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An optimization study**

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DOI

[10.1007/s10562-018-2312-9](https://doi.org/10.1007/s10562-018-2312-9)

Publication date

2018

Document Version

Accepted author manuscript

Published in

Catalysis Letters

Citation (APA)

Avhad, M. R., Gangurde, L. S., Sánchez, M., Bouaid, A., Aracil, J., Martínez, M., & Marchetti, J. M. (2018). Enhancing biodiesel production using green glycerol-enriched calcium oxide catalyst: An optimization study. *Catalysis Letters*, 148(4), 1169-1180. <https://doi.org/10.1007/s10562-018-2312-9>

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Enhancing Biodiesel Production Using Green Glycerol-Enriched Calcium Oxide Catalyst: An Optimization Study

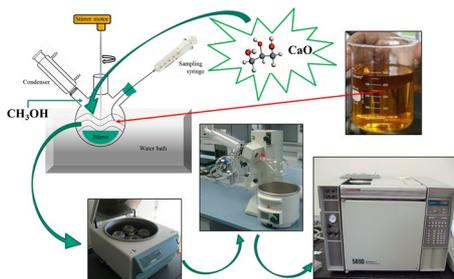
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Received: 13 December 2017 / Accepted: 12 January 2018
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Abstract

The present article demonstrates a superior catalytic performance of glycerol-enriched calcium oxide for biodiesel production than other calcium-based counterparts. The proficiency of glycerol-enriched calcium oxide in catalyzing the methanolysis of crude *Jatropha curcas* oil containing high free fatty acids content was systematically researched by examining the effects of glycerol dose, temperature, time, methanol-to-oil molar ratio and calcium oxide (CaO) amount on the process. Acid value of oil was lowered by 49 times and the maximum oil conversion of 96.1% was reported after the methanolysis reaction that indicated the improved performance of calcium oxide, after its treatment with glycerol, in accelerating biodiesel production from crude oil with very high free fatty acids amount. An interaction between the reaction variables, their influence on the methanolysis and optimum conditions affecting the process were moreover determined by means of the regression analysis (response surface methodology). The statistical analysis suggested that both CaO amount and mole ratio of methanol-to-oil had a significant impact on the current biodiesel production process.

Graphical Abstract



Keywords Biodiesel production · Calcium oxide · Glycerol · *Jatropha curcas* oil · Methanolysis

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1 Introduction

Augmenting environmental pollutants as a consequence of burning fossil fuels, fluctuating fuel prices and uncertainties related to the petroleum reserves have together contributed in triggering the need of utilizing renewable sources of energy, which are sustainable, ecologically benign and economically reasonable [1]. Certainly, biodiesel has been recognized as one of the potential replacements of petroleum diesel not only due to the fact that this oxygenated fuel can be synthesized from lipid-rich biomass but also because its

combustion offers minor environmental toxicity in comparison to the petroleum-derived diesel [2, 3]. Among several methodologies currently known for biodiesel production, the catalytic transesterification of triacylglycerols (TAGs) and esterification of free fatty acids (FFAs) have been frequently tested [1]. The ability of homogeneous catalysts to accelerate the production of biodiesel in a short reaction time using mild reaction conditions is well-recognized and has resulted in its widespread utilization. Homogeneous catalysts, however, are miscible in the reaction medium that provoked the key concerns related to its recovery and reutilization. The post-reaction treatments essential for the removal of residual homogeneous catalyst from the reaction medium have resulted in the generation of emulsion, which reduced the yield as well as the purity of biodiesel and glycerol [4, 5]. Moreover, the application of homogeneous acid catalysts could result in corrosion of the equipment [6].

Heterogeneous catalysis has offered an imperative solution to the above-mentioned drawbacks related to use of their homogeneous counterparts. The efficacy of a variety of heterogeneous base and acid catalysts for biodiesel production have been widely investigated, wherein they facilitate the phase separation; hence, reducing the neutralization step and enhancing the purity of the reaction products [7, 8]. This catalyst can be easily recovered and reutilized, directly or after treatment, for the next reaction cycle. Therefore, the research efforts have been consistently engaged in developing not only a high-performance and stable but also low cost heterogeneous catalyst for biodiesel production [9]. The base catalyst assisted alcoholysis reaction have been found to be faster than those catalyzed by the acidic materials [10, 11]. Among different basic solid catalysts, calcium oxide (CaO) has been extensively tested for the alcoholysis reaction owing to its high basicity, low solubility in short-chain alcohols and low cost [12]. Kouzu et al. [13] concluded that 0.78 g of CaO catalyst applied for transesterification of soybean oil with reflux methanol resulted in the fatty acid methyl esters (FAMES) yield of 99% after 120 min of reaction performed using 12:1 methanol-to-oil molar ratio. Because of the straightforward synthesis of CaO from inexpensive and abundant natural resources [14–16], there is augmenting research on testing its catalytic activity for biodiesel production from different lipid feedstocks. Besides, there exist the necessity to further expand research on the same also to understand its different active catalytic phases. For example, the recent studies have reported that neat CaO catalyst experiences its structural transformation during the progression of the alcoholysis reaction [17–20]. An initial stage of transesterification reaction is catalyzed by the oxide phase (CaO) of the material, after which the material interacts with the by-producing glycerol and faces its transformation to calcium diglyceroxide (CaDg)

[17]. The probability of CaDg formation is higher than that of calcium methoxide because CaO is more reactive with glycerol than with methanol. León-Reina et al. [18] described CaDg as a set of molecular calcium tetramers interlinked by hydrogen bonds. The CaDg catalyst has been reported to display superior catalytic activity for biodiesel production than CaO because of availability of basic oxygen anions as a consequence of interruption of the crystal structure at the surface that can abstract proton from –OH group of methanol and direct the formation of surface methoxide ion [18]. CaDg has been described as a chemically stable heterogeneous catalyst, weakly basic in nature and not prone for deactivation by the hydration/carbonation reaction when exposed to the surrounding air [19, 20]. CaDg has been also described as glycerol-enriched CaO [21, 22]. Considering the above-mentioned advantages of CaDg over CaO, Kouzu et al. [19] and López Granados et al. [23] have recommended to transform CaO to CaDg compound prior to its application for biodiesel production.

