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DEACIDIFICATION AND ETHYL BIODIESEL PRODUCTION FROM ACID SOYBEAN OIL USING A STRONG ANION EXCHANGE RESIN

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ABSTRACT

The objective of this work was to investigate simultaneously the deacidification and the ethyl biodiesel production from soybean oil using the Amberlyst A26 OH anion exchange resin. The behavior of the process was investigated as a function of resin loading, ethanol concentration and initial free fatty acids (FFAs) content. To obtain the acidified oil, degummed soybean oil and commercial linoleic acid were mixed. The Langmuir model was able to better describe the FFAs adsorption isotherms in comparison to the Freundlich equation. A high removal of FFAs with high deacidification rate could be obtained using lower initial ratios of FFAs per mass of dry resin, being this the more favorable condition for oil deacidification. Ester formation showed to be affected by the resin loading, initial FFA content and ethanol concentration in the medium. The adsorption of FFAs seemed to deactivate the catalytic activity of the resin sites. For this reason, a high resin loading was required, although it was still possible to obtain a satisfactory biodiesel production. The present work makes possible deeper understanding of oil processing by anion exchange resins in the presence of an alcoholic solvent.

Keywords: Strong anion exchange resin; Soybean oil; Deacidification; Biodiesel production.

1 INTRODUCTION

In recent years, alternative energy sources, such as biodiesel, have attracted great attention because of the limited traditional fossil energy resources and increased environmental concerns [1]. Biodiesel is a fuel for diesel engines, which is renewable, biodegradable and can be used in any mixture with petrodiesel fuel [2]. It can be defined as a fuel composed of mono alkyl esters of long chain fatty acids, derived from vegetable oils or animal fats [3]. Biodiesel typically comprises fatty acid alkyl esters of short-chain alcohols, mainly methanol or ethanol [2]. The use of ethanol has some advantages, since it has higher miscibility with vegetable oils that allows a better contact during the reaction step and also shows a lower toxicity [4].

Nevertheless, the total cost of biodiesel production is a disadvantage in relation to the petroleum-based diesel fuel, where the main factor to consider is the high cost of the lipid feedstock, which generally consists of refined vegetable oils [5]. Thus, low-cost raw materials have been investigated for biodiesel production; however, the question of the quality of these lipid materials is of utmost importance. A major problem associated with these lipid materials is the high content of FFAs [6].

A high FFA content is detrimental to the production of biodiesel using basic homogeneous catalysis due to the formation of soap, reducing the efficiency of the process [7–9]. The soap formed causes an increase in the viscosity or formation of gels, and interferes in the phase separation of biodiesel and glycerin [10]. Furthermore, the biodiesel quality specifications impose limit for the allowed acid value [11], requiring that FFAs be esterified or removed from raw materials with high content of these compounds.

Therefore, some changes in the biodiesel production process are required for the processing of raw materials with a high FFA content [6]. Some changes in the process are being proposed, including pretreatment from oils with alkali to removal the FFA as soaps before beginning transesterification [5], the process in two acid-alkaline steps (esterification-transesterification) [12], the use of solid acid catalysts [13,14], among others. In addition, an alternative process for the FFAs removal can be based on anion exchange resins.

The adsorption of fatty acids by anion exchange resins has been studied in different oils and resins [15–25]. The Amberlyst A26 OH resin was suitable for the removal of FFAs in a fixed-bed for different mixtures of vegetable oils with solvents [23,24], for oleic acid in sunflower oil [21] and also in the deacidification of soybean oil [25].

However, in these studies with the Amberlyst A26 OH resin, the effect of process variables on the removal of FFA was not investigated for soybean oil dissolved in ethanol. The presence of organic solvents in the medium may increase the rate of FFA removal [25]. Moreover, the use of ethanol for extraction of vegetable oils has been investigated [26,27], and in this case, the extractor outlet miscella could be sent to deacidification without previous removal of the solvent. This kind of process integration and intensification may reduce cost and increase the economic feasibility of biodiesel production. This can also mean an additional step for integrating the production of edible oils and biodiesel. As vastly proved in the Brazilian case, the simultaneous production of sugar and bioethanol allows sharing some of the requiring unit operations as well as heat integration between a variety of hot and cold streams, generating cost reducing technologies and higher economies of scale [28].

In fact, another application for anion exchange resins in fatty systems involves their use as a heterogeneous catalyst in the transesterification of oils for biodiesel production. Anion exchange resins demonstrate favorable characteristics for catalysis of biodiesel production, such as easy recovery and regeneration, operation under mild conditions and the potential for continuous biodiesel production [29,30].

Recently the production of biodiesel with anion exchange resins in the presence of acid oil was investigated [31–34]. Some papers also discussed the relationship of active site deactivation of the resin for catalysis with the adsorption of fatty acids [29, 35]. However, different behaviors are reported regarding the effect of the presence of FFAs on biodiesel production. Moreover, in these studies the removal of FFAs and the production of ethylic biodiesel with the Amberlyst A26 OH resin were not simultaneously evaluated, remaining as an interesting topic of research the behavior of both processes in these systems.

The objective of this work was therefore to investigate simultaneously deacidification and biodiesel production in the processing of soybean oil dissolved in ethanol using the Amberlyst A26 OH anion exchange resin. Understanding the behavior of these systems is an important step for process application and development.

2 MATERIAL AND METHODS

2.1 Materials

Degummed soybean oil was donated by the company Cargill Agrícola S.A. (Mairinque, São Paulo, Brazil). This oil was submitted only to the refining stages that traditionally precede deacidification, in order to represent study conditions most similar to those observed industrially. Commercial linoleic acid (Sigma-Aldrich, USA) was added to the oil in order to adjust the FFA content to the desired value when necessary.

The strong anion exchange resin Amberlyst A26 OH is a trademark of The Dow Chemical Company ("Dow") or affiliated companies of Dow, and was obtained from the company Coremal (Brazil).

According to the manufacturer [36], it is a macroreticular polymeric resin based on crosslinked styrene divinylbenzene copolymer containing quaternary ammonium groups and it has the following properties: spherical beads with particle size (harmonic mean size) in the range of 0.560 to 0.700 mm, average pore diameter of 290 Å, ionic form as shipped is hydroxide (OH), concentration of active sites ≥ 0.80 eq/L, moisture holding capacity of 66 to 75 % (OH form), shipping weight of 675 g/L and suggested maximum operating temperature of 60 ºC.

