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Study of an Ethylic Biodiesel Integrated Process: Raw-materials, Reaction Optimization and Purification Methods.

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Abstract

Up to date, no studies exist on integrated processes for ethylic biodiesel production, focusing on raw materials (including wastes), reaction optimization and product purification (using water-free methods). Therefore, the present study aims to: i) select key variables for experimental optimization of ethanolysis reaction using a virgin vegetable oil; ii) perform an optimization study on ethanolysis using a waste oil as raw material; and iii) evaluate the effectiveness of currently proposed water free methods for product purification using the waste and refined oils as raw materials. Preliminary experiments on sunflower oil ethanolysis were conducted at different temperatures (30 – 80 ºC), catalyst concentrations (0.3 – 2 wt.%), reaction times (0.5 – 4 h) and ethanol to oil molar ratios (2:1 – 12:1). Optimization experiments on waste oil ethanolysis were further performed by varying the temperature (30 – 50 ºC) and the ethanol to oil molar ratio (6:1 – 12:1), during 1 h and using 1 wt.% catalyst. Several quality parameters were measured in the products (considering EN 14214). A cation-exchange resin and a ceramic membrane were evaluated as alternative purification agents. Preliminary studies reflected the difficulties on performing ethanolysis; when successfully conducted, conversion ranged from 75.2 – 97.7 wt.%. Using both oils under optimized conditions (45 ºC and 6:1 ethanol:oil molar ratio), a product with a very high purity (> 98.0 wt.%) could be obtained after water washing purification. Better purification results were obtained using the 0.1 μm ceramic membrane compared to the cation-exchange resin, but it was not possible to obtain a good quality product under the studied conditions using both water-free processes.

Keywords: Ethanolysis; Waste oil; Optimization; Ceramic membrane; Resin.

1. Introduction

Biodiesel is being studied since several years as a renewable and environment-friendly alternative to fossil diesel [1, 2]. Chemically, biodiesel is a mono-alkyl ester obtained through a transesterification reaction, by which more complex triglyceride molecules are converted into smaller molecules of fatty acid esters (biodiesel), that present physical and chemical characteristics similar to fossil diesel [3]. Vegetable food oils, such as soybean oil, rapeseed oil, palm oil and sunflower oil are used in more than 95 % of biodiesel production plants throughout the world [4]. The transesterification reaction is reversible and involves three steps to convert the initial triglyceride into a mixture of biodiesel and the by-product glycerol (according to stoichiometry, roughly 1 kg of biodiesel and 0.1 kg of glycerol per 1 kg of oil). The technology employed by most industries dedicated to biodiesel production consists of a methanolic route for the reaction, catalysed by a homogeneous alkali reagent (e.g. NaOH, KOH, CH_3ONa, CH_3OK) [3, 5].

To contribute for a sustainable biodiesel production, there are two fundamental aspects: raw material diversification and process optimization. These aspects should be studied not only aiming the reduction of costs but also to enable the implementation of “greener” alternatives, with reduced environmental impacts.

Virgin vegetable oils might account for up to 95% of the biodiesel production costs [6]; therefore, raw-material diversification might have significant impact on improving the economic viability of the process. In order to do that, animal fats might be used [7]; in addition, when possible, waste streams, namely from the food processing industry and domestic activities, should be recycled for biodiesel production [7-9]. By using wastes as resources, both the energetic and the waste management problems might be mitigated.

Among the research work which considers the improvement of current production processes, heterogeneous catalysts appear as a very valid contribute, although catalytic activity, leaching and reusability issues still need further developments [10, 11]. Another very relevant subject is the alcohol used; the problems associated with the hazardous nature of methanol, used in most of the industrial plants, and its non-renewable origin (almost 100% is fossil derived) motivated the research towards the use of an ethanolic route, since ethanol might be easily produced from renewable resources and presents very low toxicity [12], which makes the overall biodiesel production process greener. Although the price of ethanol is higher than that of methanol [12], this alcohol presents much higher solubility in vegetable oils and its extra carbon slightly increases the energy content of the fuel [13]. The higher cost of ethanol results mostly from the fact that it derives from the conversion of biomass, and, currently, essentially from food and animal feed crops (e.g. corn and sugarcane) that have great implications on the production cost [14]. The production of bioethanol from cellulosic biomass resources has potential to lower the bioethanol production costs [15], although the complexity of cellulosic ethanol production (the difficulties in breaking down such materials, due to the plant cell wall structure) also increases associated costs. Research is still ongoing regarding the production of engineering improved energy feedstocks and other potentially alternative feedstocks for bioethanol production [14]. In the future, biomethanol produced from biomass might also be used [16], but extensive research is still required to make this alternative economically viable. The ethanolic route is in fact more promising; however, the process is much more sensitive and it still needs to be optimized, namely regarding reaction conditions and product separation constraints, to be competitive with the methanolic route [17].

Finally, biodiesel purification is also a major issue, even when using heterogeneous catalysts [10, 18]. Conventional purification process includes water washing to remove the alcohol (usually used in excess), and residual glycerol, soaps and catalyst [19]. After washing, the remaining water in biodiesel is evaporated, usually using vacuum flash processes. Water washing of biodiesel is generally implemented because it allows fulfilling the stringent biodiesel standards such as EN 14214 and ASTM D6751; however, it leads to the production of wastewater that requires further treatment, causing significant economic and environmental impacts [20]. In addition, this process is responsible for high energy and time consumptions and also for low biodiesel yields (there is always product loss during washing stages) [6, 16]. No data could be found regarding the quantification of the operational costs of biodiesel purification.

It is known that an effective biodiesel separation and purification is crucial, because impurities resulting from ineffective processes can cause operational problems during engine functioning, such as filter plugging, injector coking, additional carbon deposits, remarkable engine wear, among others [16]. Therefore, purification technologies to be developed must be effective and without risks of causing the mentioned problems.

