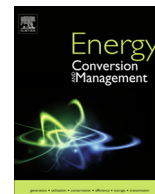




Contents lists available at ScienceDirect

## Energy Conversion and Management

journal homepage: [www.elsevier.com/locate/enconman](http://www.elsevier.com/locate/enconman)

# Modeling chemical kinetics of avocado oil ethanolysis catalyzed by solid glycerol-enriched calcium oxide

M.R. Avhad<sup>a,\*</sup>, M. Sánchez<sup>b</sup>, A. Bouaid<sup>b</sup>, M. Martínez<sup>b</sup>, J. Aracil<sup>b</sup>, J.M. Marchetti<sup>a,\*</sup>

<sup>a</sup> Department of Mathematical Science and Technology, Norwegian University of Life Sciences, Drøbakveien 31, 1432 Ås, Norway

<sup>b</sup> Chemical Engineering Department, Faculty of Chemistry, Complutense University, 28040 Madrid, Spain

## ARTICLE INFO

## Article history:

Received 7 June 2016

Received in revised form 8 July 2016

Accepted 23 July 2016

Available online xxxx

## Keywords:

Biodiesel production

Calcium oxide

Glycerol activation

Avocado oil

Ethanolysis

Kinetics

## ABSTRACT

The catalytic activity of glycerol-enriched calcium oxide for the alcoholysis reaction between avocado oil and ethanol was investigated. The calcium oxide was derived from *Mytilus Galloprovincialis* shells. This study systematically examined the influence of temperature, ethanol-to-oil molar ratio, and the catalyst amount on the variation in the concentration of triacylglycerols and biodiesel with reaction time. The interaction between the reaction variables (ethanol-to-oil molar ratio and catalyst amount), their influence on the ethanolysis process, and the optimum variables affecting the process were determined through the response surface methodology. A previously developed mathematical model was applied for the current ethanolysis process, and the model parameters were determined. The ethanolysis reaction occurred between the surface chemisorbed ethoxide ions and oil molecules in the liquid phase, while, the overall process was controlled by the ethanol-adsorption step. The physico-chemical properties of biodiesel, produced using potassium methoxide catalyst, were additionally measured.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Biodiesel, comprising fatty acid alkyl esters (FAAEs), is considered as a viable alternative or additive to current petroleum-derived diesel due to its environmental benefits, such as negligible toxicity, biodegradability, and renewability [1]. According to the American Society for Testing and Materials (ASTM), biodiesel is referred as the mono-alkyl esters derived from lipid feedstocks, such as vegetable oils and animal fats [2]. A well-known and extensively applied methodology for biodiesel production is the catalyst-assisted alcoholysis process, which is also known as the transesterification reaction of triacylglycerol (TAGs) and the esterification of free fatty acid (FFA). Since the last few years, heterogeneously catalyzed alcoholysis reactions are preferred over the homogeneous process. This is because, the utilization of heterogeneous catalysts allows an easy recovery of the materials which might be re-utilized, eliminates the neutralization process, simplifies the purifications stages, and could enable the continuous operation of the process; which in return would improve the yield and the purity of biodiesel as well as glycerol [3,4]. However, the use of heterogeneous catalysts for biodiesel production have not been yet implemented on an industrial scale. The major challenges

associated with the utilization of heterogeneous catalysts includes: (i) restricted catalytic active sites in comparison to the homogeneous counterparts, (ii) generally need of severe reactions conditions, (iii) sometimes tri-phasic reaction system (liquid-liquid-solid) resulting in the mass transfer limitations, (iv) expensive and time-consuming material synthesis procedure, and (v) catalyst poisoning due to the surrounding atmosphere. In this regards, consistent scientific efforts are involved in developing not only an active and stable but also a low-cost heterogeneous catalyst for biodiesel production.