Absolute ethanol used in the experiments was of the brand Merck (Germany) and the ethanol used in pretreatment of the resin was of the brand Synth (Brazil). Toluene (purity 99.9 %) and acetic acid (purity 99.8 %) were obtained from Sigma-Aldrich (USA) and Merck (Germany), respectively. The commercial mixture of partial acylglycerols from soybean oil was obtained from the company SGS Agriculture and Industry Ltd. (Brazil).

2.2 Experimental procedure

The fatty acid composition of degummed soybean oil and commercial linoleic acid was determined by gas chromatography of fatty acid methyl esters according to the official method Ce 1f-96 [37]. Their compositions were reported in our previous work [25]. The fatty acid in greatest concentration in soybean oil was linoleic acid. The mole percent purity of commercial linoleic acid was of 53.23 ± 0.02 %.

Pretreatment of the resin involved conditioning with ethanol, carried out in fixed bed, flowing 5 volumes of the solvent (in relation to the resin volume) through the resin with flow rate of 2 bed volumes/h. At the end, the resin was transferred to a container where it was immersed in the solvent. It was used in the experiments after separation of the excess solvent by filtration. The volatile content of the resin was determined in each experiment by gravimetry, where samples of approximately 3 g were dried in an air circulation oven (model MA 035, Marconi, Brazil) at 110 ºC until reaching constant weight. The concentration of active sites in the resin after the pretreatment was also determined. The methodology used was based on the procedure described by Cren et al. [38], using an ethanolic hydrochloric acid solution (0.2 eq/L), and from the volatile content of the sample the dry basis value of the active sites concentration can be obtained.

In the experiments the liquid phase was composed of degummed soybean oil, ethanol, and when necessary to adjust the initial FFA content, commercial linoleic acid. It should be mentioned that the resin used in the experiments has a volatile content of approximately 81 %, corresponding in large part to ethanol, the solvent used in resin conditioning. Thus, two forms of quantifying ethanol will be described, in the initial solution and in the total solution. The initial solution mass refers to the mass of solution prior to contact with the resin and the mass of the total solution corresponds to the sum of the initial solution mass and the volatile mass loaded in the cell together with the resin.

2.2.1 Analysis of the resin

The Amberlyst A26 OH resin was analyzed by nuclear magnetic resonance (NMR) and infrared spectroscopy (IR) before and after the acidic oil processing with ethanol. These spectroscopy analyses were performed at the Department of Analytical Chemistry of the Institute of Chemistry at UNICAMP.

The experimental conditions used in oil processing with the resin were: dry resin loading to neutral oil of 2 % (g dry resin/100 g neutral oil), initial FFA content in the acidified oil of 5 %, molar ratio of ethanol in the initial solution to neutral oil of 9:1 and temperature of 50 ºC. After this procedure the resin was washed with hexane to remove the oily fraction from the exterior and interior of the resin. Both samples were dried at 50 ºC in an air circulation oven (model MA 035, Marconi, Brazil) until reaching constant weight to remove excess solvent from the resin.

Solid state $^{13}C\{^{1}H\}$ NMR spectra of the resin were obtained using the Bruker AVANCE II^{+} 300 MHz (7.05 T) spectrometer, operating at a frequency of 75.5 MHz for ^{13}C. A combination of Cross-Polarization and Magic Angle Spinning (CP/MAS) was used. To obtain the spectra, beads of the resin were accommodated within a zirconia rotor (ZrO_2) using the following experimental conditions: spectral width from 250 to -50 ppm, contact time of 4.0 ms, delay of 3.0 s, acquisition time of 45 ms and sample rotation at 10 kHz.

The mean IR spectra of the resin were obtained on the Agilent FTIR Cary 630 spectrometer, using the attenuated total reflectance (ATR) accessory. To obtain the spectra, beads of the resin were positioned in the sampler and pressed by the accessory, using the following experimental conditions: spectral width from 4000 to 600 cm^{-1}, spectral resolution of 2 cm^{-1} and 64 scans.

2.2.2 Equilibrium and kinetic assays

To obtain the adsorption equilibrium and kinetic data, cells of 50 or 200 mL were used, jacketed and hermetically sealed. Stirring of the system was carried out at 500 rpm with a suspended magnetic stirrer (Trevisan Tec, Brazil). The temperature was maintained by coupling the cells to a thermostatic bath (model 12101-15, Cole Parmer, USA).

In all experiments the temperature was fixed at 50 ºC. The resin was previously weighed in the cell and heated to 50 ºC; after this the miscella (initial solution) was prepared separately and also heated to 50 ºC. The initial time of the experiments was based on mixing of both the resin and solution.

FFA adsorption isotherms were obtained for two molar ratios of ethanol in the initial solution to neutral oil, namely 9:1 and 6:1. For the construction of each adsorption isotherm the initial FFA content per neutral oil was maintained fixed at 6.4 % (g acid/100 g neutral oil) and the dry resin loading was varied from 1 to 10 %. Samples were collected after 72 h.

Samples of the initial solution and those collected after FFA removal equilibrium were analyzed with regards to the FFA content using two quantification methods in order to compare the data obtained by titration or chromatography. The adsorbed amount of FFA in the resin (solid phase concentration) was obtained by mass balance. The Langmuir and Freundlich adsorption isotherm models were fitted to the experimental data. Samples collected in the assays used to construct the isotherms were also analyzed for determining ethyl esters and ethanol contents. Thus, the ester molar yield was calculated in relation to the maximum quantity of ester that can be produced, considered equal to three times the number of moles of the initial neutral oil. In the calculation of number of moles of the initial neutral oil, the mass of oil was obtained by difference using the initial mass of ethanol and FFA.

Afterwards, the kinetics of FFA removal and formation of ethyl esters were also evaluated as a function of the resin loading, the amount of ethanol in the medium and the initial FFA content. In this case, the samples were analyzed for the content of FFAs, acylglycerols, ester and ethanol. Removal of FFAs from the solution was determined in relation to its initial FFA content, and the ester molar yield was calculated in the same way indicated above.

It should be noted that the results were calculated in a FFA free basis due to a possible decrease in the liquid solution mass caused by the adsorption of these components, considering the high molecular weight of the fatty acid compared to water, generated by the ion exchange reaction in the case of FFA adsorption. Furthermore, the initial concentrations of the liquid phase were recalculated considering the total volatiles introduced into the reaction medium with resin.

The FFA content determined by titration was performed according to IUPAC methodology 2.201 [39], using an automatic titrator model 808 Titrando (Metrohm, Switzerland). The average molar mass calculated from the commercial linoleic acid composition was used to express the results of the analysis of FFA content by titration.

