Instrumentation. The concentrations of PCG and GC in the samples from transesterification were determined using gas chromatography attached with a flame ionization detector (FID) (gas chromatography-FID, Agilent 6890). The gas chromatography was operated under the following conditions: (i) a capillary column (HP-5 5% phenyl methyl S) with 0.32 mm internal diameter, 30 m length with 0.25 μm of liquid film, (ii) helium was used as the carrier gas at flow rate of 1.0 mL/min, (iii) the temperature program was set as follows: 2 min initial hold at 60 °C, ramp rate of 10 °C/min from 60 to 150 °C, ramp rate of 20 °C/min from 150 to 310 °C, and then maintained at 310 °C for 5 min, (iv) the detector and injection temperature were set at 250 and 320 °C, respectively, and (v) the total run time was 18 min. The internal standard method was used with MeOH and isopropanol as internal standards to quantify PCG and GC, respectively. The GC yield, PCG conversion, and GC selectivity were calculated assuming PCG as the limiting reactant, using eqs 3–5

$$\text{GC yield (\%)} = \frac{\text{moles of GC}_{\text{produced}}}{\text{moles of PCG}_{\text{initial}}} \times 100 \quad (3)$$

Table 2. Characteristics of CG, PCG, and Commercial Glycerol Compared with Previous Studies

parameters	CG ^a	PCG ^a	glycerol ^b	Kongjao et al. ²⁹	Manosak et al. ³⁰
glycerol (wt %)	39.2 ± 0.2	98.4 ± 0.1	>99.5	93.34	96.2 ± 0.03
MONG (wt %)	49.8 ± 0.3	0.57 ± 0.1	0.001	5.16	1.5 ± 0.07
water (wt %)	7.2 ± 0.1	0.72 ± 0.2	<0.5	1.5	0.06 ± 0.02
ash (wt %)	3.8 ± 0.1	0.31 ± 0.1	0.002	0.00045	2.08 ± 0.06
pH	10.2 ± 0.1	7.05 ± 0.2	neutral to litmus	7.03–7.12	
density (g/cm ³ at 20 °C)	1.033 ± 0.2	1.257 ± 0.1	1.261	1.25	
viscosity (cP at 25 °C)	358.65 ± 2.2	893.8 ± 0.1	954	201–207 ^c	
color	dark brown	clear	clear	light brown	clear

^aData are provided as the mean ± standard deviation of three replicates. ^bCommercial glycerol data are obtained from the supplier. ^cViscosity (cSt at 40 °C).