Alternative water-free purification processes have been developed, employing the use of different materials such as absorbents (e.g. ®magnesol), adsorbents (e.g. activated carbon), solvents (e.g. ether), resins (e.g. Purolite®) and membranes (organic or inorganic) [16].From the existing processes, dedicated ion exchange resins are being highly promoted for biodiesel purification. For instances, Purolite® (PD206) is a commercial cation-exchange resin, manufactured to purify biodiesel with the purpose of removing residual catalyst, water and other impurities, being however known for acting mostly as an adsorbent [18, 20]. The use of membranes on the treatment of organic solutions is emerging. Taking into account biodiesel purification, inorganic, ceramic membranes, have high potential due to their very high chemical and thermal stability [19, 21].

The literature review shows that there are no studies concerning integrated processes for ethylic biodiesel production, focusing on raw materials (including wastes), reaction optimization and product purification (using water-free methods). It is therefore a novel approach towards this field of study, because it considers simultaneously the raw material diversification and the process optimization, focusing on greener alternatives (by reducing environmental impacts associated with the use of methanol, the management of wastes and the wastewater treatment) and the reduction of costs (especially by replacing raw-materials but also by avoiding wastewater treatment).

In agreement with what was previously stated, the present study aims to: i) select key variables for experimental optimization of ethanolysis reaction using a virgin vegetable oil; ii) perform an optimization study on ethanolysis, by varying reaction conditions, using a waste oil as raw material; and, iii) evaluate the effectiveness of currently proposed water free methods for biodiesel purification, obtained from waste oil or refined oil.

2. Materials and Methods

2.1. Materials

The sunflower oil (SFO) was obtained commercially and used without any treatment. The waste frying oil (WFO) was obtained from a voluntary collection system (different domestic sources) implemented at *Faculdade de Engenharia, Universidade do Porto*. Before being used, WFO was pre-treated with anhydrous sodium sulphate (25 wt.%

relative to oil mass) followed by vacuum filtration, to remove solid impurities and residual water.

The resin used was commercial Purolite®PD206. A housing G1-1/6-Swageloc and a monochannel ceramic membrane with a pore diameter of 0.1 μm 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: ethanol absolute (P.A, Panreac), sodium hydroxide powder 98 % (Sigma–Aldrich, Reagent Grade), heptane (analytical grade, Merck), ethyl pentadecanoate (Aldrich), 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 Biodiesel production procedures

To start the transesterification reaction, the necessary amount of oil (around 50 g for preliminary experiments and 120 g for optimization experiments and around 250 g in each batch for water-free purification studies) was added to a three-necked batch reactor, immersed in a temperature controlled water bath, set according to the reaction temperature (30 – 80 ºC), and equipped with a water-cooled condenser. After reaching the desired oil temperature, an ethanolic solution containing the NaOH catalyst (0.3 – 2.0 wt.%, with respect to oil) and the ethanol (2:1 – 12:1 ethanol:oil molar ratio) was added to the reactor. The transesterification reaction was carried out under atmospheric pressure, with vigorous magnetic stirring (stirring plate regulated to 600 rpm), for the desired time (0.5 – 4 h). Biodiesel and glycerol phases were separated by gravitational settling and, following, the excess ethanol was removed from both phases in a rotary evaporator, at reduced pressure.

When conducting a two-step process, the reaction was stopped after the first established period, the products were left to settle and then the glycerol phase was removed. After, the excess ethanol was recovered from the biodiesel phase that was either submitted directly to the second step or purified by washing and then used in the second step.

When water washing was performed, it was conducted as described by Dias *et al.*[4].

2.2.2. Dry purification processes

The dry purification methods were applied after excess ethanol removal. When the cation-exchange resin was used, biodiesel was treated with 2 – 40 wt.% (in respect to biodiesel mass) of resin, under magnetic stirring (magnetic stirring plate regulated to 500 rpm), during 1 h, at room temperature. After, the resin was filtered and the biodiesel was analysed according to 2.2.3.

Regarding the ceramic membrane separation system, 250 mL of crude biodiesel was poured into a feed vessel and cross-filtered once by the membrane ceramic tube, using a peristaltic pump at 6.25 L h^{-1} (Aspen, Standard model).

2.2.3. Evaluation of raw materials and biodiesel quality

The following key quality parameters were determined in the raw materials: (i) acid value, by volumetric titration according to NP EN ISO 660:2002; (ii) water content, by coulometric Karl Fischer titration (Karl Fischer titrator MKC-501) according to ISO 8534:2008; and, (iii) oil composition and iodine value, obtained from the ester profile determined by gas chromatography (GC) analysis according to NP EN 5508:1996 and EN 14103:2003.

Biodiesel quality was accessed by measuring: (i) water content, by coulometric Karl Fischer titration according to NP EN ISO 12937:2003; (ii) acid value, as reported by EN 14104:2003; (iii) kinematic viscosity, according to ISO 3104:1994; (iv) flash point, using a rapid equilibrium closed cup tester according to ISO 2160:1998; (iv) ethyl ester content, also presented as product conversion [10] (mass of ethyl esters/mass of product x 100), determined by GC analysis, after extraction with heptane, based on the standard used for methyl esters (EN 14103:2003), using ethyl pentadecanoate as internal standard; and, (v) sodium content, by atomic absorption spectrometry, using a SOLAAR UNICAM AA spectrometer.

In order to determine product conversion with time, samples were collected at each defined period and treated as referred by Dias et al. [10], before being analysed in the GC.

For sodium determination, 1 g of biodiesel was dried in a hot plate at 350 ºC, in a platinum crucible, and after calcined in a furnace at 550 ºC for 30 min, to obtain white ashes. After, the solid was treated with 5 mL of nitric acid and heated at 200 ºC until reduced to 200 μL. Finally, 5 mL of nitric acid were added and this solution was diluted with distilled water up to 50 mL, for further analysis.