Few protocols have been employed for the synthesis of CaDg material. Lukić et al. [24] applied a mechanochemical technique for the synthesis of CaDg that was used to catalyze the alcoholysis reaction between sunflower oil and methanol, wherein it is concluded that CaDg catalyst acted as an emulsifier and significantly influenced the initial rate of the methanolysis reaction. Li et al. [25] utilized the precipitation method using potassium hydroxide, glycerol and calcium chloride for the synthesis of CaDg catalyst. The synthesized catalyst was used to assist the methanolysis reaction between refined *Jatropha curcas* oil containing extremely low FFAs content. Additionally, the catalytic activity of CaDg have been tested for biodiesel production from few lipid feedstocks such as, soybean oil [21, 26, 27], sunflower oil [28], castor oil [29] and waste cooking oil [30]. Looking at the novel catalytic proficiency of glycerol-enriched CaO, the reports focused on its utilization for biodiesel production are extremely low in comparison with those of neat CaO catalyst. Moreover, no literature on the process optimization of glycerol-enriched CaO assisted biodiesel production till date is available to the best of our knowledge.

The present study preliminary demonstrates the comparison of catalytic activity of glycerol-enriched CaO with other laboratory-synthesized and commercial calcium-based catalysts for the methanolysis of crude *J. curcas* oil (CJCO) containing high FFAs amount. A novel protocol developed for the synthesis of glycerol-enriched CaO catalyst was utilized using mussel shells, which scientifically is known as *Mytilus galloprovincialis* shells. The influence of reaction temperature, time, glycerol dose, methanol-to-oil molar ratio and CaO amount on the conversion of CJCO and FAMES yield was systematically investigated. Furthermore, an interaction between the reaction variables, their influence

on the described methanolysis reaction and optimal process parameters were determined by means of the response surface methodology (RSM).

2 Experimental Section

2.1 Materials

CJCO was supplied by IBERINCO (Spain). Its fatty acid composition and physico-chemical characteristics were determined in accordance with the American Oil Chemists' Society (AOCS) official methods, and the results are reported previously [31]. CJCO was filtered using Whatman filter paper prior to its utilization for biodiesel production. Methanol (Cor Quimica, Spain), glycerol (Sigma-Aldrich), *n*-octyl octanoate (Sigma-Aldrich) and carbon disulphide (Panreac) with purity higher than 99% were utilized. The commercial reagent grade CaO (CC) was purchased from Sigma-Aldrich and used as received, while, for the synthesis of laboratory-grade CaO, *M. galloprovincialis* shells were collected from the local fish market in Madrid.

2.2 Catalyst Preparation

For the synthesis of CaO, *M. galloprovincialis* shells initially were cleaned under a flow of tap water to remove the adsorbed superfluous substances, followed with its drying in an oven set at 100 °C for 60 min. Subsequently, the shells were pulverized using a mortar-pestle, evenly placed in a silica crucible and calcined in a ceramic muffle heating furnace set at 800 °C using the heating rate of 5 °C min⁻¹ for 360 min. The obtained white colored powder (MC) was removed from the furnace and preserved carefully in a desiccator to avoid its poisoning due to moisture and carbon dioxide in ambient air while handling and weighing. The calcination process resulted in approximately 45% loss of the total fresh weight of the precursor, *M. galloprovincialis* shells. The particle size of CaO was between 0.25 and 0.5 mm. However, the particle size was observed to have a negligible impact on the process due to its macroporous features [15].

The preparation of glycerol-enriched CaO (GMC) was carried out by reacting the obtained CaO powder with a desired amount of glycerol in an airtight glass reactor. To improve the interaction between glycerol and CaO, a measured amount of CJCO was added to the reactor. This mixture was vigorously agitated at 60 °C for 60 min using 350 rpm stirring intensity under atmospheric pressure. For the synthesis of calcium methoxide (CM), an immersion of CaO in methanol was stirred at 60 °C for 60 min, followed with its filtration for the separation of the solid material. To investigate the leaching phenomenon of catalyst in the reaction

mixture, a measured amount of CaO and methanol were agitated using 350 rpm stirring intensity at 60 °C temperature for 720 min. Subsequently, the solution was filtered and only the filtrate, methanol containing leached calcium species, was used for the CJCO methanolysis reaction; this experiment was labelled as homogeneous contribution of mussel shells (HMC). The term thermal catalysis (TC) refers to the performance of the alcoholysis reaction between CJCO and fresh methanol performed at 65 °C temperature in the absence of a catalytic material.

2.3 Reaction

The methanolysis of CJCO was performed in a three-neck curved bottom glass reactor of 250 cm³ volume capacity. A mechanical stirrer equipped with an impeller of 6.0 cm diameter was inserted through the middle neck and placed centrally close to the bottom of the reactor. A water condenser was attached to one of the side necks, while, a rubber cork was fitted to the other neck of the reactor. The water condenser allowed the refluxing of methanol into the reactor. The glass reactor was placed in a thermostatically controlled water bath (Heto-Holten A/S, Denmark), the temperature of which was controlled by a PID controller with 1 °C precision. The speed of the stirrer was set by a motor (Eurostar Basic IKA). After the treatment of CaO with glycerol in the presence of CJCO, the system temperature was shifted to the desired reaction set point and a measured volume of methanol was charged into the reactor; this was considered as the starting time for the methanolysis reaction. The stirring intensity of 350 rpm was maintained for all experiments based on our previous study [15], and was adequate to avoid the external mass transfer limitations [9, 15, 16]. The post-reaction mixture was centrifuged to separate different components and the residual trace amount of methanol as well as water present in the biodiesel phase was removed using a rotary evaporator attached to a vacuum pump (10 mg Hg) set at 60 °C for 30 min. All experiments were replicated twice [except center points, which were performed four times based on the experimental design (see Sect. 2.6)] to obtain the reproducibility, and an average of the experimental values were considered.

2.4 Analysis

The reaction samples were analyzed using the gas chromatography (GC) analyzer (Hewlett–Packard HP-5890 Series II) equipped with a flame ionization detector and a fused silica capillary column (12 m length, 0.31 mm internal diameter and 0.71 μm thickness). A Hewlett–Packard 3396SA integrator was connected to the chromatograph. The injection system was split-splitless, and helium was the carrier gas at a 1 ml min⁻¹ flowrate. The injector and

detector temperature were set at 275 and 325 °C, respectively. The GC column temperature was initially held at 130 °C for 1 min, then raised at 4 °C min⁻¹ to 160 °C and finally heating at a ramp rate of 30 °C min⁻¹ to 320 °C. *n*-Octyl octanoate was used as an internal standard and the reaction samples were dissolved in carbon disulfide. The GC analysis was conducted by injecting 1 µl volume of the prepared analysis samples into the instrument. Based on the area obtained for a given weight of the sample from the chromatogram, weight was converted to molar results with the help of standards using the below mentioned expressions:

$$\text{Grams of methyl esters} = \frac{\text{Grams of internal standard} \times \text{Area of methyl esters}}{\text{Density of methyl esters} \times \text{Area of internal standard}} \quad (1)$$

$$\text{Moles of methyl esters} = \frac{\text{Grams of methyl esters}}{\text{Molar mass of methyl esters}} \quad (2)$$

The CJCO conversion (X_{CJCO}) and FAMEs yield (Y_{FAMEs}) are expressed as:

$$X_{\text{CJCO}} = \frac{\text{Initial moles of oil} - \text{Final moles of oil}}{\text{Initial moles of oil}} \quad (3)$$

$$Y_{\text{FAMEs}} = \frac{\text{Total moles of FAMEs}}{(3 \times \text{Moles of oil})} \times 100 \% \quad (4)$$

The acid value of CJCO and FAMEs was determined in accordance with the American Society for Testing and Materials (ASTM) D664 method using a Metrohm Swiss model 702SM Titrino. The titration endpoint was determined and verified automatically with the help of phenolphthalein indicator.