The recent literature demonstrated that calcium oxide (CaO) catalyst has been widely applied for the alcoholysis reactions, because of its high basicity, low solubility in short-chain alcohols, low cost, and is easy to handle [5–7]. In addition, the utilization of CaO catalyst for biodiesel production could be advantageous because the material can be generated from abundantly available natural and waste sources [8–10]. The CaO-based catalyst have been utilized in several forms, including neat [11–13], mixed oxides [14–17], supported [18–22], doped [23,24], amongst others [25,26]. Besides the above mentioned CaO-based catalysts, the catalytic activity of glycerol-CaO complex, described as glycerol-enriched CaO or calcium diglyceroxide (CaDg), for the alcoholysis reaction have been also investigated [27–31]. León-Reina et al. [32] described glycerol-enriched CaO as a set of molecular calcium tetramers interlinked by H-bonds; and reported its superior catalytic activity when compared with CaO catalyst. The superior activity

\* Corresponding authors.

E-mail addresses: [avhad.mangesh@gmail.com](mailto:avhad.mangesh@gmail.com) (M.R. Avhad), [jorge.mario.marchetti@nmbu.no](mailto:jorge.mario.marchetti@nmbu.no) (J.M. Marchetti).

of CaDg catalyst was due to the availability of basic oxygen anion as a consequence of interruption of the crystal structure at the surface which can abstract proton from OH group of methanol leading towards the formation of surface methoxide ion [22]. The CaDg catalyst was characterized as a chemically stable heterogeneous catalyst, weakly basic in nature, and not prone for deactivation due to the hydration/carbonation reaction when exposed to the surrounding air [33,34]. Because CaO catalyst experiences material transformation due to its interaction with glycerol, co-producing during the transesterification reaction, Kouzu et al. [33] and López Granados et al. [35] recommended to transform CaO to CaDg compound prior to its application for biodiesel production.

In the present study, glycerol-enriched CaO catalyst was applied for the alcoholysis reaction between avocado oil and ethanol. The CaO was derived from mussel shells (*Mytilus Galloprovincialis*), which is a waste generated from the fish industry. It is generally believed that the production of fatty acid ethyl esters (FAEEs) could be valuable from an ecological standpoint because ethanol can be synthesized through the fermentation process of a reasonable cost and abundantly available lignocellulosic biomass [36,37]. This study, therefore, addressed the utilization of only renewable resources for biodiesel production; thereby attaining total independence from petroleum-based materials and following the principles of green chemistry. Moreover, the application of ethanol for biodiesel production offers several advantages, including superior miscibility with plant oils, low toxicity, higher cetane number, lower cloud point, improved pour point, and lower nitrogen oxides as well as carbon monoxide emissions [38,39]. The synthesis of FAEEs is of high relevance because it can also be used as alcohol markers for the retrospective drug analysis in forensic cases [40,41]. Furthermore, FAEEs can be useful internal standard for the determination of fatty acid methyl esters in food and other samples [42]. Due to the previous mentioned advantages, the number of recent studies focused on the ethanolysis process of the lipid feedstocks have augmented [38,39,43–50]. The present research uses avocado oil as the lipid feedstock for the ethanolysis process. The energy analysis presented by Takahashi and Ortega [51] concluded that avocado can be used as a raw material for biodiesel production because oil can be generated from the pulp, while, ethanol can be extracted from the pit. The renewability index of avocado was reported to be higher than the other oleaginous crops used for biodiesel production, such as rapeseed, sunflower, soybean, and cotton [51]. The use of avocado as a raw material for biodiesel production could be possible because, in its oil content, avocado fruit is exceeded only by the fruits of the palm and olive trees [52]. Though literature on the alcoholysis of avocado oil are available [53,54], no studies on glycerol-enriched CaO catalyst assisted avocado oil ethanolysis and its kinetic modeling have been so far reported.

This study systematically investigated the influence of temperature, the catalyst amount, and ethanol-to-oil ratio on the described ethanolysis process. The interactions within the reaction variables, their influence on the described ethanolysis reaction, and the optimum parameters affecting the process were determined by means of the response surface methodology (RSM). A mathematical model predicting the change in the TAGs and FAEEs concentration over the applied range of the experimental conditions is also presented. Furthermore, the physico-chemical properties of FAEEs, produced using a homogeneous catalyst, were measured and compared with the ASTM D6751 and EN 14214 official standards for biodiesel.