Analysis of the contents of fatty acid alkyl esters, FFAs, acylglycerols and ethanol was performed using a high performance liquid chromatograph (HPLC model LC-20AT, Shimadzu), equipped with size exclusion column 100 Å Phenogel (300 mm x 7.8 mm ID, 5 µm) (Phenomenex, USA), and refractive index detector (model RID-10A, Shimadzu, Japan). The oven temperature of the column (CTO-10AS VP, Shimadzu) was 40 ºC. The injection system used was an automatic sampler (SIL-20A, Shimadzu) to inject 20 µL and the flow rate used was 1 mL/min and elution was performed in the isocratic form [40,41]. The mobile phase was composed of a Toluene solution containing 0.15 % acetic acid (v/v). This concentration of the mobile phase was used in order to improve the separation of ethyl esters and FFAs, particularly difficult in cases of high ester concentrations combined with low FFA concentrations. Although the elution time of FFAs was closer to the monoacylglycerols (MAG) elution time, in the experiments with high FFA concentration, the MAG concentration was negligible and vice-versa, so that the separation of FFA and MAG was not troublesome.

The compounds were identified by comparison with external standards and quantified by calibration curves constructed with the reagents of the system and with purified biodiesel obtained after reaction with the resin. To determine the classes of acylglycerols in the samples, a calibration curve elaborated with a commercial mixture of partial acylglycerols of predetermined composition was used.

Calculation of the average neutral oil molar mass of soybean oil, required to calculate the molar ratio of ethanol to neutral oil and the molar yield of ester, was made from the composition in classes and components of acylglycerols. The composition of neutral oil according to the different acylglycerol classes was determined by the chromatographic method, considering that the amount of MAG in the oil was negligible and the content of triacylglycerol (TAG) was obtained by difference using the contents of diacylglycerols (DAG) and FFAs. In addition, the DAG composition varied according to acidification of the degummed oil, being considered an average value. The probable TAG composition was estimated based on the statistical method suggested by Antoniosi Filho et al. [42] using the fatty acid composition of degummed soybean oil. In order to reduce the number of TAGs, all structural isomers were grouped into a set of components with x carbons and y double bonds, where each group was represented by the major TAG component. In addition, only groups with a total TAG concentration greater than 0.5 % were considered. The composition in DAGs was estimated considering the probability of partial disruption of triacylglycerols without preferences for specific ester bonds. The average molar mass of the ethyl ester mixture was determined from the fatty acid composition of the oil. This value was also required for calculating the ester molar yield.

3 RESULTS AND DISCUSSION

In all assays the resin pretreatment was carried out by conditioning with ethanol. This pretreatment was selected according to previous experiments, since the presence of water inside the resin impaired catalysis. Furthermore, the Amberlyst A26 OH resin is supplied in its ionic form with hydroxyl and inclusion of a regeneration step did not demonstrate to significant affect its catalytic activity. The volatile content of the resin after pretreatment was determined in each experiment, and the corresponding values ranged from 0.801 ± 0.004 to 0.810 ± 0.002 g/g (wet basis). The concentration of active sites after pretreatment was 5.5 ± 0.5 meq/g dry resin.

In this study the removal of FFAs and the formation of ethyl esters were simultaneously evaluated in the processing of soybean oil with ethanol using the

Amberlyst A26 OH anion exchange resin. First, the resin was analyzed before and after oil processing to investigate how deacidification occurs in these systems. Subsequently, FFA adsorption isotherms were obtained and the formation of esters was evaluated in these assays. Finally, the kinetics of both processes was evaluated as a function of process variables.

3.1 Resin analysis

The Amberlyst A26 OH resin was analyzed by nuclear magnetic resonance and infrared spectroscopy before and after processing of acidified soybean oil dissolved in ethanol.

Figure 1 shows the ^{13}C CP/MAS NMR spectrum of the Amberlyst A26 OH resin pretreated with ethanol, (a) before and (b) after oil processing. In Figure 1 (a) it is possible to note the signals between 40.4 and 68.8 ppm related to the aliphatic carbons and the region between 126.8 and 147.3 ppm corresponding to the aromatic carbons of the resin structure.

The signal at 160.8 ppm, observable in spectrum (a) of Figure 1, is related to the HCO_3^- (hydrogen carbonate) species, which can be formed from the reaction of the hydroxyl (OH^-), present on the resin active sites, with atmospheric CO_2 (carbon gas) [43,44]. It should be noted that in order to remove the excess of ethanol present in the resin as a result of its pretreatment, it was dried before the analysis. During this procedure the reaction may have occurred. However, to perform the experiments the resin was always immersed in ethanol and properly conditioned, and in accordance with previous experiments the resin sites were activated for catalysis. However, this result underscores the importance of proper resin storage.

It is possible to infer that fatty acids were adsorbed onto the resin, because in spectrum (b) of Figure 1 signals of these compounds can be noted, in addition to the signals already identified as belonging to the resin. The signals between 14.8 and 30.4 ppm are related to CH_2 present along the chain and to CH_3 terminals of the fatty acid chains. The signals at 128.5 and 130.4 ppm are related to olefinic carbons.

It was also possible to infer the mechanism involved in FFA adsorption. Some reaction mechanisms have been proposed for the removal of long chain fatty acids in non-aqueous medium by weak and strong anion exchange resins. Among them are the ion exchange equilibrium [20,45], and the formation of a complex via a hydrogen bond between the nitrogen pair of the amino group present in the resin and the acidic hydrogen of the fatty acid [22]. As can be seen in Figure 1 (b), the signal at 179.4 ppm is associated with deprotonated fatty acid carboxylates that would be adsorbed on the resin active sites, indicating that the mechanism associated with this system involves the exchange of anions. Furthermore, in the Amberlyst A26 OH resin spectrum after oil processing (Figure 1 (b)), the signal at 160.8 ppm related to the hydrogen carbonate ion is not identified.

Figure 2 shows the spectrum in the mid-IR region of the Amberlyst A26 OH resin which underwent ethanol conditioning, (a) before and (b) after oil processing. From the spectroscopy in the mid-IR region it is also possible to observe the effective adsorption of fatty acids to the resin. The bands at 2926 and 2855 cm^{-1} (spectrum (b) of Figure 2) are related to the asymmetric and symmetrical stretches, respectively, of the CH_2 groups resulting from fatty acids [46]. In addition, it is possible to observe the asymmetric vibration band of the carboxylate group at 1559 cm^{-1} [47]. In spectrum (a) of Figure 2, bands are noted at 1609 and 1323 cm^{-1} associated with the hydrogen carbonate ion vibrations, which again are not present in spectrum (b) [48].