2.5 Catalyst Characterization

The X-ray diffraction (XRD) patterns for the fresh and collected catalyst were recorded using a Bruker D5005 diffractometer equipped with Huber incident-beam monochromator and Braun PSD detector. The data collection was done at room temperature using monochromatic Cu K α 1 radiation ($\lambda = 0.154056$ nm) in the 2θ region between 10° and 80°, step size 0.038° 2θ . Samples of about 20 mg were deposited on a Si (510) wafer and were rotated during the measurement. The data evaluation was carried out using the Bruker program EVA. The thermogravimetric analysis (TGA) of the

samples were performed using a Thermal Advantage (SDT Q600) analyzer. The samples were placed in an alumina crucible in amounts varying between 3 and 25 mg. The experimental runs were conducted in the nitrogen atmosphere, and the purge flow rate was 100 ml min⁻¹. The thermal analysis started with a temperature equilibration at 25 °C, after which the samples were heated at a ramp rate of 5 °C min⁻¹ to 800 °C. The residence time at 800 °C was 20 min.

2.6 Experimental Design

The regression analysis was conducted by designing a set of experiments, the results of which were fitted to a two-level factorial design for the RSM application using the statistics centurion XVI software (Statpoint technologies, Inc., USA). The linear and non-linear stage of the two-level factorial design consisted of four experiments each, along with four replicates of the center points, as shown in Table 1.

Table 1 Two-level factorial design of experiments. Stages of experiments along with the natural and the coded values (X_M for methanol-to-CJCO molar ratio and X_C for CaO amount) of the reaction variables, and the obtained CJCO conversion and FAMEs yield

Type of experiments	Run	Methanol-to-oil molar ratio	CaO amount (%)	X_M	X_C	Conversion (%)	FAMEs yield (%)
Linear stage	1	12	18	1	1	96.1	78.3
	2	12	12	1	-1	94.3	77.0
	3	6	18	-1	1	93.0	79.3
	4	6	12	-1	-1	83.7	69.3
Center stage	5	9	15	0	0	92.7	75.6
	6	9	15	0	0	93.5	75.9
	7	9	15	0	0	93.5	76.3
	8	9	15	0	0	92.6	75.2
Non-linear stage	9	13.2	15	1.41	0	95.0	78.0
	10	4.8	15	-1.41	0	80.9	66.0
	11	9	19.2	0	1.41	94.7	77.3
	12	9	10.8	0	-1.41	84.3	68.7

The non-linear stage is also known as the star-points and coded as $\pm \alpha$. The distance between the origin and the star-points is expressed as $\alpha = 2^{n/4}$ (in the present study: $n = 2$ and $\alpha = 1.41$). The linear, center-points and non-linear stage of the experimental design were combined to form a central composite design and utilized to investigate the influence of methanol-to-CJCO molar ratio and catalyst amount on the methanolysis process. The successful implementation of such method requires an appropriate selection of the independent variables, levels and the response. The catalyst amount (X_C) and methanol-to-oil molar ratio (X_M) were selected as the investigating factors, while, the response chosen was CJCO conversion and FAMEs yield. The statistical analysis allowed the determination of influences associated with interactions considering the CJCO conversion and FAMEs yield at high and low values of each factor. The model equations were utilized to interpret the interaction between the variables, and predict the optimum conditions affecting the described methanolysis process.

3 Results and Discussion

3.1 Catalyst Type Selection

The proficiency of different calcium-based materials to catalyze the methanolysis of CJCO was first investigated. The methanolysis reactions were performed at 65 °C for 420 min, using methanol-to-oil molar ratio of 9:1 and 15 wt% CaO amount. The glycerol dose in the case of GMC catalyst was 10 wt% with respect to CaO amount. The experimental results for the study evaluating the ability of different catalysts to accelerate the CJCO methanolysis reaction are presented in Fig. 1. The application of a commercial CaO catalyst for the methanolysis reaction resulted in 53.8% CJCO conversion, which was 1.15 times higher than that obtained using the CaO derived from *M. galloprovincialis* shells. However, the CJCO conversion was found to be enhanced by 2.88 times when *M. galloprovincialis* shells derived CaO was treated with glycerol before its utilization for the described methanolysis reaction. The application of GMC to catalyze the methanolysis reaction using the above-mentioned reaction variables resulted in 93.5% CJCO conversion. An improved performance of GMC catalyst is anticipated due to an interaction between basic sites of CaO and glycerol that leads towards the formation of CaO–glycerol complex. The presence of hydrophobic as well as hydrophilic sites at the surface of GMC, in comparison to polar surface of CaO, is expected to favor the approach of TAGs and alcohol to the catalytic sites [18, 27]. The CJCO conversion raised from 23.8 to 47.2% when the catalytic species were converted from CaO to calcium methoxide. This significant elevation in the oil conversion suggests an

