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

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Abstract

The technologies conventional 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 after 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 pre-treated with Na_2CO_3 and after 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 pre-treatment 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.

Keywords: Biodiesel purification; Calcium soap; Membrane, Resin.

1. Introduction

Biodiesel is as 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 specification), 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 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 absorbents) 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 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 absorbents. 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 (eg. magnesium silicate - magnesol®) and ion-exchange resins (eg. 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, that 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 separation processes of this nature (presence of soaps and alcohols) due to their excellent thermal, chemical and physical stability [8,13,14]. Therefore, 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, that 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 more eco-friendly processes and was not carefully evaluated.

The present work aims to contribute for 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 after 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 an homogeneous transesterification process.

2. Material 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 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 pre-treated by vacuum filtration and presented, after pre-treatment, an acid value of 0.77 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 PUROLITE®PD206, that, according to the supplier, functions both as a dehydrating media (desiccant) as well as an ion exchange polishing media.

An 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: 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®, 1000mg/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

2.2.1Catalyst 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.* [19], 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 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 2.2.3.

2.2.3. Setup for dry purification processes

Biodiesel production and the different purification methodologies studied are summarized in the 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 Granados et. al. [18] and then using the resin, or the membrane or the water washing, to obtain samples BDR-II, BDM-II, 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 (in 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 set-up 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], causing the cross-filtering by the ceramic membrane tube. The flux through the membrane was maintained at 26.4 L m^{-2} h^{-1}. The pump was stopped when the volumetric concentrated factor reached 3.

After performing the purification procedures, biodiesel samples were analyzed according to section 2.2.4.

Experiments were performed in duplicate and all the results are expressed as mean values; the relative percentage differences in all cases were less than 5% of the mean.

2.2.4. Biodiesel quality evaluation

Taking into account that a water-free purification process was studied, that the main objective was calcium soaps removal and that a pre-treatment was conducted to convert calcium soaps to sodium soaps, the following key quality parameters were determined in the products: (i) methyl ester content using gas chromatography (GC) according to EN14103 and as described by Dias *et al*. [17]; (ii) water content, by the coulometric Karl Fischer titration method (EN ISO 12937); and, (iii) calcium and sodium content, by atomic absorption spectrometry (SOLAAR UNICAM AA spectrometer).

For water content determination, a coulometric Karl Fischer titrator MKC-501 was used. For calcium and sodium determination, 1 g of biodiesel was dried in a hot plate at 623 K in a platinum crucible and then calcined in a furnace at 823 K for 30 min. The white ashes were treated with 5 mL of nitric acid and heated at 473 K until reduced to 200 µl. Then, 5 mL of nitric acid were added and the solution was transferred to a 50 mL volumetric flask, completed with distilled water. The calcium cathode lamp was used at 5 mA to determine calcium concentration, at a wavelength of 422.7 nm and with a slit width of 0.5 nm. The sodium cathode lamp was used at 5 mA to determine calcium concentration, at a wavelength of 589.0 nm and with a slit width of 0.2 nm.

3. Results and Discussion

The crude biodiesel (before purification), obtained from soybean oil, presented a methyl ester content of 91.2 wt.% and a calcium concentration of 393 ppm. The calcium present should be essentially in the form of calcium soap [18].

3.1. Direct soybean oil biodiesel purification using an ion exchange resin and a ceramic membrane

The biodiesel washing was not considered within the first purification route studied because it was previously shown that water and acid washing of biodiesel obtained using CaO cannot reduce the Ca content to < 5 ppm [18], contrary to what happens to alkaline metals from homogeneous catalysts.

Two resin concentrations were evaluated for purification, 6 wt.% and 50 wt.% (with respect to biodiesel mass, BDRS-I). Regarding calcium removal, it was found that both concentrations were ineffective since using 6 wt.% resin the calcium concentration in biodiesel was found to be 384 ppm, showing a small reduction of around 2 wt.% after treatment and did not change when resin concentration increased to 50 wt.%.

Regarding the use of the ceramic membranes (BDMS-I), biodiesel was filtered using 0.05 and 0.1 μm pore size membranes. Although the membrane with higher porosity (0.1 μm) presented better results, both were inefficient to remove all calcium from biodiesel, with calcium concentrations measured in the permeate of 270 ppm (30% reduction), and 305 ppm (22% reduction), respectively.