3. Results and Discussion

3.1 Raw materials

In the present work, a sunflower oil (acid value of 0.19 mg KOH g^{-1}; water content of 0.06 wt.%; composition: C16:0 = 5.5 wt.%, C18:0 = 3.6 wt.%; C18:1=35.2 wt.%; C18:2 = 54.2 wt.%; others = 1.5 wt.%)) and a pre-treated waste frying oil (acid value of 0.62 mg KOH g^{-1}, water content of 0.07 wt.% ; composition: C16:0 = 7.3 wt.%, C18:0 = 3.8

wt.%; C18:1= 29.1 wt.%; C18:2 = 58.5 wt.%; others ≅ 1.2 wt.%)) were used as raw materials. The virgin oil presents the characteristics required to be used for food purposes and it was used as reference oil for preliminary experiments and for comparison with the results obtained with the waste oil. The characteristics of both oils agree with the range of values reported in the literature and reference books [3, 10, 22].

3.2 Preliminary experiments

In order to evaluate the biodiesel production process, 14 preliminary experiments were conducted, by varying the reaction temperature, time, ethanol:oil molar ratio and homogeneous catalyst (NaOH) concentration aiming to select the best conditions to obtain high conversion and identify key reaction parameters. All experiments were conducted using the reference sunflower oil.

Because these were preliminary experiments and among the fundamental aspects to ensure the viability of the process are biodiesel conversion [3] and product separation, especially in the case of ethyl esters [17], only this two parameters were evaluated in order to select the key experimental variables for further optimization studies, after which additional quality parameters were determined.

The reaction conditions were established taking into account a literature review, namely considering the review by Brunschwig *et al.* [17] that evaluates bioethanol use for biodiesel production. Taking into account the great amount of work on ethanolysis conducted at 80 °C, initially, experiments were conducted at that temperature and by varying the ethanol:oil molar ratio, the catalyst concentration and the reaction time. Results are presented in Table 1 (exp. 1 – 6).

It can be seen that using a lower ethanol to oil molar ratio, of 7:1 (experiments 1 – 4), independently of the catalyst concentration and reaction time, there was no phase separation, reason why such conditions were considered to be inefficient; also, using 2.0 wt.% of catalyst, a great amount of soap was observed. The use of a higher amount of ethanol was considered (aiming to shift the reaction towards the products) and a maximum conversion/purity of 93.4 wt.% was obtained using 0.6 wt.% catalyst and 2 h of reaction (experiment 5). For this reaction period, the use of a higher catalyst concentration (1 wt.%) had a negative impact on product conversion (experiment 6), possibly due to the reversibility of the reaction or other side reactions (this will be later explored in this section). Because the reaction temperature and time were relatively high and the maximum conversion was slightly below the standard limit imposed by EN 14214 (96.5 wt.%, for methyl esters), additional experiments were conducted at 30 ºC, being also presented in Table 1 (exp. 7 – 9). Using the best catalyst concentration and molar ratio obtained in previous studies (0.6 wt.% and 12:1, respectively), after 3 h of reaction the conversion was only 75.2 wt.% (experiment 7). Therefore, a different strategy was evaluated by conducting a two-step process and removing the glycerol formed during the first reaction step aiming higher conversion in the second step (by shifting the equilibrium towards the products). This was found to be particularly effective when using lower temperatures, according to Mendow *et al.* [23], that studied a range of temperatures between 45 and 65 ºC. Here, a lower reaction temperature was evaluated since some studies were conducted under this temperature with good results [17] and it could be very appealing from an energetic point of view. To do that, after 1 h the reaction was stopped, the products were settled and glycerol was removed as described in section 2.2.1. Then, two alternatives were studied, the first included the purification of the product obtained in the first step after ethanol recovery by water washing and drying (as presented in 2.2.1) and after using it in the second step of 1 h (experiment 8) and in the second one the product obtained from the first step was directly used in the second step, after ethanol recovery (experiment 9).

By comparing the results obtained using a one step process and a two-step process (comparing experiment 7 with 8 and 9), it is clear a great difference regarding the conversion obtained (from 75.2 to 95.3 wt.%). However, to achieve high conversion (95.3 wt.%), the purification of the product was required, both at the end of the first and second stage of the reaction. This indicates that the reagents remaining in the product after the first stage affect product conversion in the second stage, namely the excess catalyst that might lead to soap production. Taking into account that such process, although performed at relatively low temperature, would imply a great effort on product purification (requiring additional consumption of time and energy), leading also to a higher process complexity as well as to higher costs in the wastewater treatment, a final set of preliminary experiments, at 45 ºC, were conducted, using a one step process, and the results are also presented in Table 1 (exp. 10 – 14). At this temperature, a very low molar ratio, of 2:1, was also evaluated, according to the patent by Khali and Leite [24], referred by Brunschwig *et al.* [17]. Using this oil, such molar ratio, and at a catalyst concentration of 1 wt.%, immediate soap production occurred which impaired the reaction (experiment 10). By increasing 3 times the ethanol to oil molar ratio and 1.5 times the catalyst amount, still much soap was produced and after 30 min the reaction did not progressed (experiment 11). Taking into account the lower molar ratio reported by the previously mentioned patent, the other experiments were performed at 6:1 instead of 12:1, since the use of a lower molar ratio might have significant advantages in terms of purification costs. At this temperature, a catalyst concentration of 0.6 wt.% was found to be insufficient for a high product conversion (88.2 wt.% was determined, experiment 12). To have an idea of the reaction kinetics, in the experiment 13 the reaction conversion was determined after 30 min, being 89.6 wt.%. The best preliminary reaction conditions, that led to a product conversion of 97.7 wt.% were found after 1 h of reaction using 1 wt.% of catalyst (experiment 14). To evaluate the reaction progression and properly conclude about the best reaction time, as well as to evaluate the reproducibility of the results, biodiesel production, at the best conditions, was conducted, in triplicate, and the reaction was monitored for different periods, up to 2 h, to evaluate the conversion, expressed in terms of ethyl ester content. Fig. 1 shows the reaction kinetics; from that, it is clear that for a period higher than 1 h of reaction there is a decrease in the conversion, showing that some reversibility of the reaction might be occurring, or side reactions such as soap production, that reduces the ethyl ester content; this might explain what was observed in experiment 6 (Table 1).