## 2. Experimental section

### 2.1. Materials

Avocado oil was supplied by Jedwards International, Inc. (Braintree, USA). Its fatty acid composition and properties,

provided by the suppliers, are listed in the Supplementary Table S1. Ethanol (Cor Quimica, Spain), glycerol (Sigma-Aldrich), K-methylate (methanol/potassium methoxide: 68/32 wt.%, BASF, Germany), n-octyl octanoate (Sigma-Aldrich), and carbon disulfide (Panreac) with purity higher than 99% were utilized as received. The waste mussel shells needed for the synthesis of CaO were collected from the local fish market in Madrid, Spain.

### 2.2. Catalyst preparation

The detailed procedure for the synthesis of CaO material from mussel shells has been documented in the previous work [55]. The results for the characterization of CaO material, carried out earlier by means of X-ray diffraction, specific surface area analysis, induced coupled plasma atomic emission spectroscopy, and transmission electron microscopy, were published elsewhere [56]. For the synthesis of glycerol-enriched CaO catalyst, measured amount of CaO and glycerol (10% with respect to (w.r.t.) catalyst weight) were initially added into an airtight three-neck curved bottom glass reactor of 250 cm<sup>3</sup> volume capacity. Subsequently, an appropriate volume of avocado oil was poured into the reactor and the mixture was vigorously stirred at 60 °C for 60 min under atmospheric pressure. The selection of glycerol dose and the mixing temperature was based on the previous reports [55,57]. The CaO material transformation was conducted in the presence of avocado oil, and not ethanol, so as to not only produce merely glycerol-enriched CaO catalyst but also to eliminate even a minor possibility of the formation of the calcium ethoxide catalytic species [55,58]. In addition, performing the material transformation in the presence of avocado oil would prevent poisoning of CaO occurring due to the surrounding air inside the reactor.

### 2.3. Reaction and analysis

The transesterification reaction was performed in a three-neck curved bottom glass reactor of 250 cm<sup>3</sup> volume capacity. The middle neck of the glass reactor was used to insert a mechanical stirrer equipped with an impeller of 6.0 cm diameter which was placed centrally close to the bottom of the reactor. Both the diameter and the length of the glass reactor are 12.0 cm. The water condenser was attached to one of the side necks, while, a rubber cork was fitted to the other neck of the reactor through which the aliquots of the reaction mixture were periodically withdrawn using a glass syringe. The glass reactor was immersed in a thermostatically controlled water bath (Heto-Holten A/S, Denmark), the temperature of which was controlled by the PID controller with 1 °C precision. The speed of the mechanical stirrer was monitored by a motor (Eurostar Basic IKA). After the glycerol activation process of CaO, the reaction system was heated to the desired temperature. Once the system temperature reached the set point, an appropriate volume of ethanol was charged into the reactor using a conical flask; this was considered as the starting time of the ethanolysis reaction. The stirring intensity of 350 rpm was maintained for all experiments to overcome the mass transfer limitations [56]. The aliquots (approximately 1 ml) of the reaction mixture were withdrawn at a specific time intervals (1, 2.5, 5, 10, 20, 40, 60, and 120 min) to understand the progression of the reaction. The extracted samples were immediately applied to a rotavaporator, attached to a vacuum pump (10 mg Hg), set at 70 °C for 30 min to eliminate the residual ethanol. The catalyst and glycerol was separated through the centrifugation (1500 rpm for 15 min).

The potassium methoxide-catalyzed ethanolysis of avocado oil was carried out in a semi-batch 3 dm<sup>3</sup> capacity glass reactor, equipped with the mechanical stirrer, the water condenser, a distillation unit and a decantation valve. The avocado oil ethanolysis

Download English Version:

<https://daneshyari.com/en/article/7160103>

Download Persian Version:

<https://daneshyari.com/article/7160103>

[Daneshyari.com](https://daneshyari.com)