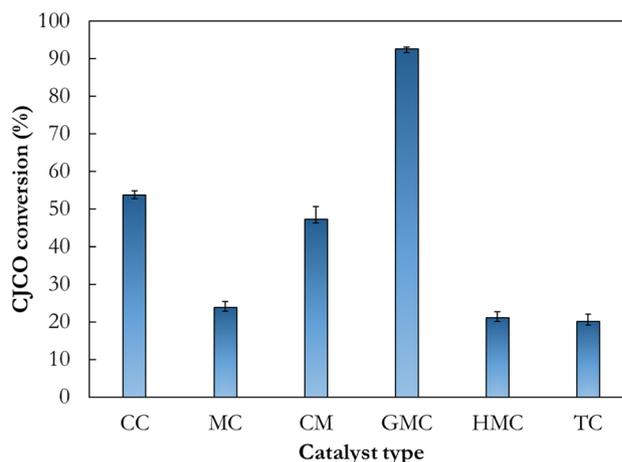


Fig. 1 CJCO conversion using different types of catalyst. *CC* commercial CaO, *MC* mussel shells derived CaO, *CM* calcium methoxide, *GMC* glycerol-enriched CaO, *HMC* homogeneous contribution of mussel shells derived CaO, *TC* thermal catalysis. Reaction temperature: 65 °C, time: 420 min, CaO amount: 15 wt%, glycerol dosage: 10 wt% (in the case of GMC), methanol-to-CJCO molar ratio: 9:1, stirring intensity: 350 rpm

existence of interaction between CaO and methanol. Therefore, the current study applied a novel protocol for the preparation of GMC in the presence of oil, instead methanol, as a medium for enhancing the interaction between CaO and glycerol. This strategy ensured the elimination of even a minor possibility for the generation of catalytic methoxide species, and generated only glycerol-enriched CaO catalytic material. Previous studies have reported the formation of glycerol-enriched CaO species in the presence [21, 22, 32] and absence [18, 27] of methanol. Understanding the reaction between CaO and methanol that results in the formation of calcium methoxide as reported by Kawashima et al. [33] and well-known poisoning phenomenon of CaO because of atmospheric CO₂ and H₂O, this study used an alternative method for the preparation of only glycerol-enriched CaO species in the presence of oil. Based on a mechanism proposed by Esipovich et al. [27], CaO and calcium methoxide treated with glycerol might possess similar ability to catalyze transesterification reaction because calcium methoxide would react with glycerol with the release of methanol molecule and direct the formation of CaDg. The final catalytic material, therefore, could be similar when either CaO or calcium methoxide is treated with glycerol. A negligible lixiviation of CaO in methanol solution was found, and therefore, an insignificant difference in the CJCO conversion was obtained between homogeneous contribution of catalyst (HMC) and TC. This behavior indicated that CaO derived from *M. galloprovincialis* shells is a good solid material for its application as catalyst for biodiesel production.

3.2 Reaction Variables Effect

3.2.1 Glycerol Dose Effect

The use of appropriate amount of glycerol for its adequate interaction with CaO is of high importance as confirmed also in the previous report that concluded the deactivation of catalyst because of availability of surplus amount of glycerol in the reaction mixture during its by-production during the methanolysis reaction [34]. Also, Ferrero et al. [21] reported that glycerol dosage higher than the optimum amount resulted in decreasing of biodiesel yield. This study investigated the impact of different glycerol dosage (5, 10 and 15 wt% of CaO wt.) on the CJCO conversion. It is worth noting that the amount of glycerol used for the catalyst synthesis in this study is below the stoichiometric value. This is because of the fact that glycerol is producing during the methanolysis process and would interact with the available untransformed CaO; hence, the glycerol amount would never be too high to cause the catalyst deactivation as observed by Li et al. [25], and shift the reaction equilibrium towards the formation of the product. The impact of glycerol dosage on the methanolysis was studied keeping reaction temperature of 65 °C, methanol-to-CJCO molar ratio of 9:1, CaO amount of 15 wt% and 420 min reaction time. The results presented in Fig. 2 shows rise in the CJCO conversion from 85.6 to 93.5% with increasing the glycerol dosage from 5 to 10 wt%; however, further increment in the glycerol dosage showed an insignificant improvement on the CJCO conversion. López Granados et al. [23] observed a similar pattern of experimental findings that suggested the addition of glycerol to the reaction mixture augmented the methanolysis reaction rate,

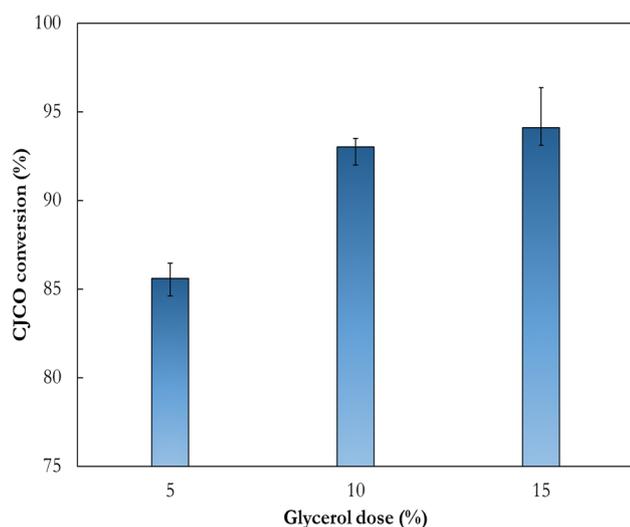


Fig. 2 Effect of glycerol dosage for CaO activation. Reaction temperature: 65 °C, time: 420 min, CaO amount: 15 wt%, methanol-to-CJCO molar ratio: 9:1, stirring intensity: 350 rpm

but increasing its amount above the optimal value showed a negligible impact on the biodiesel yield. The present experimental findings are in agreement with the previously reported study [23], and concludes that the glycerol dose of 10 wt% (of CaO amount) was adequate to ensure high activity of glycerol-enriched CaO for the described methanolysis reaction.

3.2.2 Reaction Temperature Effect

Agreeing with the suggestions presented in the previous reports [23, 34], an adequate temperature would be essential not only to promote miscibility and reactivity between the reactants but also for the activation of glycerol-enriched CaO catalytic phases. Therefore, understanding the temperature effects on the described methanolysis process could be of foremost relevance. The experimental results indicating the effect of different temperatures (45, 55 and 65 °C) on the CJCO conversion are presented in Fig. 3. The reaction temperature of 75 °C caused the evaporation of methanol despite having the water condenser. This could lead towards the incomplete methanolysis reaction, and therefore, was not included in the present reaction system. The methanolysis reaction performed at 65 °C resulted in the highest oil conversion of 93.5% after 420 min of reaction time. Unexpectedly, approximately similar value of oil conversion obtained using 45 and 55 °C reaction temperature. This could be because the catalytic phases of glycerol-enriched CaO were not activated at this temperature conditions, and the activation energy was not sufficient at 45 and 55 °C temperature to