The adsorption mechanism of FFAs, involving anion exchange, can also be inferred via the IR spectrum, considering that the band at 1559 cm^{-1} is associated with stretching of the carboxylate anion, $\nu_{ass}(COO^{-})$ and that the band at approximately 1710 cm^{-1}, corresponding to the carbonyl vibration of the carboxyl group [49], is not present in Figure 2(b).

Thus, based on both spectroscopic techniques, NMR and IR, it was possible to characterize the FFA adsorption on the resin after oil processing with ethanol. Despite some controversies on the issue [33,34,50], other works in the literature agree that even with the presence of alcoholic solvents, deacidification occurs by adsorption on the anion exchange resin.

Cren and Meirelles [45] studied the removal of oleic acid from solutions composed of ethanol and water and obtained similar results for the quantity adsorbed on the resin by mass balance and by analytical measurements after resin regeneration, and thus reported that the FFA adsorption occurred by the ion exchange mechanism. Díaz and Brito [20] analyzed the Dowex monosphere 550A anion exchange resin by FT-IR before and after acid oil processing with and without the presence of methanol. These authors found that in both treatments the FFAs were adsorbed on the resin and there was no esterification. Furthermore, other works also agree that FFAs are adsorbed with anion exchange resin and esterified with cationic resins in the presence of an alcoholic solvent [18,32].

3.2 Adsorption isotherm and ethyl esters yield

FFA adsorption isotherms for the molar ratios of ethanol in the initial solution to neutral oil of 9:1 and 6:1 were determined and are shown in Figure 3. Different amounts of ethanol were used in the medium in order to evaluate the effect on the adsorption behavior of FFAs. The conditions used were similar to those investigated in previous work with anion exchange resin [29].

As expected, for experiments with higher resin loading the FFA removal was higher due to the greater presence of active sites available for adsorption. However, since the amount of solute in the initial solution was the same, the larger quantity of solute adsorbed will be divided by the larger quantity of resin added to the system. Thus, as long as the total amount of fatty ions present is sufficient to saturate the active sites, the ratio of fatty ions adsorbed per unit mass of dry resin at saturation is constant and, outside this region, this ratio decreases. The variation of ethanol concentration in the medium did not seem to affect the behavior of FFA removal, being the maximum quantity adsorbed similar for both systems.

The Langmuir and Freundlich models are commonly found in literature to describe the behavior of the adsorption equilibrium in processes similar to those studied in this work [17,18,21,45,51]. Both models were tested in this set of experiments, based on the mathematical expressions of the Langmuir and Freundlich models described in our previous work [25].

Adjustment of the Langmuir and Freundlich models is also shown in Figure 3. The parameters obtained for these models are shown in Table 1. The values of the n parameter, of Freundlich's Isotherm were greater than 1, indicating favorable conditions for adsorption [52]. It was observed that the Langmuir model allows a higher coefficient of determination, better describing the data in both systems. In general, no significant difference was observed in the parameter values of this model for both ratios of ethanol to neutral oil.

The maximum adsorption capacities (q_m) for the systems with molar ratios of ethanol in the initial solution to neutral oil of 9:1 and 6:1 were 1.105 and 1.109 g acid/g dry resin, respectively. Cren et al. [51] found the maximum adsorption capacity value to be 1.107 g acid/g dry resin for the adsorption of linoleic acid in the Amberlyst A26 OH resin from ethanol + water solutions. Additionally, in this work the best fit was also obtained for the Langmuir isotherm. Thus, the presence of the oil does not appear to have affected adsorption.

In the data presented in Figure 3, the analysis method for FFA content was based on titration. In order to compare different analytical methodologies, the FFA content in all samples was also analyzed by chromatography, according to the method described previously. The isotherms obtained with both methodologies are shown in Figure 4. It may be considered that the two methodologies presented similar results. However, because the chromatographic analysis requires a much smaller amount of collected samples, this methodology was selected in order to obtain the kinetic data. In fact, using this technique it was not necessary to remove large amounts of sample from the reaction medium.

In order to evaluate the effect of FFA adsorption behavior on the production of biodiesel, the formation of ethyl esters was also investigated in the same assays used to determine the isotherms. The ethyl ester yield as a function of the resin loading is shown in Figure 5. It should again be noted that because the initial FFA quantity was the same in all experiments represented in Figure 5, when the resin loading is increased outside the saturation region, there are more active sites that are not occupied with FFAs, i.e., more free sites available for catalysis.

The formation of ethyl esters was observed in all the experiments, being smaller for tests with lower dry resin loading. It is known that with the increase in resin loading the amount of active sites for catalysis increases. However, the observed behavior shows not only a growing trend. In fact, there is a practically constant tendency of low ester formation corresponding to the tests with the dry resin loading of 1 to 5 %. These assays correspond to the saturation region of the adsorption isotherm, which indicates that occupation of the active sites with fatty acids is the determining factor for the formation of ethyl esters. Thus, the production of biodiesel is directly related to the quantity of free active sites.

This behavior is in agreement with what was discussed by Shibasaki-Kitakawa et al. [29] and Kim et al. [35], who report that the catalytic activity of the resin may decrease due to the occupation of active sites with fatty acids and suggest the corresponding deactivation of the basic catalytic sites.

3.3 FFA removal kinetics and ethyl esters yield

The effect of process variables was evaluated via the FFA removal and ethyl ester formation kinetics during the processing of acidic soybean oil dissolved in ethanol with the Amberlyst A26 OH resin. The influence of resin loading, amount of ethanol, initial FFA content and the interaction between resin loading and initial FFA concentration were evaluated.

3.3.1 Effect of the resin loading

First the effect of the resin loading on the kinetics of FFA removal and yield of ethyl esters was evaluated (Figures 6 and 7). In these experiments, the initial FFA content per neutral oil was maintained at approximately 6.5 %, the molar ratio of ethanol in the initial solution to neutral oil was fixed at 9:1 and the dry resin loading per neutral oil varied from 1 to 20 %.

It was observed that the stabilization time for the FFA removal is dependent on the resin loading present. For the experiment with dry resin loading of 1 %, the FFA removal stabilized after 45 min of processing and reached a removal of approximately 18 %. For the experiment with dry resin loading of 5 % the FFA removal stabilized only after 1 h and 40 min and presented a removal of approximately 87 %. For the experiments with dry resin loading of 10, 15 and 20 %, the FFA removal stabilized after approximately 20, 8 and 4 min, respectively, and in all of these assays a removal greater than 98 % was achieved.

