



Water-free process for eco-friendly purification of biodiesel obtained using a heterogeneous Ca-based catalyst



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ABSTRACT

The technologies conventionally used for biodiesel purification imply high consumptions of both energy and water. In the present work, biodiesel was produced by transesterification using a very active calcium glyceroxide catalyst and purified using water-free processes. The study focused on soaps removal that was the main product impurity. The best results were obtained when the crude biodiesel (methyl ester content of 90.2–91.2 wt.% and calcium content of 372–393 ppm) was pretreated with Na_2CO_3 and afterward treated by an ion-exchange resin (6 wt.%) or a ceramic membrane (0.1 μm). The purification was effective using biodiesel produced from both soybean oil and waste frying oil and the quality of the product agreed with the one obtained using the conventional water washing process. The effectiveness of the treatment could be explained by calcium elimination through precipitation as CaCO_3 during pretreatment and sodium soaps removal by absorption into the resin or filtration by the ceramic membrane, according to the micelle formation mechanism. The studied process presents a high potential to remove calcium soaps from biodiesel.

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1. Introduction

Biodiesel is a renewable fuel (produced from biomass), that can replace petro-diesel with several advantages. The more relevant are its high biodegradability, and the lower emissions that result from the combustion, namely regarding CO_2 , CO, particulate matter, unburned hydrocarbons and sulfur [1]. Being a petro-diesel replacer/additive, biodiesel operates in diesel engines such as those used in private and commercial vehicles as well as the ones used in farm equipment [2]. However, because biodiesel is generally more expensive, due to the raw-materials and the processing costs, subsidies are required for commercialization outside of niche markets [3,4].

Raw material costs relate mostly to the vegetable food oils, used in more than 95% of the biodiesel production plants in the world [5]. Such difficulty could be surpassed, in part (according to the availability and considering also the use of blends to ensure compliance with quality specifications), using low cost feedstock such as waste cooking oils, animal fats and other fatty wastes derived from industrial activities, that can be converted into biodiesel [4,6].

Taking into account biodiesel processing costs, separation and purification of the final product are also extremely relevant. The conventional technologies used for biodiesel separation (gravitational settling and filtration) and purification (washing with water, acid or ether and use of adsorbents) are known for being inefficient

from an economic point of view, due to the high consumption of time and energy [7].

Focusing on biodiesel purification, water washing is generally conducted although some “dry washing” methods have been proposed [8–10]. Water washing is used mostly to remove impurities such as the remaining methanol and glycerol, as well as soaps and the remaining catalyst [11]. After water washing, biodiesel is dehydrated, generally by using vacuum flash processes, anhydrous salts (such as Na_2SO_4) or other water adsorbents. Water washing is the most used purification process due to the fact that the purified biodiesel usually satisfies the stringent quality standards imposed by EN 14214 or ASTM D6751 [2]. However, this process leads to the production of high amounts of wastewater, which results in significant economic and environmental impacts.

Aiming to develop more environment-friendly technologies, with fewer costs, research is being conducted to replace the water washing by water-free biodiesel purification processes that generally imply the use of synthetic adsorbents (e.g. magnesium silicate – Magnesol®) and ion-exchange resins (e.g. Purolite®) to eliminate the homogeneous catalysts and, in part, the fatty acid salts (soaps) and glycerol present in biodiesel after the reaction [12]. Such materials are however unable to remove all the methanol and glycerol, which should be removed as much as possible during the first separation stage (usually settling) to ensure that the product is in agreement with quality standards [12]. Ceramic membranes have high potential to be used in the separation processes of this nature (presence of soaps and alcohols) due to their excellent thermal, chemical and physical stability [8,13,14]. Therefore,

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the ceramic membranes might be effective for biodiesel purification, by removing glycerol from the FAME produced [11,14,15] or by retaining the un-reacted triglycerides [13] or soaps [8].

Aiming to reduce biodiesel impurities and also to improve glycerol quality, heterogeneous catalysts have been studied in more detail [16]. Calcium oxide derived catalysts are promising alternatives [17]. Granados et al. [18] showed that it was possible to produce a very active catalyst towards biodiesel production through transesterification, by using glycerol and CaO as precursors, sunflower oil as raw material and inert reaction conditions. Such catalyst could be reused and easily separated; however, calcium soaps were found to be present in biodiesel, which still required purification to fulfill the stringent biodiesel quality standards [17–19]. A process to produce biodiesel using such catalysts under ambient air conditions (aiming reduced costs) and using different raw materials is yet to be studied. In addition, the application of water-free processes for the removal of the calcium soaps would be an innovative and cleaner alternative aiming at more eco-friendly processes, which was not carefully evaluated.

The present work aims to contribute to the development of a cleaner integrated technology for biodiesel production. For that, an active calcium glyceroxide catalyst was prepared and used for biodiesel production in ambient air conditions and afterward the product purification was performed using water-free processes. The following specific objectives were established: (i) to produce biodiesel using a calcium-glyceroxide catalyst under ambient air conditions; (ii) to evaluate the efficiency of a resin and a ceramic membrane for biodiesel water-free purification, focusing on calcium soaps removal; (iii) to evaluate the influence of the raw material, by using both a virgin vegetable oil as well as waste oil; and, (iv) to assess the applicability of the selected method for biodiesel purification after a homogeneous transesterification process.