Biodiesel was produced under the same conditions using the WFO and fundamental quality parameters were evaluated in both products. Results are presented in Table 2. The ethyl ester content of waste frying oil biodiesel (WFOB) is very close to the one obtained with the SFOB, meaning that the reaction time of 1 h is also adequate for the conversion of this oil.

Both products presented generally very good quality, compared to the European standard for methyl esters (EN 14214). The viscosity of the waste frying oil biodiesel (WFOB) was just on the limit. The iodine value in both cases and the acid value regarding the WFOB did not fulfil the standard. The iodine value relates to the raw-material characteristics. Since the European Standard is based on rapeseed oil, it makes sense the differences found, that agree with studies on the use of such type of oil [3]; the iodine value of the WFOB shows similar degree of unsaturation. The acid value of the products is one of the main differences between them; in fact WFOB presents an acid value around 3 times higher than that of the SFOB (Table 2), being also higher than the

EN 14214 limit. This fact should be related to the higher initial acid value of the WFO and, perhaps, a higher susceptibility of this product towards degradation, due to previous exposure of the oil to higher temperatures and air during usage and storage.

3.2 Optimization experiments

Taking into account the importance of using waste raw-materials and the results obtained in section 3.1, which showed different results for the different conditions studied on product conversion, an optimization study was conducted to evaluate the influence of selected reaction conditions on product conversion. The selected variables were: temperature (30 – 50 ºC) and ethanol to oil molar ratio (6:1 – 12:1). The experimental planning included performing all experiments in duplicate except for the central point that was performed in triplicate (19 experiments were performed). The experiments were performed in a random order. Two biodiesel properties were determined in all cases: ethyl ester content and viscosity of the product. The mean purity/ conversion ranged between 88.9 and 95.4 wt.% whereas the viscosity ranged between 4.71 and 5.13 $mm^2\ s^{-1}$. Figure 2 shows effects of varying the reaction conditions in the quality parameters. It can be seen that, using a 9:1 ethanol:oil molar ratio, minor effects were found on varying the temperature; in this case, the purity was, in average 92.3 ± 0.7 and the viscosity 4.76 ± 0.04 $mm^2\ s^{-1}$.

When using 6:1 and also when using 12:1 ethanol:oil molar ratio, a more significant effect was found by varying the temperature, with the highest purity being obtained at 40 ºC and 6:1 ethanol:oil molar ratio and at 30 ºC, using 12:1, being in both cases very similar (close to 96 wt.%). The lowest conversion was obtained using the lowest temperature and molar ratio of ethanol to oil. This product was the only one that did not agree with the limits imposed in terms of viscosity, according to EN 14214. Apparently, no trend existed concerning the effect of the variables on the product quality. To confirm this fact it, model fits were performed, considering all the experimental results and the linear, quadratic and interaction effects of both variables (ethyl ester content and viscosity) on each property (temperature and ethanol:oil molar ratio). It was not possible to find statistically significant models that could explain the experimental results. However, it seems clear from the results that, under the conditions studied, to achieve high conversions and low viscosity at a relatively low temperature, of 30 ºC, a high ethanol:oil molar ratio is required (12:1); on the other hand, the ethanol:oil molar ratio can be reduced to 6:1 but it should be compensated by an increase of the reaction temperature. By comparing the optimization results using WFO as raw material with the ones obtained using SFO during preliminary experiments (Table 1), although some of the conditions used were different, it can be seen that they agree with each other in terms of the main studied variables since the best preliminary results were obtained at 30 ºC and 12:1 (experiment 7) and at 45 ºC and 6:1 (experiment 13); and, in the optimization studies the best conditions were 40 ºC and 6:1 ethanol to oil molar ratio and 30 ºC and 12:1 ethanol to oil molar ratio. This fact indicates that these variables are in fact very determining aiming reaction optimization when performing ethanolysis. Taking into account the results obtained during preliminary studies and also that the use of high alcohol:oil molar ratios in the transesterification reaction is known to significantly increase separation and purification costs [20], the optimized conditions were selected as 45 ºC and 6:1 ethanol to oil molar ratio.

3.3 Evaluation of purification methods

In order to perform an integrated study on all the fundamental aspects of the biodiesel production process, through ethanolysis, alternative water-free product purification methods were also explored, using both the sunflower oil and the waste frying oil biodiesel. The water free selected methods were based on previous work [19-21, 25-27]. Here the objective was not to perform optimization studies but rather evaluate how some of the previously studied methods could be applied to the raw products obtained. In this case, the biodiesel was produced under the same conditions for both oils (45 ºC, 6:1 ethanol:oil molar ratio, 1 wt.% NaOH, 1 h of reaction). The processes included using an ion-exchange resin (Purolite®PD 206) and a ceramic membrane (monochannel with 0.1 μm pore diameter). In addition, to select the resin concentration, a study was performed by using 6 – 40 wt.% of resin (with respect to biodiesel mass) and the ethyl ester content as well as the water content of the purified biodiesel were determined, as key parameters on biodiesel quality. The results are presented in Fig. 3.

The ethyl ester content of SFOB was always higher than the one of WFOB, except for the experiment using 40 wt% of resin, where values were very similar (around 92 wt.% in both cases) (Figure 3A). This might be due to a higher degree of impurities in the WFO that are removed by adsorption/absorption when higher resin concentrations are used. The best product for both raw materials was obtained using the higher resin amount; however, the ethyl ester content was still slightly below the reference value for methyl esters (> 96.5 according to EN 14214) and significantly below the values obtained using the water washing purification process (solid lines, Figure 3A).