In all experiments the same quantity of FFA was maintained in the initial solution, therefore as the resin loading was increased, the number of active sites available for FFA removal increased. The longer time required for stabilization of FFA removal in the case of the 5 % dry resin loading experiment compared to the 1 % dry resin loading one may result from faster saturation of the active sites in the latter case. In the other three experiments (10, 15 and 20 % resin loading), the process conditions did not involve resin saturation and the increase in active sites allowed for a higher adsorption rate.

It should be mentioned that in these experiments the amount of ethanol in the initial solution was fixed. As discussed previously, two forms of quantifying ethanol were considered: in the initial solution and in the total solution. The initial solution mass refers to the solution mass prior to contact with the resin and the total solution mass corresponds to the sum of the initial solution mass and the volatile mass added to the system as part of the resin loaded in the cell. Thus, as the resin loading was increased, the amount of ethanol in the medium was increased due to the presence of this solvent within the resin, as a result of its pretreatment. In the experiments performed outside the resin saturation region, the molar ratio of ethanol in the total solution to neutral oil was greater than 16:1, and it was observed that in this range the amount of ethanol in the medium had no influence on deacidification and biodiesel production, as will be presented later.

The ester yield was also determined as a function of resin loading (Figure 7(a)). As noted previously, for experiments under the conditions of resin saturation with the FFAs (dry resin loading of 1 and 5 %), the ester yield was very low. Ester formation stabilized together with the stabilization of FFA removal, indicating deactivation of the active resin sites for catalysis of the biodiesel production reaction. For the experiments in which there was no resin saturation with FFAs (10, 15 and 20 % dry resin loading), an increase in the ester formation rate was observed with increased resin loading. This behavior was also observed in other studies using anion exchange resin for transesterification [29,53].

It was also observed that, depending on the resin loading, very low ester formation kinetics were obtained. Figure 7(b) shows the ester formation for the last three experiments as a function of longer processing times. The experiment with resin loading of 10 % only achieved an ester yield of approximately 78 % in around 10 days. With the resin loading of 15 % stabilization occurred in approximately 2 days, but reaching ester yield values similar to the resin loading of 20 %. Marchetti and Errazu [34] also observed very slow reaction kinetics in the production of biodiesel with acid oil using basic resin.

Although higher resin loading are required, it is possible to obtain a satisfactory level of biodiesel production even from acidic oils, being required just a higher concentration of free anion exchange resin sites. In this case, it is possible that both the deacidification process and biodiesel production occur satisfactorily. However, the resin loading required for deacidification was less than that required for a high rate of ester formation. Furthermore, in the experiments performed, when the FFA removal stabilized, the maximum ethyl ester yield found was of approximately 5 %. In fact, with operating conditions that did not result in saturation of the resin with the FFAs the kinetics of both processes were very different.

3.3.2 Effect of ethanol quantity in the medium

In this operation, besides the acting of the ethanol as a reagent in the medium, this solvent is also used to remove the water of inside the resin and maintain its swelling, also acting on the modification of the physical properties of the initial solution. To verify the influence of the ethanol quantity in the medium on the removal of FFA and ethyl esters yield, two sets of experiments were performed. In the first, the initial FFA content per neutral oil was fixed at 6.5 %, the dry resin loading per neutral oil at 20 % and the molar ratio of ethanol in the total solution to neutral oil was varied from 16 to 24:1. In the second set of experiments the initial FFA content per neutral oil was fixed at approximately 1.6 %, the dry resin loading per neutral oil at 5 % and the molar ratio of ethanol in the total solution to neutral oil varied from 4 to 17:1. Because of the selected values for the resin loading and initial FFA content, all these experiments were conducted outside the resin saturation region with FFAs.

The first set of experiments allowed for evaluating the effect of the ethanol quantity on obtaining high ester yields, but only by taking into account the amount of volatile carried by the resin loading, the molar ratio of ethanol in the total solution to neutral oil was approximately 15 to 16:1. Therefore, in order to evaluate smaller amounts of the solvent, the experiments with smaller resin loading were used.

The results obtained for FFA removal as a function of time for the first and second sets of experiments are shown in Figures 8 and 9, respectively. For the conditions evaluated, there was a small influence of the ethanol content on the FFA removal rate, especially for molar ratios of ethanol in the total solution to neutral oil below 16:1. There was no interference on the final value of removal under the investigated conditions.

The results of ester yield versus time for the first and second experiment sets are shown in Figures 10 and 11, respectively. As can be seen, the decrease in the ethanol quantity affected the ethyl ester yield kinetics only when the molar ratio of ethanol in the total solution to neutral oil was less than 16:1, making the process slower and tending to a lower final ester content.

As was described by Fillières et al. [54], considering that the transesterification reaction is an equilibrium one, an excess of alcohol can increase ester conversion by shifting the reaction equilibrium to the product side. In addition, the effect of the other functions of this solvent in the process must be considered.

Shibasaki-Kitakawa et al. [29] studied the transesterification reaction of triolein with ethanol using the resin Diaion PA306s and also observed this behavior, but above certain ethanol concentration no significant change in the maximum conversion was observed.

By observing the initial period of the process, it can be noted that the smaller quantity of ethanol in the solution increased initially the reaction rate. However, over time a larger amount of the solvent becomes more beneficial. Marchetti and Errazu [34] also observed similar behavior, obtaining higher ester conversions with the increase in ethanol content, but with slower initial reaction rates.

It should be noted that in experiments with the 20 % dry resin loading (Figure 10), only by using the ethanol present in the resin sample a satisfactory biodiesel production was obtained, similar to the results attained for the other ethanol contents in the initial solution. Thus, it is possible to avoid the unnecessary addition of ethanol by considering the ethanol present in the resin. It should be remembered that pretreatment of the resin, with ethanol conditioning, is advantageous in order to eliminate water usually present in the resin.

3.3.3 Effect of the initial FFA content

In order to investigate the influence of the initial FFA content on the removal of FFAs and the ethyl ester yield, experiments were performed where the dry resin loading per neutral oil was fixed at 20 %, the molar ratio of ethanol in the total solution to neutral oil fixed at 16:1 and the initial FFA content per neutral oil varied from 1.5 to 19.9 %. Due to the resin loading, even with the highest FFA content studied, all experiments are outside the adsorption saturation region of the resin.

The removal of FFAs as a function of time is shown in Figure 12. In the experiments with lower initial FFA contents (1.5 and 6.5 % per neutral oil) a very rapid removal was observed. In the experiment with a higher initial FFA content, a more gradual removal was observed, reaching equilibrium after 30 min of processing. In all cases, the FFA removal was satisfactory.