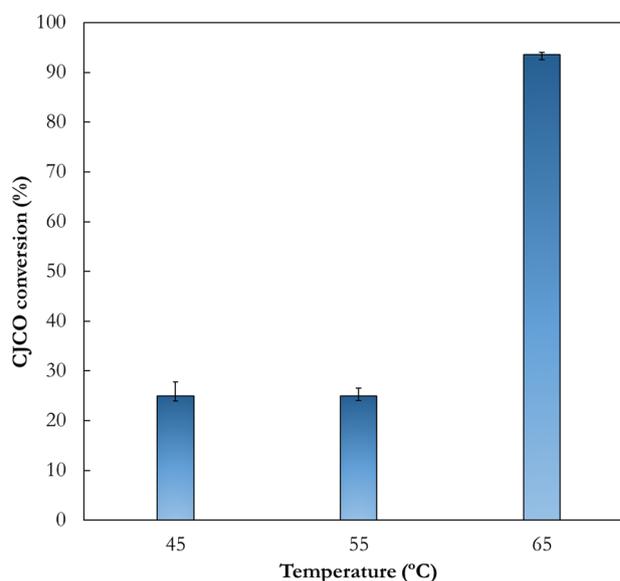


Fig. 3 Effect of temperature on CJCO conversion. Reaction time: 420 min, CaO amount: 15 wt%, glycerol dosage: 10 wt%, methanol-to-CJCO molar ratio: 9:1, stirring intensity: 350 rpm

carry out the reaction. Such behavior of experimental results was reported also by Kouzu et al. [34], wherein it was concluded that CaDg catalyst was active for the methanolysis only above 60 °C reaction temperature. Therefore, the reaction temperature of 65 °C was found to be adequate for the described methanolysis process.

3.2.3 Reaction Time Effect

The effect of reaction time (60, 180, 300, 420 and 540 min) on the CJCO conversion was further studied using constant reaction temperature of 65 °C, CaO amount of 15 wt%, glycerol dose of 10 wt% (of CaO weight) and 9:1 methanol-to-CJCO molar ratio. The experimental results for change in the oil conversion at different reaction time are shown in Fig. 4. The glycerol-enriched CaO assisted CJCO methanolysis reaction performed for 420 min enabled 93.5% oil conversion. However, further continuation of the reaction showed an insignificant variation in the oil conversion. Hence, all experiments in the present study were performed for 420 min reaction time.

3.2.4 Methanol-to-Oil Molar Ratio Effect

Stoichiometrically, a single molecule of TAGs reacts with three molecules of alcohol to produce three molecules of FAMES and a molecule of glycerol. However, it has been well understood by now that an excess amount of alcohol is utilized to promote the forward reaction that directs the transformation of TAGs to biodiesel [1]. The effect of mole ratio of methanol-to-CJCO, varied from 4.8 to 13.2:1, on the CJCO conversion is presented in Fig. 5. The experimental results indicated that the oil conversion augmented gradually with increasing amount of methanol. The highest oil conversion of 95.0% was achieved using methanol-to-CJCO molar ratio of 13.2:1. Increasing methanol-to-CJCO molar ratio

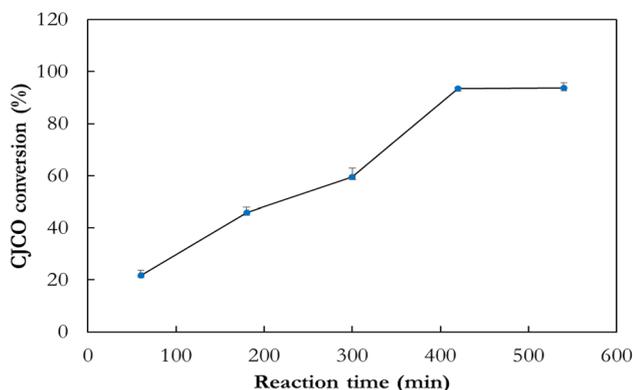


Fig. 4 Effect of reaction time on CJCO conversion. Reaction temperature: 65 °C, CaO amount: 15 wt%, glycerol dosage: 10 wt%, methanol-to-CJCO molar ratio: 9:1, stirring intensity: 350 rpm

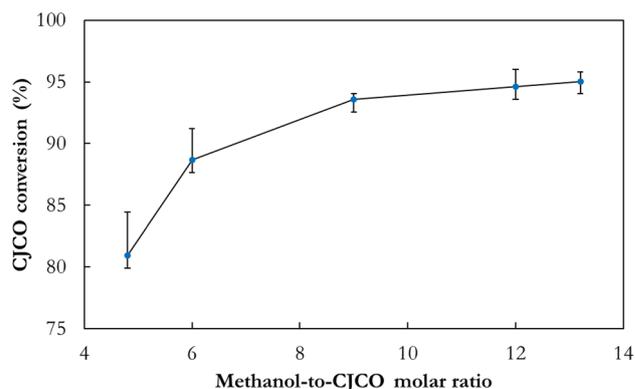


Fig. 5 Effect of methanol-to-CJCO molar ratio on CJCO conversion. Reaction temperature: 65 °C, time: 420 min, CaO amount: 15 wt%, glycerol dosage: 10 wt%, stirring intensity: 350 rpm

from 4.8 to 9:1 resulted in the elevation of oil conversion from 80.9 to 93.5%. However, further increasing in methanol-to-CJCO molar ratio resulted in slight improvement in the oil conversion. Increasing the methanol-to-oil molar ratio from 9 to 12:1 resulted in the rise of oil conversion only by around 1.1%. Therefore, methanol-to-oil molar ratio of 9:1 was considered adequate for the further investigations considering the amount of methanol has been used to obtain a reasonable value of CJCO conversion.

3.2.5 Calcium Oxide Amount Effect

The effect of five different CaO amount on the methanolysis reaction was further studied using constant glycerol dosage of 10 wt% (of CaO amount), temperature of 65 °C, time of 420 min and 9:1 methanol-to-CJCO molar ratio. The effect of CaO amount, ranging between 10.8 and 19.2 wt%, on the CJCO conversion is presented in Fig. 6. The experimental results indicated that increasing CaO amount from 10.8 to

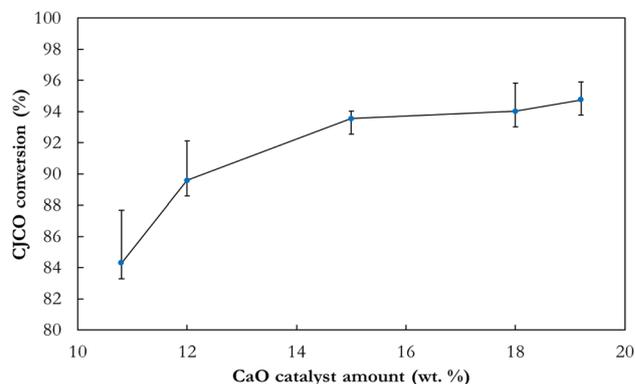


Fig. 6 Effect of CaO amount on CJCO conversion. Reaction temperature: 65 °C, time: 420 min, glycerol dosage: 10 wt%, methanol-to-CJCO molar ratio: 9:1, stirring intensity: 350 rpm