Taking into account the water content of the product, previous research showed negligible effect of the studied resin on this parameter [26, 28]. From those studies, the one by Faccini *et al.* [26], comparable to the present study, evaluated a batch process at 65 ºC using low resin concentrations, of 1 wt.% or 2 wt.%, to purify soybean oil biodiesel. After treatment, the products presented similar water content than before, being 1200 mg kg^{-1} and 1100 mg kg^{-1}, using 1 wt.% or 2 wt.% of resin, respectively.

It can be observed that, under the conditions studied in the present work (ambient temperature and concentration from 2 – 40 wt.%), the resin amount has a great influence on the water content of the product (Figure 3B).Using 2 and 6 wt.% of resin it was not possible to have low biodiesel water content; in fact, when 2 wt.% of resin was used, the water content of the product was close to 2 times higher than the maximum imposed by EN14214, which agrees with the values observed in the previously mentioned study. Using 30 or 40 wt% of resin, the water content was low being in agreement or even lower than that obtained using the conventional water washing process and significantly below the one imposed by EN 14214.To evaluate other quality parameters and compare with the results obtained using the ceramic membrane, the product purified using 40 wt.% of resin was used. The quality parameters obtained using both water free methods are presented in Table 3.

The high flash point of the product indicates effective ethanol removal. By comparing the results obtained for all these parameters with the ones obtained using water washing it is possible to verify that the higher differences relate to the ethyl ester content, water content and acid value. In terms of the acid value, the resin was not effective to reduce this parameter to acceptable values. Berrios and Skelton [28] showed previously an increase in the acid value of biodiesel after using resin BD10 (Rohm & Haas) and PD 206 (Purolite) for purification; this fact was attributed to the acidic properties of this type of resins.

On the other hand, the ceramic membrane seemed to retain the fatty acids [20] allowing the reduction of this parameter to acceptable values. The raw materials water content was between 600 and 700 ppm (section 3.1) and although the resin selectively absorbs hydrophilic components, the membrane did not retain the water molecules and did not enable a low water content of the product. As previously stated, the final purity obtained was lower than that obtained with the water washing method. Similar values for methyl esters obtained from waste cooking oil and purified using water free purification processes are reported [29]. Finally, although these methods are referred to as effective for catalyst removal [20, 21, 25], to confirm the efficiency towards sodium removal, sodium was measured in the water washed product as well as in the product purified with the water free methods, when the virgin oil was used as raw material. No sodium was detected in the water-washed product; on the other hand, both water-free processes led to sodium contents in the product, higher than the EN 14214 limit (< 5 ppm). The membrane purified product presented 69 ppm of Na, whereas the product purified with the resin presented 108 ppm of Na. Wang *et al.* [21] showed that a ceramic membrane with a pore size between 0.1 and 0.6 μm was effective to reduce the content of metal from the catalyst to values below the maximum imposed by EN 14214 (5 ppm). In that case, using a membrane with 0.1 μm, the metal content was less than the one using water washing (< 2 ppm). Better results might be achieved by optimization studies, since membrane separation efficiency depends upon conditions such as temperature, transmembrane pressure and flow [19]. Berrios and Skelton [28] showed high efficiency of this ion exchange resin towards the removal of glycerol and soaps by treating biodiesel in a column with a fixed resin bed at ambient temperature. The high sodium content obtained in the present study indicates that further optimization is also still required for the resin used, namely considering changing not only the concentration (Figure 3), but also the temperature and mixing intensity. For instances, in a study by Faccini *et al.* [26], the use of this resin at only 2 wt.% but at a temperature of 65 ºC, as previously mentioned, enabled metal removal to trace values. This study shows that both water-free methods have good potential for purifying ethanolic biodiesel; however, further optimization is still required to allow their effective use.

Conclusions

The present work allowed the study of an integrated biodiesel production process through ethanolic route, using virgin and waste oil as raw materials. The preliminary results on ethanolic biodiesel production using sunflower oil showed the importance of optimizing reaction conditions and the difficulties and complexity of this process. Considering all theexperiments conducted, by varying temperature (30 – 80 ºC), catalyst concentration (0.3 – 2 wt.%), reaction time (0.5 – 4 h) and ethanol to oil molar ratio (2:1 – 12:1), in around 40% of the cases it was not possible to separate the product or high soap production occurred whereas in the remaining, more successful experiments, conversion ranged from 75.2 – 97.7 wt.%. The preliminary experiments showed as key reaction parameters, the temperature and ethanol:oil molar ratio. The optimization experiments on ethanolic biodiesel production from waste oil validated the results obtained in preliminary experiments. The results showed that to achieve high conversions at a relatively low temperature, of 30 ºC, a high ethanol:oil molar ratio is required (12:1); on the other hand, no benefit results from increasing the temperature up to 50 ºC using such a high ethanol:oil molar ratio. To reduce the costs of separation and purification that result from using a high molar ratio, this parameter can be reduced to 6:1 but it should be compensated by an increase of the reaction temperature. Taking into account the results from preliminary and optimization experiments, the best conditions were selected as: reaction temperature of 45 ºC and 6:1 ethanol:oil molar ratio (considering 1.0 wt.% of catalyst and 1 h of reaction). Under such conditions, a good quality product could generally be obtained after water washing, using both the virgin and the waste oil. Under the conditions studied for water-free processes, better results were obtained using the 0.1 μm ceramic membrane compared with the cation-exchange resin; the major problems related with the lower product purity, compared to the water washing product; the acid value in the case of the resin and the sodium content in both methods (although with the membrane a much higher metal removal was achieved) ,which did not allow obtaining a good final quality of the product. Although showing good potential, such water-free methods require further improvements.