The ester yield as a function of time is shown in Figure 13. As in the case of the resin loading influence, the initial FFA content affects the ester yield. At lower levels, higher reaction rates are obtained. In fact, with the lowest FFA content evaluated (degummed oil content without addition of linoleic acid), biodiesel production occurred satisfactorily in a reduced time. Meanwhile, for the initial FFA content per neutral oil of 19.9 %, with only more of 9 days an ester yield of approximately 64 % was achieved.

In these experiments the amount of ethanol in the medium and the amount of resin were maintained constant, and consequently the quantity of active sites present. However, variation of the ester yield with the FFA concentration confirms the importance of the active sites being available for catalysis. Another relevant fact is that a higher FFA content provided a lower ester yield at the every time evaluated, which is contrary to the assumption that FFAs were esterified rather than adsorbed. However, an additional factor to consider is the formation of water with the ion exchange in the adsorption of FFAs. Díaz and Brito [20], commented that for some catalysts water can affect the active sites used for catalysis.

3.3.4 Interaction effect of the initial FFA content and resin loading

With the results obtained, it was observed that an increase in resin loading, as well as a decrease in the initial FFA content, resulted in higher reaction rates and ester yields. Thus, for satisfactory ester formation not only is the presence of active sites in the medium necessary, but that these sites be not occupied and be free for catalysis. For each initial FFA content in the oil, there would be therefore an optimum resin loading condition, in which the number of sites that are not occupied with the FFAs is sufficient to catalyze the transesterification reaction of all neutral oil present.

In order to investigate the interaction of these variables a set of experiments was performed, varying the initial FFA content and the dry resin loading in order to obtain a similar condition of free sites per neutral oil present after adsorption of the FFAs. The calculation of free sites, in the equilibrium condition of FFA adsorption, was performed using the number of sites that were occupied with the FFAs and the concentration of active sites in the resin conditioned with ethanol.

In these experiments the molar ratio of ethanol in the total solution to neutral oil was fixed at approximately 16:1, the dry resin loading per neutral oil was varied from 6 to 20 % and the initial FFA content per neutral oil varied from 1.6 to 19.9 %. The initial condition was planned so that, as the amount of sites occupied by FFAs increased, the resin loading was increased to maintain the ratio of free sites per neutral oil similar in the FFA adsorption equilibrium (0.3 to 0.4 meq/g neutral oil).

The amount of FFAs adsorbed as a function of time for the experiments performed is shown in Figure 14. In the tests where the initial ratio of FFA per dry resin was lower, faster adsorption kinetics was obtained. In these cases, the number of sites occupied by FFA per resin weight is lower.

The ester yield as a function of time is shown in Figure 15. As can be observed, the experiments with higher quantities of resin-occupied sites produced lower ester formation at the time analyzed. It should be emphasized that in these experiments the resin loading was also increased in order to obtain similar amounts of free sites per neutral oil after the FFA adsorption equilibrium. This behavior indicates that the ester yield is not linked only to the quantity of free sites per neutral oil present, but also to the proportion of sites occupied with FFAs to the total number of sites. In fact, the sites considered available may not be more accessible, or active for catalysis due to the FFA adsorption.

This fact may also be related to the fatty acid composition, being in the present case linoleic acid the major fatty acid present in soybean oil. Furthermore, to obtain a higher FFA content commercial linoleic acid was added. As reported by Kanicky and Shah [55], the presence of “cis” unsaturations generates folds in the fatty acid structure, preventing unsaturated fatty acid molecules from being more closely arranged when they are distributed in monolayers, when compared to saturated acid molecules. This may prevent accessibility to some sites considered as available. Another factor to be considered would be the increased water formation with higher adsorption of FFAs, which could deactivate the sites for catalysis.

It should be noted that the FFA adsorption kinetics is also a factor to be considered, since when evaluating the behavior of the experiments during a shorter time, it is observed that the experiment with higher FFA content obtained a higher initial reaction rate due to slower occupation of the active sites.

A second set of experiments was performed maintained the molar ratio of ethanol in the total solution to neutral oil at approximately 16:1 and the initial ratio of FFA per dry resin similar, varying the dry resin loading per neutral oil from 5 to 20 % and the initial FFA content per neutral oil from 1.7 to 6.5 %.

The quantity of FFAs adsorbed as a function of time for the different experiments is shown in Figure 16. It was observed that the FFA adsorption behavior practically did not change and a similar final condition was reached. Thus, by establishing initial ratios of FFA per dry resin it is possible to find combinations of resin loading and initial FFA content which result in similar adsorption behavior. It should be noted that in the studied conditions the process occurred very quickly and with high removal of FFA. Under the conditions studied, the simultaneous formation of esters does not appear to affect deacidification, especially by the faster FFA removal kinetics.

In these experiments, practically the same ratio of active sites occupied per resin was obtained, and consequently the ratio of free sites per resin was similar. Thus, with the lower resin loading, the number of free sites per neutral oil present was reduced (0.2 – 0.9 meq/g neutral oil). The ester yield as a function of time for the experiments is shown in Figure 17. As expected, as the resin loading was increased the rate of biodiesel production was greater. This also reinforces the importance of achieving an adequate quantity of free sites. Thus, to optimize the ester yield it would be important to consider the amount of sites occupied by the FFAs and the resin loading.

As it was mentioned, although a higher resin loading is required, it is possible to obtain a satisfactory level of biodiesel production for acid oils catalyzed by anion exchange resins. This behavior has advantages over acid oil processing with basic homogeneous catalysts because, although the catalyst deactivation by FFAs will be the same, but the heterogeneous catalysis by anion exchange resin avoids soap formation and the corresponding prejudicial effect on the separation of glycerol [10].

Although in the process with the strong anion exchange resin the FFAs would be adsorbed rather than esterified, as occurs in processing with cationic resins, similar to homogeneous acid catalysts, the lower catalytic activity of the heterogeneous acid catalysts can lead to higher reaction temperature and time requirements for biodiesel production [11]. In addition, two factors can be considered. This process may be especially applicable for oils such as degummed soybean oil, which have low FFA contents. Another issue is that the recovery of pure fatty acids retained in the resin is viable to be conducted after the transesterification step and they can be considered as a byproduct of market value. Furthermore, the recovery of the fatty acids retained in the resin could be investigated together with esterification of these compounds.

3.4 Quantification of biodiesel production

Monitoring of process kinetics involved the collection of many points, requiring the quantification of biodiesel production using the concentration of samples and the solution mass. However, this quantification is not simple because it involves diluting the solution with the volatile compound initially present in the resin, the liquid phase composition inside and outside the resin and the adsorption of glycerol.