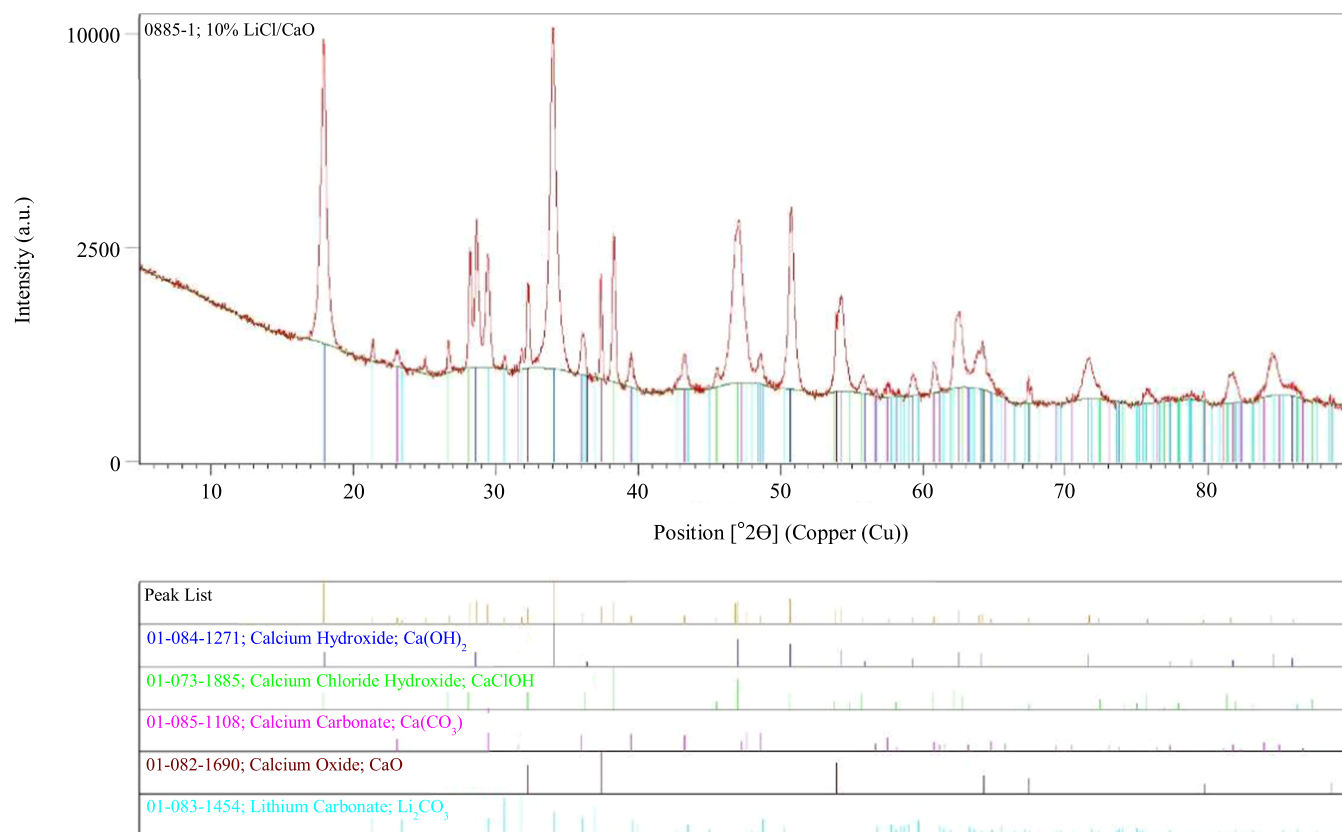


Figure 3. XRD LiCl/CaO catalyst patterns were calcined at 900 °C for 3 h.

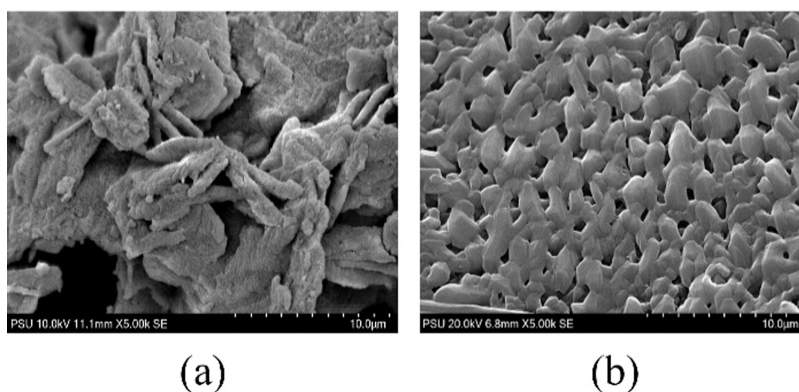


Figure 4. SEM magnification of (a) synthesized LiCl/CaO and (b) purchased Na₂CO₃.

$$\text{PCG conversion (\%)} = \frac{\text{moles of PCG}_{\text{initial}} - \text{moles of PCG}_{\text{unreacted}}}{\text{moles of PCG}_{\text{initial}}} \times 100 \quad (4)$$

$$\text{GC selectivity (\%)} = \frac{\text{GC yield}}{\text{PCG conversion}} \times 100 \quad (5)$$

3. RESULTS AND DISCUSSION

3.1. Characterization of CG and PCG. The chemical compositions of CG, PCG, and commercial glycerol are described by four components, i.e., glycerol, MONG, water, and ash. The CG collected from Specialized R&D Center for Alternative Energy from Palm Oil and Oil Crops was a dark brown liquid with a pH of 10.2. It has a higher pH than

