



# Renewable production of value-added jojobyl alcohols and biodiesel using a naturally-derived heterogeneous green catalyst



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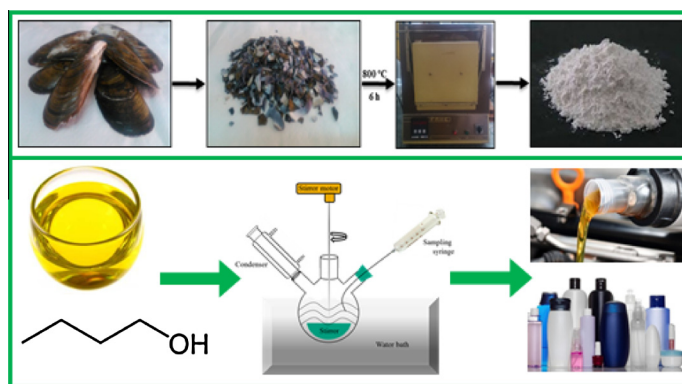
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## HIGHLIGHTS

- Green catalyst for the production of value-added alcohols and biodiesel.
- All raw materials could be obtained from the underutilized natural resources.
- Butanol-to-jojoba oil molar ratio had a major impact on the alcoholysis process.
- The surface reaction controlled the overall butanolysis process.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The present article addresses the generation of value-added jojobyl alcohols and biodiesel using the underutilized renewable natural resources. The butanolysis reaction of jojoba oil required for its transformation to jojobyl alcohols and fatty acid butyl esters was performed over mussel shells derived calcium oxide as a heterogeneous base catalyst. This study systematically investigated the influence of temperature, time, n-butanol concentration and catalyst loading on the butanolysis process. The results of the present study indicated that n-butanol concentration had a major impact on the reaction. The maximum jojoba oil conversion of 96.11% was registered after 1800 min of transesterification reaction performed at 85 °C using butanol-to-oil molar ratio of 10:1, 12 wt.% catalyst amount and 350 rpm stirring intensity. A mathematical model for its kinetics was developed based on a three-step mechanism equivalent to the Eley–Rideal one. It was concluded that the butanolysis reaction occurred between the surface chemisorbed butoxide ions and jojoba oil molecules in the liquid phase, whereas, the overall process was controlled by the surface reaction.

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## 1. Introduction

Plant biomass, the only current sustainable source of organic carbon, has been considered as the promising equivalent to

petroleum for the production of fuel and value-added chemicals. The establishment of plant biomass-based energy is anticipated to minimize the entire dependency on the utilization of fossil fuels [1]. Additionally, biomass feedstocks feature a closed carbon cycle in which the carbon dioxide released during the energy conversion is recaptured by the existing plants via photosynthesis during biomass regrowth. The “Roadmap for Biomass Technologies”, set by

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the U.S. Department of Energy, has predicted that by 2030, 20% of transportation fuel and 25% of chemicals would be produced from biomass [2]. The occurring dynamic transition of the global dependence on fossil fuels to renewable energy is understood not only for the effective management of environmental situations but also to augment the agriculture-based economy. However, the nature of biomass feedstock applied for the large-scale production of fuel and chemicals is an important aspect affecting the economics of the process [3]. Consistent scientific efforts are underway in finding a cost-effective and abundantly available non-edible oil-rich biomass. Jojoba oil is a light golden color fluid that differs profoundly from other seed oils because of the absence of glycerol molecules. Its chemical structure could be explained as a mixture of esters of straight long-chain fatty acids and fatty alcohols [4,5]. The available reports indicate that jojoba oil is not poisonous to human, but is poorly digestible and is not considered a part of human food chain; hence, is categorized as the non-edible oil [4]. The presence of 20–44 carbon atoms make it good combustion substance and is utilized as lubricant in high-speed machinery in the automotive industry [6,7]. The studies reported by Al-Widyan and Al-Muhtaseb [8] and Al-Hamamre and Rawajfeh [9] suggested that jojoba oil, having energy content higher than  $40 \text{ MJ kg}^{-1}$ , can possibly be used as direct fuel for the compression-ignition engines. However, the high kinematic viscosity of oil could cause several operational problems, such as poor atomization of the fuel spray, carbon deposits due to incomplete combustion, and gelling of lubricating oil. Since the last few years, several methodologies have emerged as a possible way to lower the kinematic viscosity of oil, out of which the alcoholysis procedure is well known and extensively applied. The alcoholysis process would enable the transformation of jojoba oil to fatty acid alkyl esters (FAAE) and jobobyl alcohol (11-eicosenol, 13-docosenol and 15-tetracosenol). The derivatives of jojoba oil, such as jobobyl alcohols finds their high relevance in the pharmaceuticals, cosmetics and coating industries, while, the fatty acid alkyl esters (biodiesel) could be utilized as biofuel in the automotive industries [6,7]. After the synthesis of jobobyl alcohols and biodiesel, the seed residue, having heating value higher than  $13 \text{ MJ kg}^{-1}$ , could be used for direct combustion or as a substrate for the biogasification process [8,9]. Therefore, the environmental and economic benefits gained through the appropriate utilization of jobobyl alcohols, FAAE and jojoba leftover could lead to a successful jojoba-based biorefinery and encourage the expansion of agriculture of jojoba plant.