The results show that the water-free methods alone, under the conditions studied, although having a slight impact on catalyst removal, are not enough to purify the product as required. The results agree with the ones obtained by Granados et al. [18] where calcium removal was not effective when acid/ water washing was used, and with Wang et al [8], where the ceramic membrane was not very efficient to remove the calcium soap (raw biodiesel presented a different metal content compared to the present study).

3.2. Soybean oil biodiesel purification, after pre-treatment, using an ion exchange resin, a ceramic membrane and water washing

The effectiveness of the studied resin is reported by the supplier for the removal of the ionic and hydrophilic compounds from biodiesel; however, for the removal of the hydrophobic calcium soap it was ineffective, as demonstrated in section 3.1.

To increase the efficiency of the purification treatments, a pre-treatment was conducted to exchange calcium by sodium, since sodium soaps might be more easily removed using both, water/acid treatment, or water-free purification processes [8,18]. This happens because, for the same fatty acid, R, sodium soap will have the form of RNa^+; whereas calcium soap, due to the bivalency of calcium ions, will have the form of R_2Ca^{2+}; therefore, this kind of soap has a more prevalent non-polar end, being, consequently, less water soluble and therefore more prone to dissolve in biodiesel, which increases separation difficulty.

In agreement with the results retained from section 3.1, the biodiesel was after treated with 6 wt.% of resin in respect to biodiesel mass, and membrane filtration was conducted using the membrane with a pore size of 0.1 μm. The results are presented in the Table 1. The calcium content after the pretreatment with Na_2CO_3 should be the same as the one obtained for the purified biodiesel, since this pre-treatment is used to eliminate calcium in the inorganic form. Sodium soaps that result from pre-treatment are expected to be further removed using the water-free processes.

The results show an effective removal of calcium by pre-treatment and sodium using both water-free treatments (BDRS-II, BDMS-II). The products obtained fulfill all the quality parameters analyzed taking into account the requirements established by EN 14214 since the differences concerning the methyl ester content are less than 2%, and agree with an acceptable margin of error. The results obtained using the water washing (BDWS-II) agree with the ones obtained in a previous study [18]. The results also show high potential of using the heterogeneous process under ambient air conditions.

3.3. Waste oil biodiesel purification, after pre-treatment, using an ion exchange resin, a ceramic membrane and water washing

In order to evaluate the effectiveness of the method to purify biodiesel produced from waste oil and the heterogeneous studied catalyst, the biodiesel production was performed using waste frying oil as raw material followed by the same pre-treatment as in section 3.2. Then, the product was purified using the dry methods selected as well as the water washing method to compare.

Methyl ester and calcium content of raw-biodiesel (before purification), obtained using waste frying oil, were 90.2 wt.% and 372 ppm, respectively, indicating a slightly lower conversion than that obtained using the virgin oil. The results obtained using the different purification procedures (samples BDRW-II, BDMW-II, BDWW-II) are presented in Table 2.

The results show no significant differences between the different methods concerning the catalyst removal, showing a great potential of using the water-free process also with this kind of raw material. However, the calcium amount of biodiesel obtained using the waste oil was higher than that of the virgin oil, possibly due to the differences between the acid value of both raw-materials (0.17 mg KOH g^{-1}).

3.4. Water-free purification of soybean oil biodiesel obtained using a homogenous catalyst with the selected membrane process

The resin is used commercially to remove sodium from biodiesel when sodium hydroxide is used as catalyst. In fact, the effectiveness of the resin has been demonstrated for the removal of sodium resulting from homogeneous transesterification [20]. However, to compare the effectiveness of the resin with the one of the membrane, biodiesel obtained using a homogeneous process (NaOH catalyst) was directly purified using the membrane of 0.1 μm, and the results are presented in Table 3. The results reveal that no sodium elimination occurred since sodium content of the ester phase after performing the membrane treatment (BDMS-IV) was close to the one of the non-purified sample (BDMS-III).

In order to increase the sodium-micelle affinity with the membrane and improve the removal of sodium, 400 μL of water (eight times the water content imposed by EN 14214), at ambient temperature, were added to 100 g of biodiesel to promote soap production according to the following chemical reaction:

$$CH_3\text{-OCO-}R_1 + H_2O \xrightarrow{NaOH} NaOCO\text{-}R_1 + CH_3\text{-OH} \quad (1)$$

Due to the residual amount of water used, such methodology should not affect the methyl ester content.