15.0 wt% resulted in the rise of oil conversion from 84.3 to 93.5%. However, an insignificant improvement in the oil conversion was observed when CaO amount was further increased. This scenario was occurred due to increasing in the viscosity of the reaction mixture that caused a stagnation in the advancement of the methanolysis process. It has been previously reported that the by-production of glycerol limited the FAMES yield to around 95% because of a reverse transformation of CaDg catalyst [34]. The experimental findings concluded that the oil conversion and biodiesel yield of 93.5 and 76.3%, respectively, was obtained when the methanolysis reaction was performed at 65 °C for 420 min using glycerol dosage of 10 wt% (of CaO amount), CaO amount of 15 wt% and 9:1 methanol-to-oil molar ratio. It is important to note that a high amount of catalyst was required for the present study, which could be due to the use of crude lipid feedstock containing very high amount of FFAs (24.75 mg KOH g⁻¹). The acid value of oil was 24.75 mg KOH g⁻¹, which subsequently dropped to 0.18 mg KOH g⁻¹ after its transformation to biodiesel. It is important to note that the water-washing step of biodiesel phase was applied. The acid value of biodiesel followed the specifications set by the EN 14214 and ASTM D6751-08 official methods, which allowed the maximum acid value of biodiesel of 0.5 mg KOH g⁻¹ [35].

3.3 Catalyst Characterization

The XRD patterns for CaO (MC) and glycerol-enriched CaO (GMC) are presented in Fig. 7. The diffraction peaks at 2θ of 32°, 37°, 54°, 64° and 67° were attributed to the CaO species. In the case of CaO, the absence of characteristic peaks for calcium carbonate (CaCO₃) at 2θ of 29.4° as well as for calcium hydroxide (Ca(OH)₂) at 2θ of 18°, 34°, 47.2° and 50.8° confirmed that the calcination process of

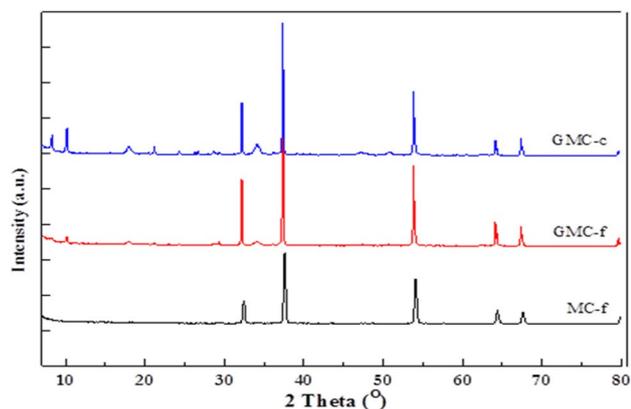


Fig. 7 XRD patterns for CaO and glycerol-enriched CaO. *MC-f* mussel shells derived CaO-fresh, *GMC-f* glycerol-enriched CaO-fresh, *GMC-c* glycerol-enriched CaO-collected

M. galloprovincialis shells at 800 °C resulted in the formation of only CaO species. The calcination resulted in the decomposition of both CaCO₃ and (Ca(OH)₂). The characteristic peaks at 2θ of 8.2°, 10.2°, 24.4°, 26.6°, 34.4°, and 36.2° in the diffractogram confirmed the formation of the glycerol-enriched CaO species (GMC-f). The characteristic peaks for GMC are coincident with the previously reported values [28]. The XRD pattern for the collected GMC catalyst (GMC-c) was also obtained and its characteristics were compared with that of the fresh catalysts. The intensity of diffraction peaks at 2θ of 8.2°, 10.2°, 24.4°, 26.6°, 34.4° and 36.2° increased that indicated the further interaction between the untransformed CaO and glycerol that is produced during the methanolysis reaction. It is worth noting that the amount of glycerol used for the CaO–glycerol complex synthesis was below the stoichiometric value (see Sect. 3.2.1). The consistent generation of CaO–glycerol complex during the methanolysis reaction was anticipated to promote the activity of GMC catalyst.

The TGA profiles for the synthesized MC and GMC are shown in Fig. 8a, b, respectively. In the case of MC, a weight loss of 3.1% was observed after heating the sample from 25 to 800 °C. The two minor weight loss found at 100 °C, and between 325 and 375 °C could be due the removal of the physisorbed moisture and decomposition/oxidation of organic components, respectively. In the case of fresh GMC, a total weight loss of 17.8% was obtained. The high weight loss indicated the formation of the CaO–glycerol complex. A well-defined weight loss takes place between 150 and 450 °C, which corresponds to the decomposition of glyceroxide ions to give calcite. The final weight loss registered between 600 and 700 °C attributed to the decarbonation process to give CaO. The obtained pattern of weight loss for GMC was in a good agreement with those reported by León Reina et al. [18] and Reyero et al. [28]. Above 700 °C, GMC seemed to be converted into CaO, because of the flat TGA line. The TGA profiles of the collected GMC is shown in Fig. 8c. The weight loss in the case of the collected GMC increased from 17.8 to 25.9%. The increase in the weight loss could be correlated to the occurring reaction between untransformed CaO and glycerol producing during the methanolysis reaction.

3.4 Statistical Analysis

The statistical analysis of glycerol-enriched CaO assisted methanolysis of CJCO was performed considering methanol-to-CJCO molar ratio and CaO amount as investigating factors, with all experiments keeping fixed reaction temperature of 65 °C, glycerol dosage of 10 wt% (of CaO wt.) and time of 420 min. The reaction temperature was not included in the experimental design because glycerol-enriched CaO catalyst was activated only at 65 °C temperature, and