Table 3. Pore Properties of Catalysts

catalyst	pore size (Å)	pore volume (cm ³ /g)	surface area (m ² /g)
CaO	106.6315	0.061802	23.1833
LiCl/CaO	159.7646	0.031104	4.4471
Na ₂ CO ₃	175.1903	0.001999	0.4564

commercial glycerol because the CG, as a byproduct from the transesterification reaction, uses NaOH as a catalyst. The CG also contains a high MONG, water, and ash but a small amount of glycerol (39.2 wt %), as shown in Table 2; it is shown that the MONG (49.8 wt %) is the main impurity in CG, composed of contaminants from the biodiesel processes, including FFA,²⁹ soap, alcohol, and methyl esters.¹¹ The water content in CG (7.2 wt %) before acidification was from the biodiesel cleaning. Still, most of the water content in PCG

Table 5. Optimal Model Fit Summary Statistics of GC Yield and PCG Conversion

model	std. dev.	R ²	Adj-R ²	Pred-R ²	p-value	
GC yield						
linear	5.93	0.2125	0.0550	-0.7132	0.3029	
2FI	5.99	0.2785	0.0379	-0.6297	0.3880	
quadratic	1.32	0.9729	0.9535	0.7989	<0.0001	suggested
cubic	0.8843	0.9913	0.9790	0.9625	0.0590	aliased
PCG conversion						
linear	4.04	0.3715	0.2457	-0.3658	0.0981	
2FI	4.08	0.4234	0.2312	-0.3069	0.3915	
quadratic	0.7926	0.9831	0.9709	0.885	<0.0001	suggested
cubic	0.7688	0.9886	0.9727	0.0879	0.3703	aliased

Table 6. P-Value Obtained in the ANOVA Analysis of Quadratic Models for the GC Yield and PCG Conversion

source	GC yield	PCG conversion
terms	quadratic	quadratic
model	<0.0001 ^a	<0.0001 ^a
x_1 : molar ratio ^b	0.0002	<0.0001
x_2 : reaction time	0.4050	0.6355
x_1x_2	0.0044	0.0024
x_1^2	<0.0001	<0.0001
x_2^2	0.0008	0.0017
lack of fit	0.1646	0.0778
std. dev.	1.32	0.7926
R ²	0.9729	0.9831
Adj-R ²	0.9535	0.9709
Pred-R ²	0.7989	0.8850
CV (%)	2.07	1.17

^ap-value less than 0.05 indicates that model terms are significant.
^bPCG/DMC molar ratio.

Table 7. CCD Matrix with Actual and Predicted Values of Responses for the Transesterification Reaction of DMC with PCG

run	variables ^a		GC yield (%)		PCG conversion (%)	
	x_1	x_2	actual	predicted	actual	predicted
1	5	1.5	49.25	48.37	55.80	55.25
2	3	1.5	69.55	68.52	71.43	70.97
3	3	1.5	69.15	68.52	71.28	70.97
4	3	1.5	67.20	68.52	71.12	70.97
5	3	0.5	62.58	61.68	68.18	67.47
6	3	2.5	62.25	63.02	67.80	67.92
7	3	1.5	67.93	68.52	70.45	70.97
8	2	2.0	70.71	69.18	72.50	72.42
9	2	1.0	62.93	63.08	67.77	68.52
10	4	2.0	58.06	58.17	62.65	63.08
11	3	1.5	69.05	68.52	71.75	70.97
12	4	1.0	61.14	62.92	65.26	66.53
13	1	1.5	58.79	59.54	66.61	66.57

^a x_1 : Molar ratio (mol) and x_2 : reaction time (h) on the transesterification reaction of DMC with PCG. Reaction conditions: Na₂CO₃ dosage = 2.1% mol of PCG and T = 75 °C.

should be noted that among these different catalysts investigated, the GC yield was found to be lower than the PCG conversion. This discrepancy can be attributed to the decomposition of GC leading to the formation of glycidol, as depicted in Figure 5. Liu et al.³¹ have reported that glycidol formation primarily arises from the decomposition of GC