The membrane filtration was performed and the results are presented in Table 3 (BDMS-V), where a notorious difference in the removal of sodium as sodium soap can be observed, which confirms the potential of this technology to retain larger molecules. The result obtained might be explained by the membrane filtration mechanism presented in Fig. 3, that derives from what is proposed by Wang et al [8] on inverse micelle formation, mentioned also in the review by Attadashi *et al.* [7]. In fact, the transformation of sodium to sodium soap favors the inverse micelle formation, that cannot cross the membrane as verified in section 3.2 (no sodium was detected in the permeate). In addition to what was reported in the section 3.2, the reason why this phenomenon is not prevalent for the calcium soap should be the fact that the micelle formation is promoted also by the presence of the residual water and glycerol (Fig. 3), which are polar molecules, and the calcium soap is a more hydrophobic molecule. However, not all sodium was converted to sodium soap. This could be because the water was kidnapped by the polar center of inverse micelle, so it was not available to react with the methyl esters. The application of acid treatment, namely using HCl solution, is not recommended because it will cause the production of NaCl salt and free fatty acids, which could cross the membrane. Experiments to evaluate optimal conditions to produce sodium soaps (temperature, time and water amount) should be conducted in the future to optimize the application of this methodology to purify biodiesel resulting from a homogeneous process.

4. Conclusion

Biodiesel with good quality was produced using an environment-friendly integrated process and both a virgin vegetable oil and a waste frying oil as raw material. The process consisted of: heterogeneous transesterification using a calcium glyceroxide catalyst, under air atmosphere conditions, followed by a water-free biodiesel purification process, using either a resin or a ceramic membrane.

The main findings are resumed in the following topics:

1) For effective removal of calcium soaps, pre-treatment using Na_2CO_3 was required to remove calcium as $CaCO_3$.

2) Sodium soaps produced by pre-treatment could be removed using 6% of resin or by filtering through a ceramic membrane with a pore size of 0.1 μm.

3) The ceramic membrane was not effective to remove the sodium resulting from the use of the homogeneous catalyst. By adding a small amount of water to biodiesel, allowing a controlled conversion of sodium to sodium soap, sodium removal significantly improved, due to the micelle formation mechanism; further studies should be conducted to optimize such process.

4) The established eco-friendly route to produce biodiesel might present high economic and environmental savings compared to the conventional route taking into account the costs and impacts associated with catalyst, drying processes and wastewater treatment.

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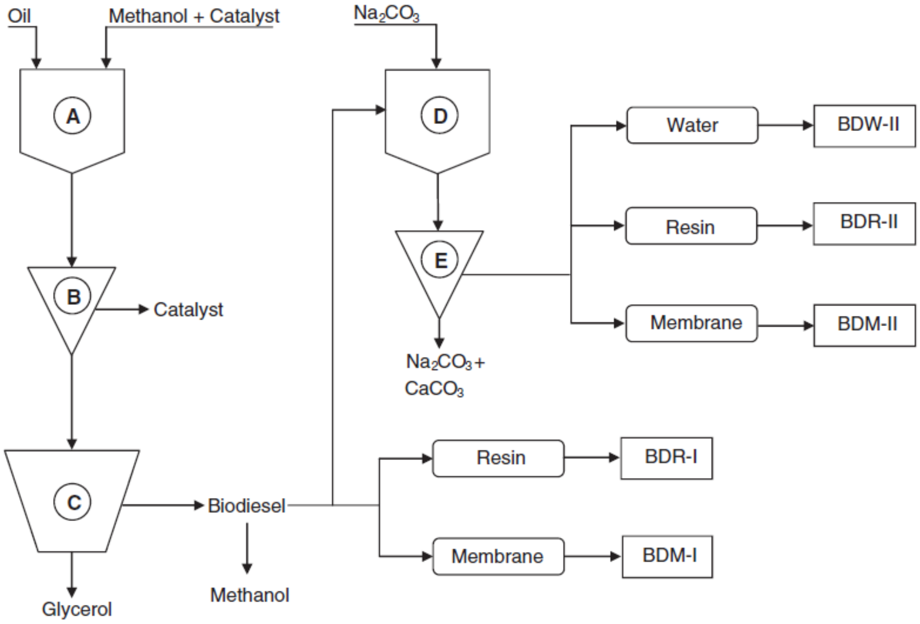

Fig. 1. Scheme of the production and purification steps studied in the present work and identification of samples.