2. Materials and methods

2.1. Materials

The soybean oil was obtained commercially and used without any treatment. The oil presented an acid value of $0.60 \text{ mg KOH g}^{-1}$ and a water content of 539 ppm. The waste frying oil was obtained from a voluntary collection system (different domestic sources) implemented at *Faculdade de Engenharia, Universidade do Porto*. Waste frying oil was pretreated by vacuum filtration and presented, after pretreatment, an acid value of $0.77 \text{ mg KOH g}^{-1}$ and a water content of 652 ppm. The low acid value of this oil indicates a low degree of both oxidation and hydrolysis reactions that might be justified by the domestic source of the oil, as verified by Dias et al. [17].

The resin used was commercial Puralite® PD206, which, according to the supplier, functions both as a dehydrating media (desiccant) as well as an ion exchange polishing media.

A housing G1-1/6-Swageloc and two monochannel ceramic membranes with a pore diameter of 0.05 and 0.1 μm , respectively, were supplied by Atech Innovations GmbH. The ceramic membrane tube presented an outside diameter of 10 mm and a length of 250 mm, providing a filtration area of approximately 0.0048 m^2 for the entire membrane.

The most relevant reagents used during synthesis, purification and quality evaluation procedures were as follows: methanol 99.5% (analytical grade, Fischer Scientific), calcium carbonate (analytical grade, Merck), glycerol (reagent grade, Aldrich), sodium carbonate (analytical grade, Merck), sodium hydroxide powder 98% (Sigma-Aldrich, Reagent Grade), heptane (analytical grade, Merck), methyl heptadecanoate (analytical standard, FLUKA), nitric acid (analytical grade, Merck), calcium standard for AAS (TraceCERT®, 1000 mg/L Ca in nitric acid, FLUKA), sodium standard for AAS (TraceCERT®, 1000 mg/L Na in nitric acid, FLUKA) and CombiCoulomat frit Karl Fischer reagent for the coulometric water determination for cells with diaphragm (Merck).

2.2. Methods

2.2.1. Catalyst preparation

CaO was prepared in a tubular furnace, by calcination of 1.78 g of CaCO_3 at 1173 K, during 4 h under N_2 atmosphere. The resulting CaO was after inserted into a small flask with 15.00 g of methanol and 1.60 g of glycerol. The slurry was sonicated during 15 min, as indicated by Granados et al. [18], to obtain the catalyst.

2.2.2. Biodiesel production procedures

The solid catalyst was weighted and added at 0.4 wt.% (with respect to oil) to a three-necked glass batch reactor, equipped with a water cooled condenser and immersed in a temperature controlled water bath that already contained the methanol (at 14:1 methanol:oil molar ratio) at 333 K. The methanol and the catalyst were then stirred during 15 min, in air atmosphere, before adding the oil. Finally, 250.00 g of vegetable oil at 333 K were added to the reactor. The subsequent transesterification reaction was carried out at the same temperature, under atmospheric pressure, with vigorous magnetic stirring (stirring plate regulated to 1000 rpm), during 2 h. The separation/purification of the products was after performed as described in Section 2.2.3.

Biodiesel produced using the conventional NaOH homogeneous catalyst was prepared using the same reaction conditions and procedures described for the heterogeneous process. After the reaction, biodiesel and glycerol were separated by settling. Methanol was further recovered from each phase, using a rotary evaporator. When water washing purification was performed, it was conducted according to Dias et al. [5]. The dry purification process was performed according to Section 2.2.3.

2.2.3. Setup for dry purification processes

Biodiesel production and the different purification methodologies studied are summarized in Fig. 1.

Biodiesel purification using heterogeneous catalyst started in all cases by catalyst filtration (B), and was followed by glycerol separation by settling (C) and methanol recovery using a rotary evaporator. Further, two alternative processes were studied.

The first process considered using the resin and the membrane directly to purify the product, resulting in samples BDR-I and BDM-I, respectively; and the second one considered treating biodiesel according to Alba-Rubio et al. [19] and then using the resin, or the membrane or the water washing, to obtain samples BDR-II, BDM-II, and BDW-II, respectively. To identify the product obtained using both raw-materials, the acronym included also the letter S for soybean and W for waste frying oil (e.g. BDRS-II or BDRW-II).

In the second process, treatment included using methanol (biodiesel:methanol mass ratio of 2) containing an excess of anhydrous Na_2CO_3 (5% in respect to the biodiesel mass), at 338 K for 5 h under vigorous stirring (magnetic stirring plate regulated to 1200 rpm) (D), filtering to remove the calcium as calcium carbonate and the remaining Na_2CO_3 (E), and, finally, settling to separate methanol from biodiesel.

When using the ion-exchange resin, biodiesel was treated with either 6 wt.% or 50 wt.% of resin (with respect to biodiesel mass), under magnetic stirring (magnetic stirring plate regulated to 500 rpm), during 2 h, at room temperature.

A membrane separation system was assembled, being presented schematically in Fig. 2. Two ceramic membranes were used (as referred in Section 2.1). The crude biodiesel was poured into the feed vessel, forced to pass through the membrane tube using a peristaltic pump and recirculated at a controlled rate by adjusting, manually, the outlet valve. The following setup was considered: 250 mL in the feed vessel, recirculated at room temperature using a peristaltic pump (Aspen, Standard model) at 2.11 mL min^{-1} , in order to have a minor perturbation and maintain the inverse micelle size [8],

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