rather than the direct dehydration of glycerol. Therefore, the main criterion for selecting a suitable catalyst is the PCG conversion. Na₂CO₃ exhibited the highest 81.82% PCG conversion and 79.89% GC yield, indicating superior performance compared to LiCl/CaO. However, it should be noted that the GC yield achieved with Na₂CO₃ was slightly lower than CaO. The catalytic performance in CaO and LiCl/CaO when using PCG with water and MONG content was 0.72 and 0.57 wt %, respectively, as a reactant, showed PCG conversion lower than Na₂CO₃ since water can cause the deactivation of the catalyst, i.e., CaO/Al₂O₃.^{13,25} The turbidity of the solution supports the possible effect of water on the dissolution of CaO after exposure to the calcined CaO in the air for 3 h.²⁶ Moreover, in the reviews of de Caro et al.,¹⁰ Teng et al.,¹³ and Ochoa-Gómez et al.,¹⁴ they found that most of the synthesis conditions of this trans-carbonation have been studied from pure glycerol or glycerol containing less than 2 wt % of catalyst. Considering the high activity PCG conversion of Na₂CO₃, the subsequent optimization experiments were carried out to investigate the impact of catalyst dosage.²⁰

3.3.2. Effect of Catalyst Dosage. The effect of catalyst dosage on GC yield, PCG conversion, and GC selectivity was studied using Na₂CO₃ with different dosages ranging from 0.3 to 3% mol of PCG. The transesterification reaction of DMC with PCG was maintained at 75 °C, with the PCG/DMC molar ratio of 1:3 for 2 h. As shown in Figure 6, GC yield, PCG conversion, and GC selectivity increased to the highest point with the increase of catalyst dosage from 0.3–2.1% mol. When the catalyst 0.3% mol was used to catalyze the transesterification of DMC with PCG, GC yield, PCG conversion, and GC selectivity were 46.76, 55.44, and 84.64%, respectively. When the catalyst dosage reached 2.1% mol, GC yield, PCG conversion, and GC selectivity were 78.15, 79.93, and 97.78%, respectively. However, when the catalyst dosage of Na₂CO₃ was further increased to 3% mol, GC yield, PCG conversion, and GC selectivity were decreased. This phenomenon can be explained by the increase in the catalyst dosage, providing more active sites for the reaction.³² The results indicate that the optimum dosage of Na₂CO₃ was 2.1%mol.

3.4. Summary of Optimal Model Fit for the GC Yield and PCG Conversion. The optimal model was developed with the aim of maximizing the adjusted coefficients of determination (Adj-R²) and the predicted coefficients of determination (Pred-R²). The cubic model produced the highest Adj-R² values for both GC yield and PCG conversion, which were 0.9790 and 0.9727, respectively, as presented in Table 5. However, the Pred-R² values were not the highest. It is also important to consider selecting the highest-order

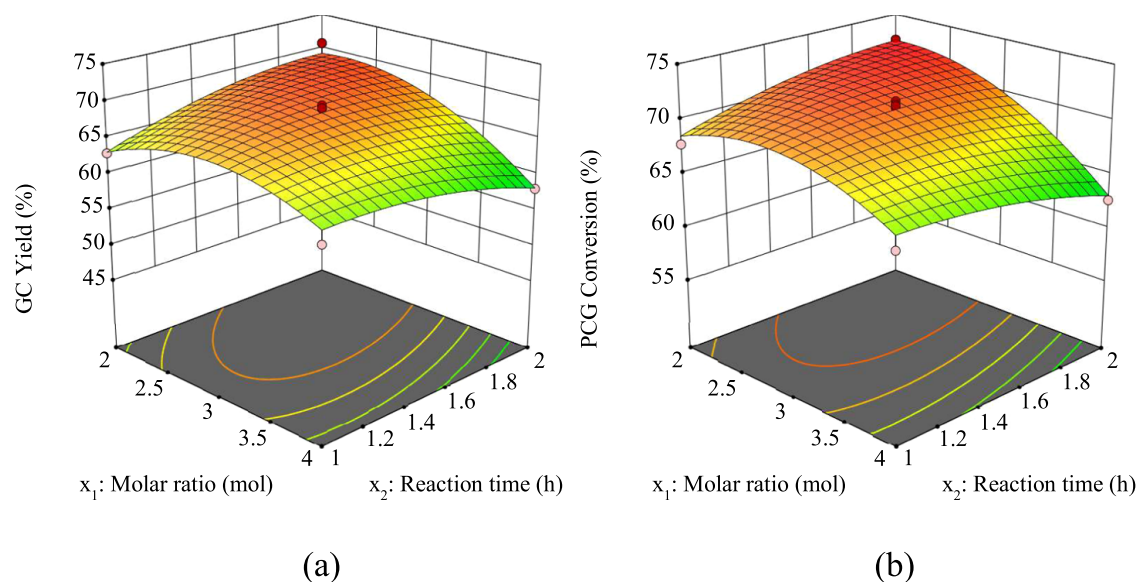


Figure 7. Response surface plots of (a) GC yield and (b) PCG conversion. Effect of x_1 : molar ratio and x_2 : reaction time on the transesterification reaction of DMC with PCG. Reaction conditions: Na_2CO_3 dosage: 2.1% mol of PCG and $T = 75\text{ }^\circ\text{C}$.