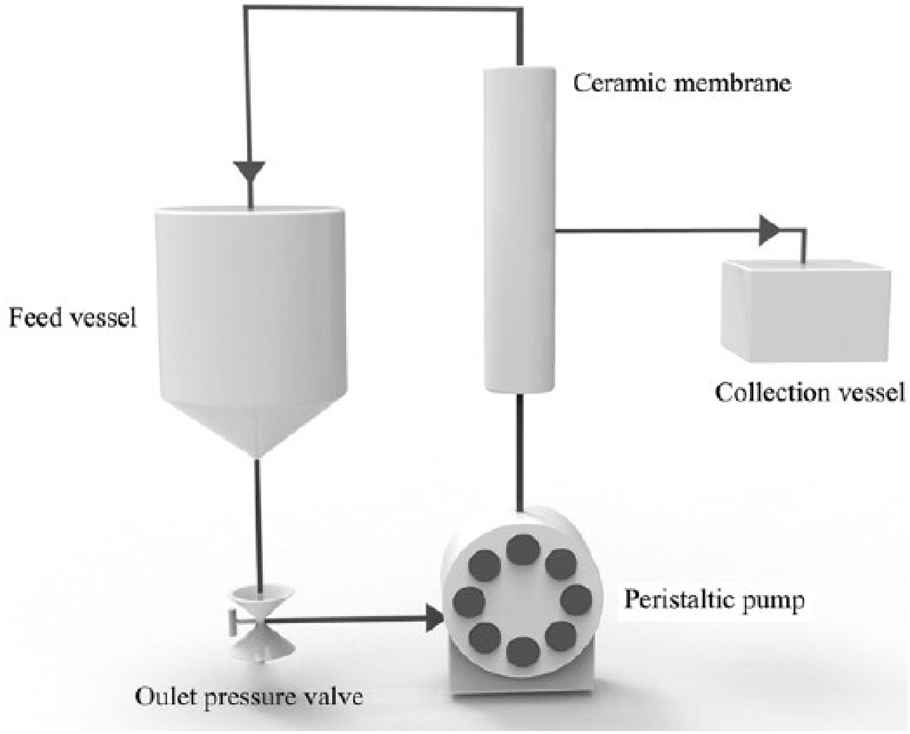

Fig. 2. Schematic diagram of membrane purification process for refining biodiesel.