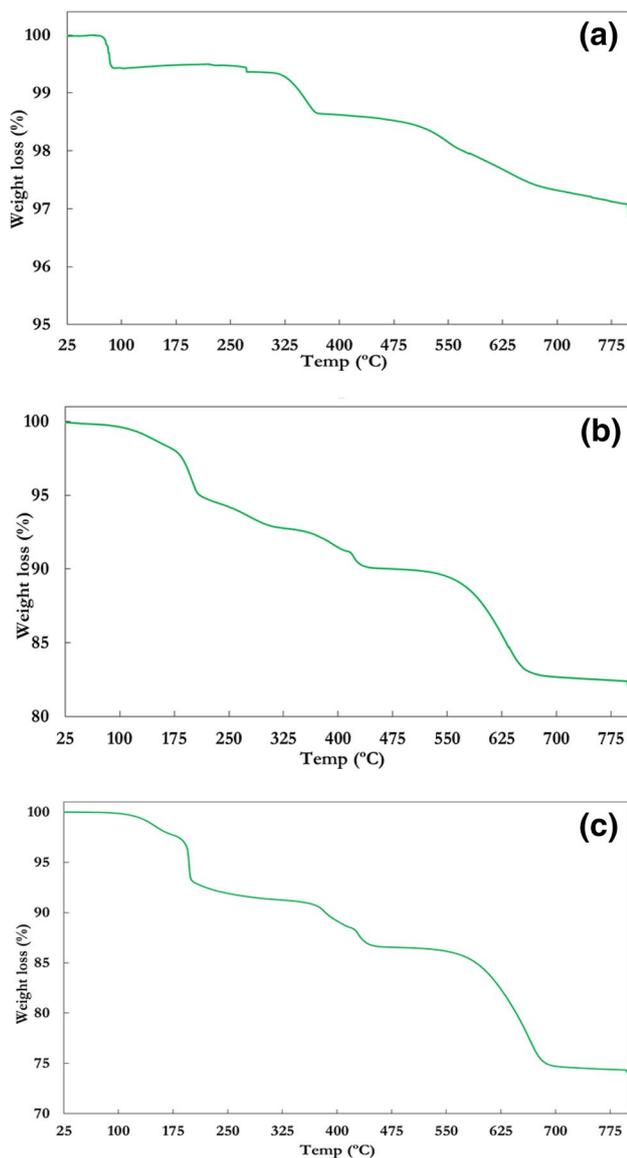


Fig. 8 Thermal analysis for CaO and glycerol-enriched CaO. **a** Muschel shells derived CaO-fresh, **b** glycerol-enriched CaO-fresh, **c** glycerol-enriched CaO-collected

displayed insignificant activity at 45 and 55 °C to assist the methanolysis process (Fig. 3). The water condenser attached to the reactor enabled the refluxing of methanol into the reactor when the methanolysis reaction was performed at 65 °C. However, increasing reaction temperature to 75 °C resulted in the evaporation of methanol despite having the water cooling condenser, and therefore, in incompleteness of the methanolysis process. The reaction time was also not included in the statistical design because low reaction time resulted in too low CJCO conversion, while, high reaction time showed an insignificant improvement in the CJCO conversion (Fig. 4). The real factors, the coded factors and the experimental CJCO conversion and FAMES yields for the

described methanolysis reaction are summarized in Table 1. The value of the oil conversion is higher than the yield of biodiesel because diacylglycerols and monoacylglycerols are available in the reaction medium through the transesterification route, while, the FFAs co-produced water through the esterification pathway.

3.4.1 Linear Stage

The linear stage and center points of the experimental design were utilized to investigate the interaction within the reaction variables, and its influence on the glycerol-enriched CaO assisted methanolysis process. The results of the statistical analysis are presented in Table 2. The evaluated parameters showed that the influence of methanol-to-CJCO molar ratio and CaO amount was higher than the confidence interval, and therefore, both parameters significantly affected the described methanolysis process. The natural and coded values of the experimental parameters were utilized for the setting the linear statistical and industrial mathematical regression models, respectively, for the described methanolysis process. The linear statistical (superscript ‘S’) and industrial (superscript ‘I’) model for the CJCO conversion, under the investigated range of experimental conditions, are presented in Eqs. 5 and 6, respectively. Whereas, the linear statistical (superscript ‘S’) and industrial (superscript ‘I’) model for the FAMES yield are presented in Eqs. 7 and 8, respectively.

$$X_{\text{CJCO}} = 91.80 + 3.39X_M^S + 2.76X_C^S - 1.87X_{MC}^S \quad (5)$$

$$X_{\text{CJCO}} = 40.42 + 4.24X_M^I + 2.79X_C^I - 0.20X_{MC}^I \quad (6)$$

$$Y_{\text{FAMES}} = 76.0 + 1.68X_M^S + 2.82X_C^S - 2.15X_{MC}^S \quad (7)$$

$$Y_{\text{FAMES}} = 24.55 + 4.15X_M^I + 3.10X_C^I - 0.24X_{MC}^I \quad (8)$$

3.4.2 Non-linear Stage

The results of the regression analysis, presented in Table 2, showed that the curvature had a positive influence on the described methanolysis process under the investigated experimental range. In the case of CJCO conversion, the non-linear stage of the experimental design was also taken into consideration because the curvature was found to be higher than the confidence curvature interval. The present analysis involves all the independent variables and their corresponding interactions. In the case of FAMES yield, the confidence curvature interval is higher than the curvature, and therefore, the curvature has no significance and is not necessary to obtain a quadratic model for predicting the variation in biodiesel yield. The response surface statistical (superscript ‘S’) and industrial quadratic (superscript ‘I’) mathematical model for the glycerol-enriched

Table 2 Results for the statistical analysis of the experimental design

Parameters	Response ^a	Response ^b
Main influence and interactions	$\bar{Y} = 91.8$ $I_M = 6.79$ $I_C = 5.52$ $I_{MC} = -3.74$	$\bar{Y} = 76.0$ $I_M = 3.36$ $I_C = 5.64$ $I_{MC} = -4.31$
Significance test: <i>c</i> confidence level: 95%		
Mean response (only center points)	93.1	75.8
Standard deviation	$t = 3.18$; $s = 0.52$	$t = 3.18$; $s = 0.45$
Confidence interval	± 0.83	± 0.71
Significant variables	M, C, MC	M, C, MC
Significance of curvature		
Curvature	1.31	0.20
Confidence curvature interval	1.18	1.02
Significance	Yes	No

M Methanol-to-oil molar ratio, *C* CaO amount, \bar{Y} mean response, *s* standard deviation, *t* Student's *t*

^aResponse for oil conversion

^bResponse for biodiesel yield

CaO assisted CJCO methanolysis process, under the studied range of experimental conditions, are expressed in Eqs. 9 and 10, respectively.

$$X_{\text{CJCO}} = 93.12 + 4.19X_M^S + 3.23X_C^S - 1.80X_{M^2}^S - 1.87X_{MC}^S - 1.03X_{C^2}^S \quad (9)$$

$$X_{\text{CJCO}} = -5.39 + 8.13X_M^I + 6.32X_C^I - 0.20X_{M^2}^I - 0.20X_{MC}^I - 0.11X_{C^2}^I \quad (10)$$

The statistical quadratic regression expressions were applied to achieve the response surface graphical representation for CJCO conversion and FAMEs yield. A three-dimensional surface plot of the predicted CJCO conversion and FAMEs yield with varying methanol-to-CJCO molar ratio and CaO amount is presented in Fig. 9a, b, respectively. Within the studied experimental range, the oil conversion augmented with the increase in methanol-to-CJCO molar ratio and CaO amount that indicated a possible interaction between methanol and glycerol-enriched CaO catalyst. The presented regression analysis provided an appreciable correlation between the predicted values and experimental findings, which validated the statistical quadratic mathematical model to be appropriate for describing the glycerol-enriched CaO assisted methanolysis process of CJCO within the studied range of reaction conditions. The graphical representation for the comparison between predicted values and experimental results for both CJCO conversion and FAMEs yield is shown in Fig. 10a, b, respectively.