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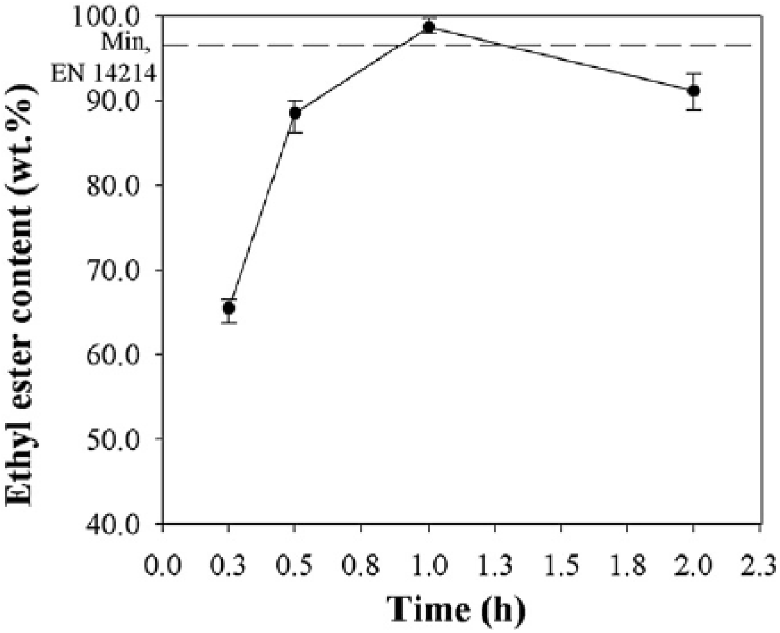


Fig.1. Reaction progression under the best preliminary conditions (45 ºC, 6:1 ethanol:oil molar ratio, 1 wt.% NaOH).

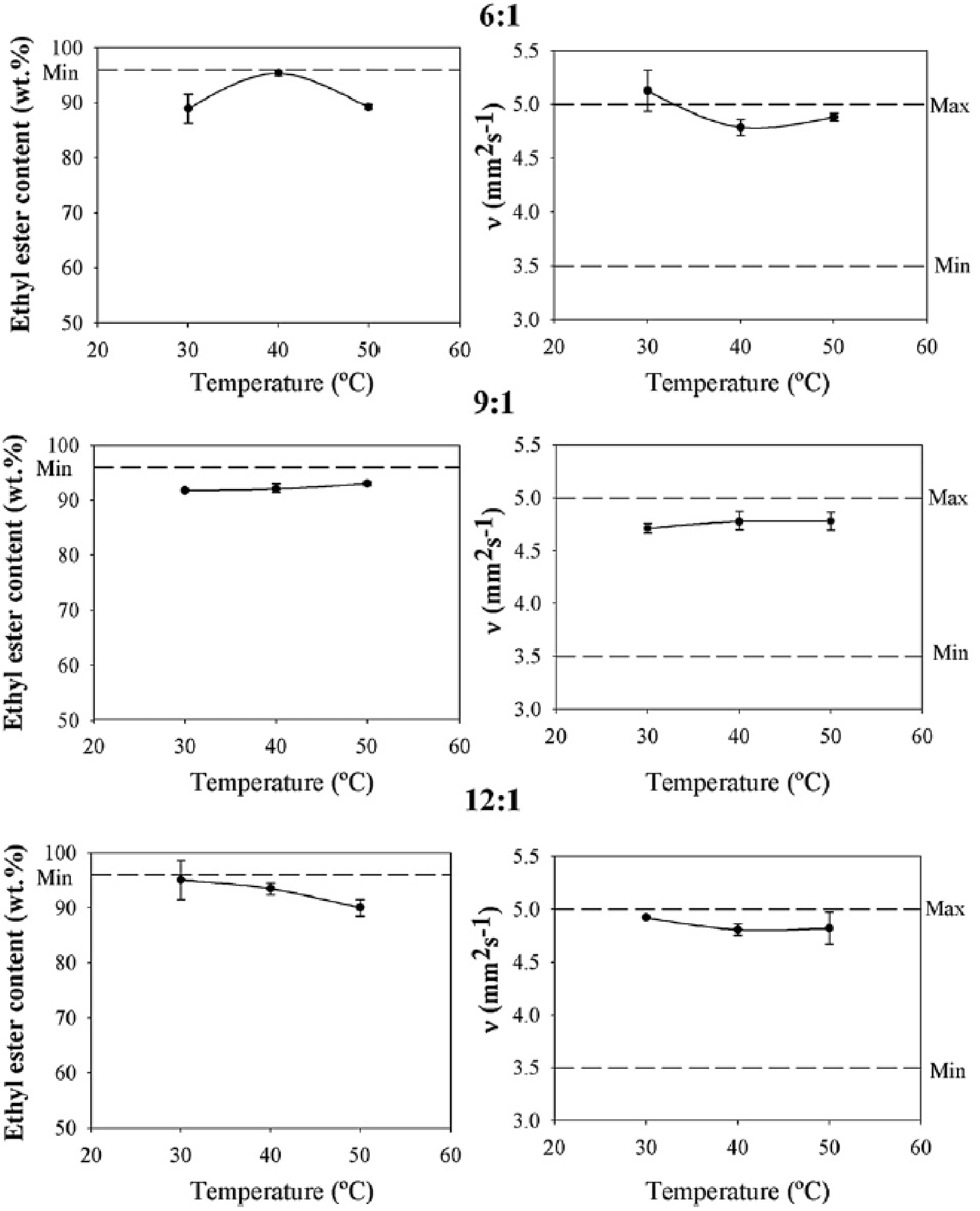


Fig. 2. Ethyl ester content and viscosity of the waste frying oil biodiesel, obtained in the optimization experiments; max and minimum values relate to standard EN 14214 on methyl esters.