In some experiments shown in the kinetics study, an ester yield slightly above 100 % was observed. This fact may be especially related to the adsorption of glycerol, which would alter the solution mass considered in the yield calculation. In fact, this kind of problem arises because the present investigation involved simultaneously different mass transfer and reaction processes: i) the anion exchange process involving fatty acid and water diffusions into and out of the resin porous structure, meaning that the liquid and solid phases change continuously their compositions and total amounts; ii) the corresponding change in the polarity of the resin internal environment, now partially occupied by long chain fatty acids that can cause additional changes in the liquid concentrations within and outside the resin structure; iii) the transesterification reaction, consuming the low polar acylglycerol compounds and generating the strong polar glycerol molecules, which further contributes to changes of phase concentrations and may cause changes in the quantities of the phases if some of the new components are also physically adsorbed by the resin surface. Despite all these simultaneous phenomena, the entire process should be mainly monitored by changes in the liquid phase concentration. Although the monitoring of the resin phase is, in principle, possible, as indicated by the NMR and IR spectra shown in this work, this monitoring is not viable in quantitative terms from a practical point of view, if one takes into account the already enormous experimental effort involved just in accompanying, in quantitative terms, the FFA adsorption and ethyl ester formation kinetics reported in this work.

Other calculation methods were also investigated, including neutral oil conversion and ester concentration. The proximity between the results of each calculation varied with the assay condition. However, the different calculation methods did not affect the conclusion on the effect of process variables. Furthermore, the values of a ester concentration, calculated such a reference of the ester quantity in relation to neutral oil in the liquid phase outside the resin, was always close to that obtained for the ester yield, demonstrating very similar behavior. In order to maintain the same reference in the quantification of biodiesel production, it was selected the ester yield (ester yield referring to the initial quantity of neutral oil).

4 CONCLUSIONS

Processing of soybean oil with ethanol using the Amberlyst A26 OH resin was evaluated in terms of FFA removal and biodiesel production. Deacidification showed to be viable, with favorable conditions for the adsorption of FFAs. The FFA adsorption isotherm was better described by the Langmuir model in comparison to the Freundlich model. Using lower initial ratios of FFA per dry resin it was possible to obtain different combinations of resin loading and initial FFA content that promote a high removal of FFAs.

Under operational conditions that did not result in resin saturation with FFAs, increasing the resin loading and decreasing the initial FFA content increased the rate of ester formation. The results indicated deactivation of the active sites of the resin for catalysis with the adsorption of FFAs. With the increase to a certain ethanol concentration it was also possible to obtain faster ester yield kinetics, but with a lower initial reaction rate. In addition, it is possible to avoid the unnecessary addition of solvent while accounting for ethanol present in the resin as a result of its pretreatment.

Although a higher resin loading is required, it is possible to obtain a satisfactory level of biodiesel production using acidic oils by heterogeneous catalysis with a higher reaction rate and without the formation of soaps during the process. Furthermore, deacidification using a strong anion exchange resin and alcoholic solvent also may be used as a pre-step in biodiesel production, at least as a promising way of obtaining a partial formation of fatty esters.

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6 TABLES CAPTIONS

Table 1 – Parameters of the Langmuir and Freundlich models for adsorption isotherms of FFAs on Amberlyst A26 OH resin from solutions composed of degummed soybean oil, commercial linoleic acid and ethanol with different molar ratios of ethanol in the initial solution to neutral oil.

7 FIGURES CAPTIONS

Figure 1 – ^{13}C CP/MAS NMR spectra of the pretreated Amberlyst A26 OH resin (a) before and (b) after processing of the miscella of acidic oil and ethanol.

Figure 2 – Spectra in region of mid-IR of the pretreated Amberlyst A26 OH resin (a) before and (b) after processing of the miscella of acidic oil and ethanol.

Figure 3 – Adsorption isotherms of FFAs on Amberlyst A26 OH resin at 50 °C with solution composed of degummed soybean oil, commercial linoleic acid and ethanol, initial FFA content per neutral oil of 6.4 % and molar ratio of ethanol in the initial solution to neutral oil of: (■) 9:1 and (●) 6:1. (—) Langmuir model and (----) Freundlich model.

Figure 4 – Adsorption isotherms of FFAs on Amberlyst A26 OH resin at 50 °C with solution composed of degummed soybean oil, commercial linoleic acid and ethanol, initial FFA content per neutral oil of 6.4 %, being the AGL content determined by titration (filled markers) or chromatography (open markers) and molar ratio of ethanol in the initial solution to neutral oil of: (■ or □) 9:1 and (● or ○) 6:1.

Figure 5 – Molar yield of ethyl ester as a function of dry Amberlyst A26 OH resin loading per neutral oil with solution composed of degummed soybean oil, commercial

linoleic acid and ethanol, temperature of 50 °C, initial FFA content per neutral oil of 6.4% and molar ratio of ethanol in the initial solution to neutral oil of: (■) 9:1 and (●) 6:1.

Figure 6 – Kinetics of FFA removal using Amberlyst A26 OH resin, solution composed of degummed soybean oil, commercial linoleic acid and ethanol, temperature of 50 ºC, initial FFA content per neutral oil of approximately 6.5 %, molar ratio of ethanol in the initial solution to neutral oil of 9:1 and dry resin loading per neutral oil of: (■) 1 %, (●) 5 %, (▲) 10 %, (▼) 15 % and (♦) 20 %.

Figure 7 – Kinetics of ester yield obtained with Amberlyst A26 OH resin, solution composed of degummed soybean oil, commercial linoleic acid and ethanol, temperature of 50 ºC, initial FFA content per neutral oil of approximately 6.5 %, molar ratio of ethanol in the initial solution to neutral oil of 9:1 and dry resin loading per neutral oil of: (■) 1 %, (●) 5 %, (▲) 10 %, (▼) 15 % and (♦) 20 %.

Figure 8 – Kinetics of FFA removal using Amberlyst A26 OH resin, solution composed of degummed soybean oil, commercial linoleic acid and ethanol, temperature of 50 ºC, initial FFA content per neutral oil of 6.5 %, dry resin loading per neutral oil of 20 % and molar ratio of ethanol in the initial and total solution to neutral oil respectively of: (■) 0:1 and 16:1, (●) 6:1 and 21:1, (▲) 9:1 and 24:1.