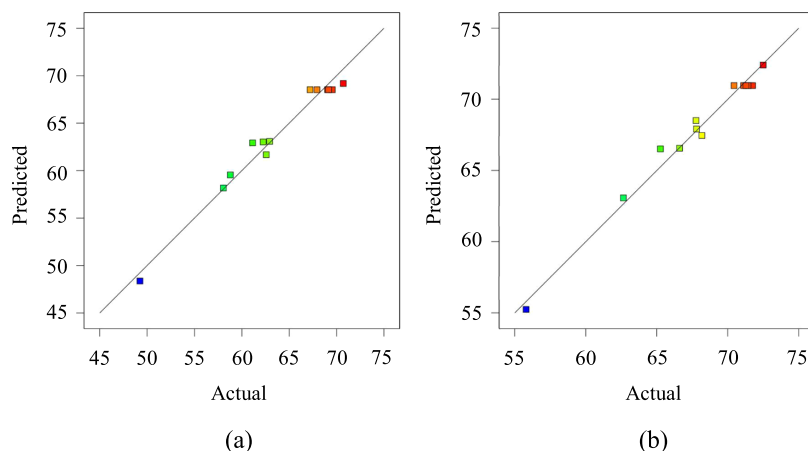


Figure 8. Plot of predicted versus actual values for the (a) GC yield and (b) PCG conversion. Effect of x_1 : molar ratio and x_2 : reaction time on the transesterification reaction of DMC with PCG. Reaction conditions: Na_2CO_3 dosage = 2.1% mol of PCG and $T = 75\text{ }^\circ\text{C}$.

Table 8. Analysis of RSM Numerical Optimization for GC Yield and PCG Conversion

	variables ^a		responses ^b (%)		desirability
	x_1	x_2	y_1	y_2	
predicted	2.37	1.83	69.52	72.24	0.944
observed			72.13	78.39	

^a x_1 : Molar ratio (mol) and x_2 : reaction time (h) on the transesterification reaction of DMC with PCG. Reaction conditions: PCG/DMC molar ratio = 1:2.37, Na_2CO_3 dosage = 2.1% mol of PCG, $T = 75\text{ }^\circ\text{C}$, and $t = 1.83\text{ h}$. ^b y_1 : GC yield (%) and y_2 : PCG conversion (%).

polynomial that includes significant additional terms and is not aliased. The fit summary revealed that the p-value of the suggested quadratic model was lower than 0.05 (<0.0001) for both the yield of GC and conversion of PCG, indicating the significance of the quadratic model.

3.5. Statistical Analysis of the Response Model. The optimization of process parameters, PCG/DMC molar ratio, and reaction time were conducted. The models were analyzed

using ANOVA to assess the goodness of fit to the empirical data, as indicated in Table 6. The results show that the models were statistically significant ($p < 0.05$). Quadratic models produced the best fit for the GC yield and PCG conversion, and the models were highly effective with a tiny p -value ($p < 0.0001$). However, the lack of fit of GC yield and PCG conversion were 0.1646 and 0.0778, respectively, which were insignificant. The results implied that the model performed well and was an excellent fit for the data derived from the experiment.