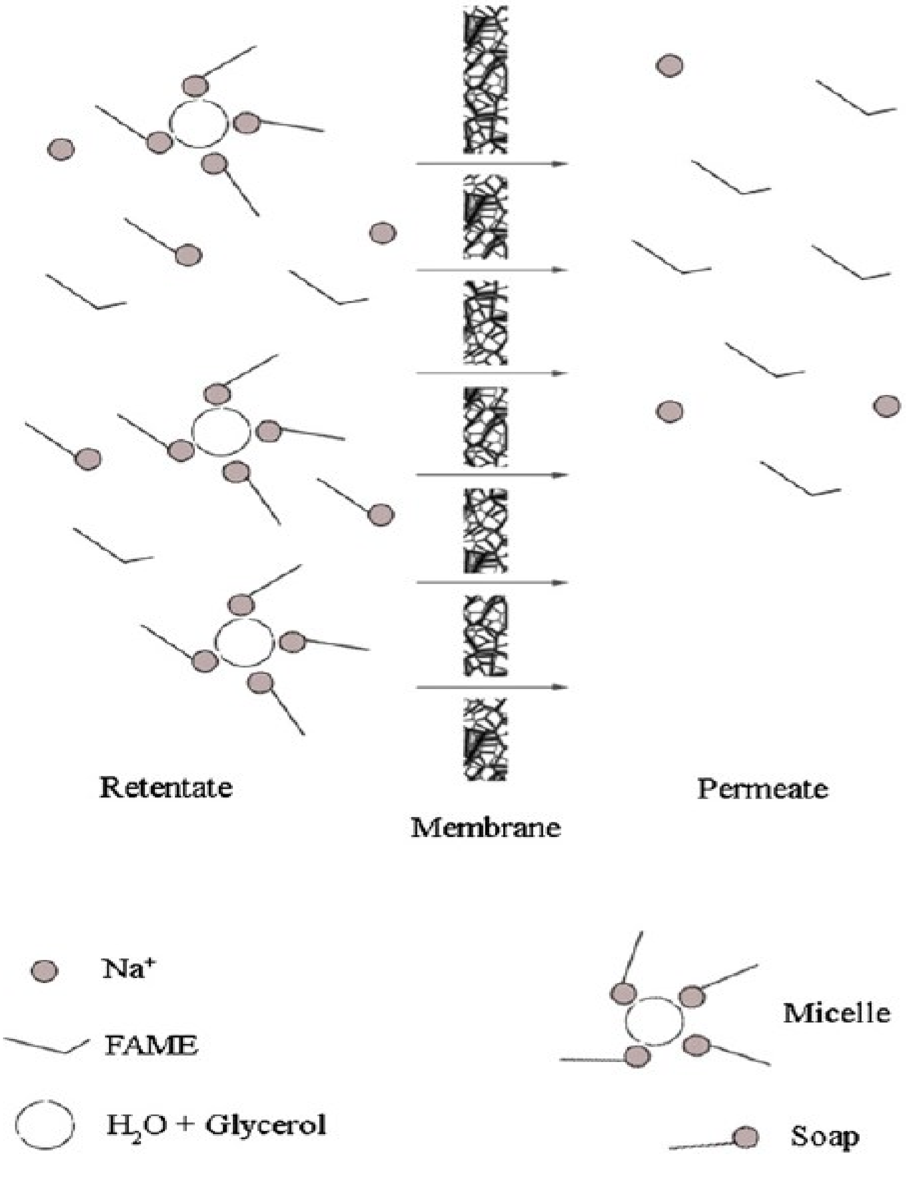

Fig. 3. Mechanism of biodiesel purification using a ceramic membrane (biodiesel produced using homogeneous NaOH as catalyst).

Table 1

Comparison of water-free soybean oil biodiesel purification procedures, after pretreatment, and limits imposed by the European biodiesel quality standard EN 14214.

Property	BDRS-II	BDMS-II	BDWS-II	EN 14214
Methyl ester content (wt.%)	95.7	94.5	98.0	Min. 96.5
Na in ester phase (ppm)	ND	ND	ND	Max. 5.0
Ca in ester phase (ppm)	2.3	1.9	2.8	Max. 5.0
Water content (ppm)	367	458	125	Max. 500

ND: not detected. BDRS-II: soybean oil biodiesel purified using 6 wt.% of resin. BDMS-II: soybean oil biodiesel purified using membrane of 0.1 μm pore size. BDWS-II: soybean oil biodiesel purified using conventional water washing.

Table 2

Comparison of water-free biodiesel purification procedures after pretreatment and limits imposed by the European biodiesel quality standard EN 14214, using waste oil as raw material.

Property	BDRW-II	BDMW-II	BDWW-II	EN 14214
Methyl ester content (wt.%)	95.8	95.7	95.4	Min. 96.5
Na in ester phase (ppm)	ND	ND	ND	Max. 5.0
Ca in ester phase (ppm)	3.4	3.2	4.7	Max. 5.0
Water content (ppm)	319	331	213	Max. 500

ND: not detected. BDRW-II: biodiesel obtained from waste oil, purified using 6 wt.% of resin. BDMW-II: biodiesel obtained from waste oil, purified using membrane of 0.1 μm pore size. BDWW-II: biodiesel obtained from waste oil, purified using conventional water washing.

Table 3

Results regarding product quality by performing purification using ceramic membranes of soybean oil biodiesel obtained using NaOH as catalyst.

Property	BDMS-III	BDMS-IV	BDMS-VI	EN 14214
Methyl ester content (wt.%)	90.0	90.2	92.8	Min. 96.5
Na in ester phase (ppm)	57.1	53.6	25.9	Max. 5.0
Water content (ppm)	157	212	241	Max. 500

BDMS-III: soybean oil biodiesel non-purified. BDMS-IV: soybean oil biodiesel purified using membrane of 0.1 μm pore size. BDMS-V: soybean oil biodiesel purified using membrane of 0.1 μm pore size, after soap production.