In the present study, the alcoholysis reactions were performed between jojoba oil and n-butanol, the rate of which was accelerated using calcium oxide (CaO) catalyst. The utilization of n-butanol for the alcoholysis reaction could be advantageous because it can be synthesized through the Acetone–Butanol–Ethanol fermentation process using the reasonable cost and easily available lignocellulosic materials, such as wood forestry residues, corn stover, wheat and barley straw [10,11]. In comparison to fatty acid methyl esters (FAME), the synthesis of fatty acid butyl esters (FABE) is beneficial as the extra carbon atoms introduced by the butanol molecule will improve the cetane number, oxidation stability, cold filter plugging point, cloud point, pour point and heating value of biodiesel [12]. However, the kinematic viscosity of FABE is higher than that of FAME. The production of FABE could be of considerable relevance because, unlike methanol, butanol is renewable and is safe to handle. Additionally, the CaO catalyst was derived from mussel shells (*Mytilus Galloprovincialis*), which is a waste generated from the fish industry. Therefore, all the raw materials utilized for the production of fuel and chemicals are available from natural resources; following the principles of green chemistry. To the best of our knowledge, no studies on the CaO-catalyzed jojoba oil butanolysis process and its kinetic modeling have been so far reported. The influence of temperature,

catalyst amount, n-butanol concentration and time on the CaO-catalyzed butanolysis process of jojoba oil was systematically investigated. The interaction between the reaction variables and the optimal conditions affecting the process were determined by means of the response surface methodology (RSM). Furthermore, the Eley–Rideal approach was used to select a mathematical model capable of describing the kinetics of the CaO-catalyzed butanolysis process of jojoba oil over the applied range of experimental conditions.

## 2. Experimental section

### 2.1. Materials

Jojoba oil was supplied by Jojoba Israel (Kibbutz Hatzerim, Israel). Its physico-chemical properties were determined in accordance to the AOCS official methods, and published elsewhere [13]. The n-butanol (Cor Quimica, Spain), n-octyl octanoate (Sigma–Aldrich) and carbon disulphide (Panreac) were utilized as received. The waste mussel shells required for the synthesis of CaO catalyst were obtained from the local fish market in Madrid, Spain.

### 2.2. Catalyst preparation

The mussel shells were carefully washed under the flow of tap water to remove the adsorbed superfluous materials. The cleaned shells were dried in an oven, set at  $100 \text{ }^\circ\text{C}$ , for 60 min. The shells were subsequently pulverized, placed in a silica crucible and calcined in a ceramic muffle heating furnace, set at  $800 \text{ }^\circ\text{C}$ , for 360 min. The selection of the calcination temperature was based on the former investigation performed in the same laboratory [14]. This is because the appliance of too low temperatures could result in the incomplete formation of the oxide species, whereas, too high temperatures could direct the undesired material transformation and reduction in the basic strength of the catalyst. The heating furnace was shut down after 360 min. of the calcination process and allowed to cool. The obtained white colored solid was removed from the furnace, preserved in an airtight container to avoid poisoning due to ambient air while handling or weighing, and utilized instantaneously to assist the butanolysis reaction. The results obtained for the characterization of the catalytic material by means of X-ray diffraction, specific surface area analysis, induced coupled plasma atomic emission spectroscopy and transmission electron microscopy have been reported elsewhere [14].

### 2.3. Reaction and analysis

The CaO-catalyzed butanolysis reaction between jojoba oil and n-butanol was conducted in a three-neck curved bottom glass reactor of  $250 \text{ cm}^3$  volume capacity. Both the diameter and the length of the glass reactor is equivalent to 12.0 cm. The middle neck of the reactor was used to insert the mechanical stirrer equipped with an impeller of 6.0 cm diameter placed centrally close to the bottom. One of the side necks was fitted with the water cooling condenser; while the other neck, was fitted with a rubber cork through which the aliquots of the reaction mixture were periodically withdrawn using a glass syringe. The glass reactor was immersed into a thermostatically controlled water bath (Heto-Holten A/S, Denmark), the temperature of which was controlled by a PID controller with  $1 \text{ }^\circ\text{C}$  precision. The speed of the mechanical stirrer was monitored by a motor (Eurostar Basic IKA).

Initially, the measured quantities of jojoba oil and CaO catalyst were added to the glass reactor and heated to the desired temperature. Once the temperature reached the set point, an appropriate

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