Additionally, these models' fit was assessed using R^2 , Adj- R^2 , Pred- R^2 , and coefficients of variation (CV%). The Adj- R^2 changed the R^2 value by considering the number of variables or predictors in the model. The R^2 value is the actual multiple determination value, reflecting how much of the variability in the data was accounted for by the model.³³ The quadratic model will be adequately adjusted to the experimental data due to this R^2 .^{34,34} The R^2 values of the GC yield and PCG conversion were 0.9729 and 0.9831, respectively. Moreover, all R^2 values were roughly near 1, indicating an excellent fit to the data and showing a high correlation between the actual and

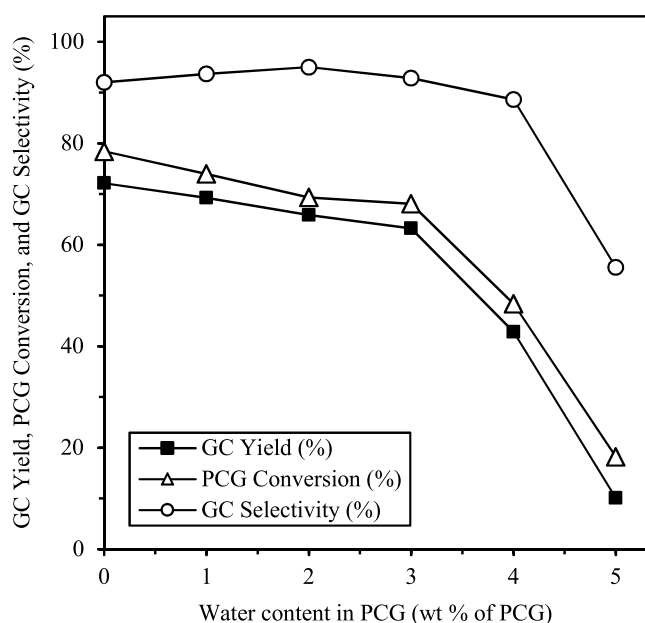


Figure 9. Effect of water content in PCG on the transesterification reaction of DMC with PCG. Reaction conditions: PCG/DMC molar ratio = 1:2.37, Na_2CO_3 dosage = 2.1% mol of PCG, $T = 75^\circ\text{C}$, and $t = 1.83$ h.

predicted values.³⁵ Moreover, the CV% is the ratio of the standard deviation to the mean, and the CV% of the GC yield and PCG was 2.07 and 1.17%, respectively, based on the replicated experiments. These low values of CV% also show the high reliability of the data from this experiment.³⁶

3.6. Effect of PCG/DMC Molar Ratio and Reaction Time on the GC Yield and PCG Conversion. The experiments were investigated at 75°C . The GC yield and PCG conversion responses were evaluated in a simulated run; the results from the CCD are summarized in Table 7. It was found that the highest actual GC yield and PCG conversion were 70.71 and 72.50%, respectively, in run number 8, which was achieved with a PCG/DMC molar ratio of 1:2 and 2 h of reaction time. The quadratic model for the GC yield and PCG conversion is expressed in eqs 6 and 7 below

$$\text{GC yield} = 4.788 + 27.205x_1 + 35.485x_2 - 5.430x_1x_2 - 3.642x_1^2 - 6.174x_2^2 \quad (6)$$

$$\text{PCG conversion} = 32.605 + 17.763x_1 + 21.062x_2 - 3.670x_1x_2 - 2.515x_1^2 - 3.275x_2^2 \quad (7)$$

The effect of the PCG/DMC molar ratio and reaction time on the GC yield and PCG conversion is illustrated by the three-dimensional (3D) RSM plot, as shown in Figure 7a,b, respectively. When the PCG/DMC molar ratio increased from

1 but did not exceed 3, this resulted in a higher GC yield and PCG conversion, but when the PCG/DMC molar ratio increased above 3, the GC yield and PCG conversion decreased. This is in agreement with previous studies, which have also reported the transesterification of DMC with pure glycerol using CaO as a catalyst; the results show that the GC yield reaches a maximum of 85.4% at the glycerol/DMC molar ratio of 2 and then decreases when the glycerol/DMC molar ratio increases up to 10. Moreover, in the transesterification of DMC with pure glycerol using 15 wt % Na_2CO_3 -CS-800 as a catalyst, it was found that the GC yield and PCG conversion increased with the increase of glycerol/DMC molar ratio was lower than 5:1, but when the glycerol/DMC molar ratio was higher than 5:1, there was no apparent change in the GC yield and PCG conversion, respectively.²⁴ Additionally, the excess DMC will limit the complete contact between glycerol and the catalyst.³⁷

Figure 8 a,b shows the model predictions versus the observations of the GC yield and PCG conversion, respectively. The plot shows that the data are generally linear, demonstrating that the model predictions and the empirical observation are closely related. As a result, the GC yield and PCG conversion response model adequacy assessments showed the model's accuracy in fitting the data.