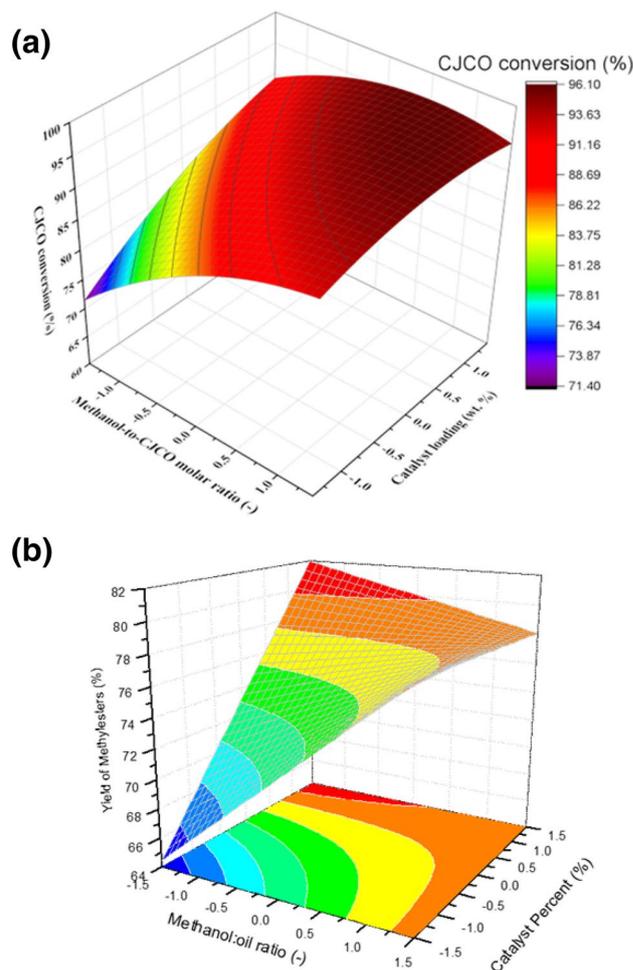


Fig. 9 Response surface 3D plot indicating the influence of methanol-to-oil molar ratio and catalyst amount on **a** CJCO conversion and **b** FAMEs yield. Temperature: 65 °C, time: 420 min, glycerol dose: 10 wt% (of CaO amount), stirring intensity: 350 rpm

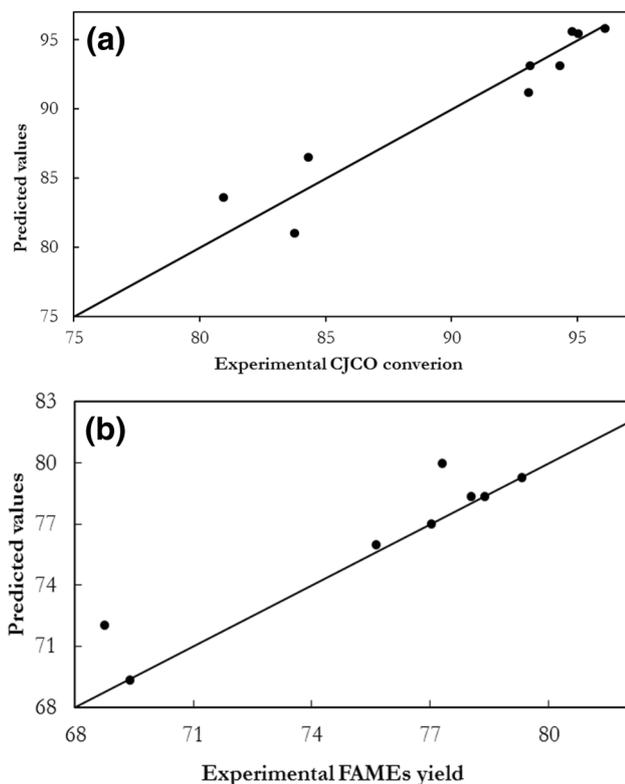


Fig. 10 Parity plot between predicted and experimental values for **a** CJCO conversion and **b** FAMES yield. Line corresponds to zero error between the experimental data and predicted values

4 Conclusion

This research article addresses high catalytic activity of glycerol-enriched calcium oxide for biodiesel production from crude *J. curcas* oil containing high FFAs amount. *M. galloprovincialis* (mussel) shells, which could be waste from fishing industry, has been utilized for the synthesis of CaO material. Both experimental as well as regression investigations were performed to better understand the effects of different parameters on the oil conversion and biodiesel yield. The experimental investigation suggests that temperature had significant impact on the glycerol-enriched CaO activation, and catalyzed the methanolysis reaction at 65 °C temperature. The catalytic performance of CaO was enhanced by 2.88 times after its interaction with 10 wt% of glycerol. The acid value of crude *J. curcas* oil was 24.75 mg KOH g⁻¹, which dropped by 49 times after the methanolysis reaction catalyzed by glycerol-enriched CaO was performed using methanol-to-CJCO molar ratio of 9:1 and 15 wt% CaO amount. The regression analysis suggested that both mole ratio of methanol-to-oil and CaO amount had a significant impact on the methanolysis process under the studied range of experimental conditions. A waste from fishing industry can be satisfactorily used for a straight-forward

synthesis of CaO, and the catalytic performance of latter can be significantly enhanced via glycerol treatment. The catalytic performance of CaO after glycerol-enrichment for biodiesel production has been, so far, seldomly researched in comparison to other solid catalysts, and the additional number of studies could be an asset in understanding its true potential for biodiesel production from a variety of lipid biomass. This in return is expected to help the fraternity in finding a new industrial-scale and cost-effective heterogeneous catalyst for biodiesel production from crude lipid feedstocks.

Acknowledgements The authors would like to express their gratitude to the Norwegian University of Life Sciences (Project No. 1301051406), Universidad Complutense de Madrid, and NILS mobility grants (009-ABEL-CM-2013) for their financial support. The authors extend their gratitude to Prof. Dr. Andrzej I. Stankiewicz for allowing the material characterization at the Delft University of Technology.

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