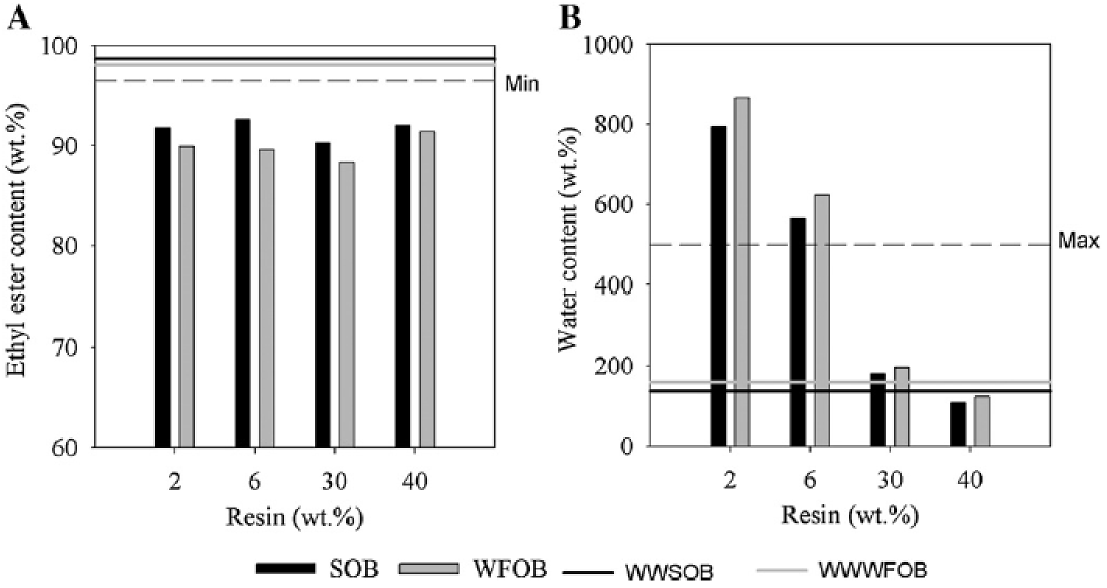


Fig. 3. Ethyl ester content (A) and water content (B) of soybean oil biodiesel (SOB) and waste frying oil biodiesel (WFOB) after treatment with different amounts of resin; results for water washed soybean oil biodiesel (WWSOB) and water washed waste frying oil biodiesel (WWWFOB), in solid line, as well as the EN 14214 standard requirement for methyl esters (dashed line) are presented for reference.