3.7. Optimization of the Independent Variables for the GC Yield and PCG Conversion. The numerical optimization of the GC yield and PCG conversion was achieved by optimizing all of the independent variables, as shown in Table 8. The optimum values for 2 independent variables were 2.37 mol (x_1) and 1.83 h (x_2). At these reaction conditions, the predicted GC yield (y_1) and PCG conversion (y_2) were achieved at 69.52 and 72.74%, respectively. The desirability function of the suggested optimum conditions is about 0.944. The observed GC yield (y_1) and PCG conversion (y_2) were achieved at 72.13 and 78.39%, respectively.

3.8. Effect of Water Content in PCG on GC Yield and PCG Conversion. The effect of water content in PCG on GC yield, PCG conversion, and GC selectivity was studied by using Na_2CO_3 with water content ranging from 0–5 wt % of PCG, as shown in Figure 9. The reactions were maintained at 75°C with the optimized reaction conditions: a PCG/DMC molar ratio of 1:2.37 for 1.83 h. The GC yield, PCG conversion, and GC selectivity showed a slow tendency to decrease; the GC yield, PCG conversion, and GC selectivity were 63.2, 68.1, and 92.80%, respectively, at the water content 3 wt % of PCG. However, when the water content increased above 3 wt % of PCG, the result showed that the GC yield, PCG conversion, and GC selectivity decreased. The effect of water content was due to 2 main reasons. Since water can deactivate the catalyst, most syntheses have been studied using pure glycerol or glycerol containing <2 wt % water.²⁰ Additionally, the presence of water in PCG might affect the GC yield due to the hydrolysis reaction between DMC and water,³¹ as shown in Figure 10. This hydrolysis reaction leads to the generation of

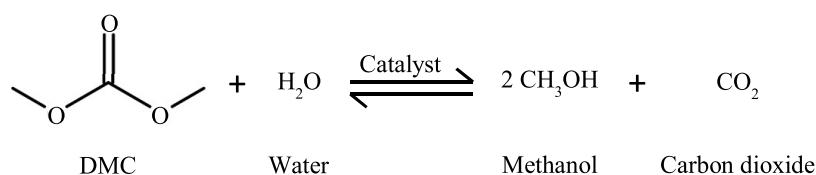


Figure 10. Hydrolysis reaction of DMC with water.

MeOH and CO₂.³⁸ The presence of excess DMC, intended for GC synthesis, might lead to a hydrolysis reaction with water instead. Therefore, it is crucial to ensure that the water content in PCG, as an impurity, does not exceed 3 wt % of PCG.

4. CONCLUSIONS

This study presents a straightforward approach to transesterifying DMC with PCG obtained from biodiesel production. The acidification process successfully purified PCG, resulting in a purity of 98.4 wt %. Among the catalysts tested, Na₂CO₃ exhibits the highest suitability for synthesizing GC from PCG, considering its composition of 0.72 wt % water and impurities such as MONG and ash. By employing a Na₂CO₃ dosage of 2.1% mol, optimal results were achieved. By utilizing a CCD to optimize the reaction conditions, the analysis of 13 experiments led to the determination of the following optimal parameters: PCG/DMC molar ratio of 1:2.37 and reaction time of 1.83 h. The reaction temperature was maintained at 75 °C. As a result, the observed GC yield was found to be 72.13%, and the PCG conversion reached 78.39%. It is worth noting that despite the purification process for CG, a byproduct of biodiesel production, it is challenging to completely eliminate the presence of water in PCG. The results demonstrate that Na₂CO₃ can withstand water content in PCG up to 3 wt %. The investigations presented in this study not only contribute to the efficient utilization of CG in the biodiesel industry but also provide inspiration and guidance for future research in the field of sustainable chemical processes.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c06287>.

Components of the catalyst were identified through XRD analysis; a summary of the key peaks, their 2θ values; and corresponding phases (Table S1); the identified phases include Ca(OH)₂, CaClOH, Ca(CO₃), CaO, and Li₂CO₃ (PDF)

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Notes

The authors declare no competing financial interest.

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