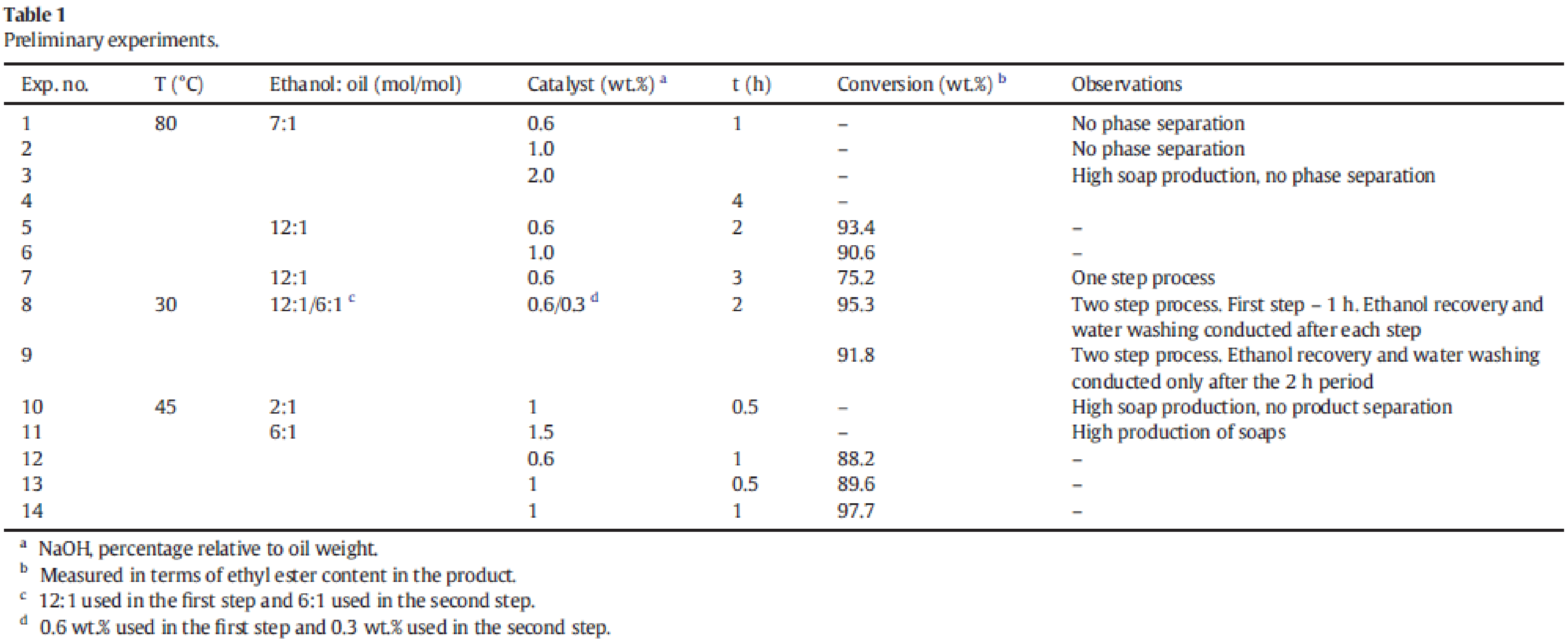


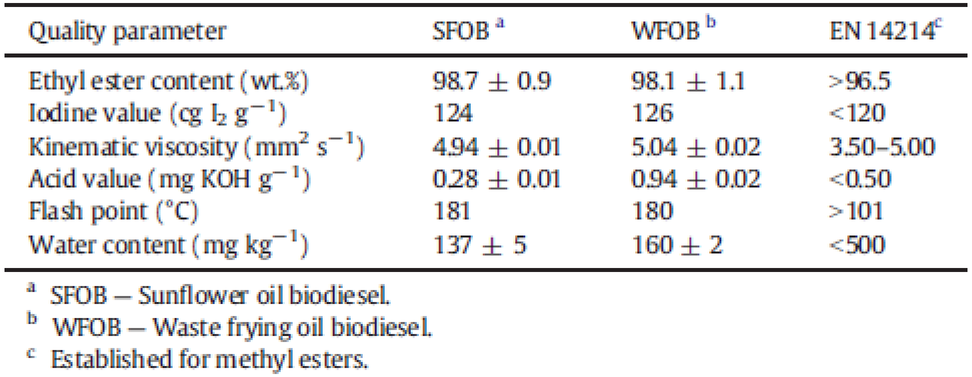
Table 1
Preliminary experiments.

Exp. no.	T (°C)	Ethanol: oil (mol/mol)	Catalyst (wt.%) [a]	t (h)	Conversion (wt.%) [b]	Observations
1	80	7:1	0.6	1	–	No phase separation
2			1.0		–	No phase separation
3			2.0		–	High soap production, no phase separation
4				4	–	
5		12:1	0.6	2	93.4	–
6			1.0		90.6	–
7		12:1	0.6	3	75.2	One step process
8	30	12:1/6:1 [c]	0.6/0.3 [d]	2	95.3	Two step process. First step – 1 h. Ethanol recovery and water washing conducted after each step
9					91.8	Two step process. Ethanol recovery and water washing conducted only after the 2 h period
10	45	2:1	1	0.5	–	High soap production, no product separation
11		6:1	1.5		–	High production of soaps
12			0.6	1	88.2	–
13			1	0.5	89.6	–
14			1	1	97.7	–

[a] NaOH, percentage relative to oil weight.
[b] Measured in terms of ethyl ester content in the product.
[c] 12:1 used in the first step and 6:1 used in the second step.
[d] 0.6 wt.% used in the first step and 0.3 wt.% used in the second step.

Table 2

Biodiesel quality, obtained using the best conditions from preliminary experiments, and biodiesel quality standard requirements.



Quality parameter	SFOB [a]	WFOB [b]	EN 14214[c]
Ethyl ester content (wt.%)	98.7 ± 0.9	98.1 ± 1.1	>96.5
Iodine value (cg I_2 g^{-1})	124	126	<120
Kinematic viscosity (mm^2 s^{-1})	4.94 ± 0.01	5.04 ± 0.02	3.50–5.00
Acid value (mg KOH g^{-1})	0.28 ± 0.01	0.94 ± 0.02	<0.50
Flash point (°C)	181	180	>101
Water content (mg kg^{-1})	137 ± 5	160 ± 2	<500

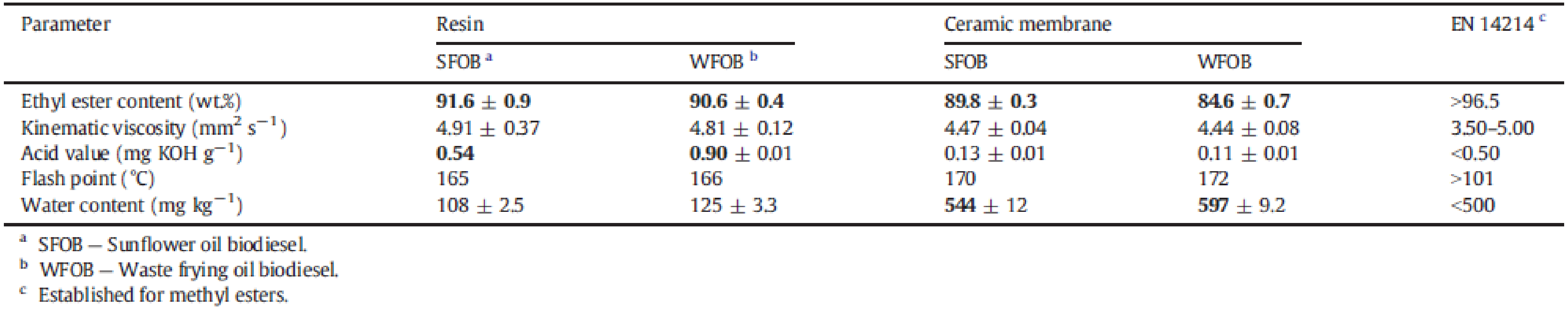
[a] SFOB – Sunflower oil biodiesel.

[b] WFOB – Waste frying oil biodiesel.

[c] Established for methyl esters.

Table 3

Biodiesel quality, obtained using 40 wt.% resin and cross filtered by a 0.1 μm ceramic membrane to purify biodiesel and quality standard requirements; values significantly affected by purification process are presented in bold.



Parameter	Resin		Ceramic membrane		EN 14214 [c]
	SFOB [a]	WFOB [b]	SFOB	WFOB	
Ethyl ester content (wt.%)	**91.6 ± 0.9**	**90.6 ± 0.4**	**89.8 ± 0.3**	**84.6 ± 0.7**	>96.5
Kinematic viscosity (mm^2 s^{-1})	4.91 ± 0.37	4.81 ± 0.12	4.47 ± 0.04	4.44 ± 0.08	3.50–5.00
Acid value (mg KOH g^{-1})	**0.54**	**0.90** ± 0.01	0.13 ± 0.01	0.11 ± 0.01	<0.50
Flash point (°C)	165	166	170	172	>101
Water content (mg kg^{-1})	108 ± 2.5	125 ± 3.3	**544** ± 12	**597** ± 9.2	<500

[a] SFOB – Sunflower oil biodiesel.

[b] WFOB – Waste frying oil biodiesel.

[c] Established for methyl esters.