Figure 9 – Kinetics of FFA removal using Amberlyst A26 OH resin, solution composed of degummed soybean oil, commercial linoleic acid and ethanol, temperature of 50 ºC, initial FFA content per neutral oil of approximately 1.6 %, dry resin loading per neutral oil of 5 % and molar ratio of ethanol in the initial and total solution to neutral oil respectively of: (■) 0:1 and 4:1, (●) 4:1 and 8:1, (▲) 13:1 and 17:1.

Figure 10 – Kinetics of ester yield obtained with Amberlyst A26 OH resin, solution composed of degummed soybean oil, commercial linoleic acid and ethanol, temperature

of 50 ºC, initial FFA content per neutral oil of 6.5 %, dry resin loading per neutral oil of 20 % and molar ratio of ethanol in the initial and total solution to neutral oil respectively of: (■) 0:1 and 16:1, (●) 6:1 and 21:1, (▲) 9:1 and 24:1.

Figure 11 – Kinetics of ester yield obtained with Amberlyst A26 OH resin, solution composed of degummed soybean oil, commercial linoleic acid and ethanol, temperature of 50 ºC, initial FFA content per neutral oil of approximately 1.6 %, dry resin loading per neutral oil of 5 % and molar ratio of ethanol in the initial and total solution to neutral oil respectively of: (■) 0:1 and 4:1, (●) 4:1 and 8:1, (▲) 13:1 and 17:1.

Figure 12 – Kinetics of FFA removal using Amberlyst A26 OH resin, solution composed of degummed soybean oil, ethanol and commercial linoleic acid, when necessary the adjustment of the initial FFA content, temperature of 50 ºC, dry resin loading per neutral oil of 20 %, molar ratio of ethanol in the initial and total solution to neutral oil of 0:1 e 16:1 respectively and initial FFA content per neutral oil of: (■) 1.5 %, (●) 6.5 % and (▲) 19.9 %.

Figure 13 – Kinetics of ester yield obtained with Amberlyst A26 OH resin, solution composed of degummed soybean oil, ethanol and commercial linoleic acid, when necessary the adjustment of the initial FFA content, temperature of 50 ºC, dry resin loading per neutral oil of 20 %, molar ratio of ethanol in the initial and total solution to neutral oil of 0:1 e 16:1 respectively and initial FFA content per neutral oil of: (■) 1.5 %, (●) 6.5 % and (▲) 19.9 %.

Figure 14 – Kinetics of FFA adsorption on Amberlyst A26 OH resin with solution composed of degummed soybean oil, commercial linoleic acid and ethanol, temperature of 50 ºC, molar ratio of ethanol in the total solution to neutral oil of approximately 16:1 and: (■) initial FFA content per neutral oil of 1.6 % and dry resin loading per neutral oil of 6 %, (●) initial FFA content per neutral oil of 6.6 % and dry resin loading per neutral

oil of 10 %, (▲) initial FFA content per neutral oil of 19.9 % and dry resin loading per neutral oil of 20 %.

Figure 15 – Kinetics of ester yield obtained with Amberlyst A26 OH resin, solution composed of degummed soybean oil, commercial linoleic acid and ethanol, temperature of 50 ºC, molar ratio of ethanol in the total solution to neutral oil of approximately 16:1 and: (■) initial FFA content per neutral oil of 1.6 % and dry resin loading per neutral oil of 6 %, (●) initial FFA content per neutral oil of 6.6 % and dry resin loading per neutral oil of 10 %, (▲) initial FFA content per neutral oil of 19.9 % and dry resin loading per neutral oil of 20 %.

Figure 16 – Kinetics of FFA adsorption on Amberlyst A26 OH resin with solution composed of degummed soybean oil, commercial linoleic acid and ethanol, temperature of 50 ºC, molar ratio of ethanol in the total solution to neutral oil of approximately 16:1 and: (■) initial FFA content per neutral oil of 1.7 % and dry resin loading per neutral oil of 5 %, (●) initial FFA content per neutral oil of 3.2 % and dry resin loading per neutral oil of 10 %, (▲) initial FFA content per neutral oil of 6.5 % and dry resin loading per neutral oil of 20 %.

Figure 17 – Kinetics of ester yield obtained with Amberlyst A26 OH resin, solution composed of degummed soybean oil, commercial linoleic acid and ethanol, temperature of 50 ºC, molar ratio of ethanol in the total solution to neutral oil of approximately 16:1 and: (■) initial FFA content per neutral oil of 1.7 % and dry resin loading per neutral oil of 5 %, (●) initial FFA content per neutral oil of 3.2 % and dry resin loading per neutral oil of 10 %, (▲) initial FFA content per neutral oil of 6.5 % and dry resin loading per neutral oil of 20 %.

Table 1

		Molar ratio of 9:1	Molar ratio of 6:1
Langmuir[a]	q_m	1104.92 ± 22.91	1108.69 ± 12.42
	b	22.87 ± 3.51	17.25 ± 1.39
	R^2	0.9139	0.9852
Freundlich[b]	k_f	924.18 ± 28.33	901.91 ± 42.05
	n	15.73 ± 2.82	14.10 ± 3.39
	R^2	0.8336	0.8018

[a] q_m (mg acid/g dry resin) and b (mg acid/g non-acid components)$^{-1}$, [b] k_f ((mg acid/g dry resin)·(g non-acid components/mg acid)$^{1/n}$).

Fig. 1

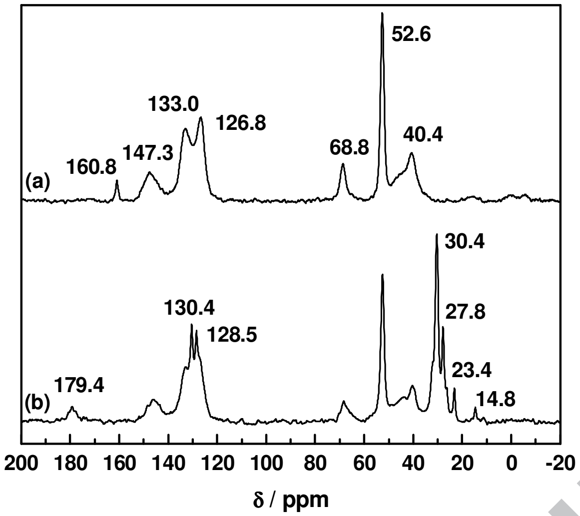

52.6
133.0
126.8
147.3
160.8
68.8
40.4
(a)
30.4
130.4
128.5
27.8
179.4
23.4
14.8
(b)
200 180 160 140 120 100 80 60 40 20 0 -20
δ / ppm

Fig. 2

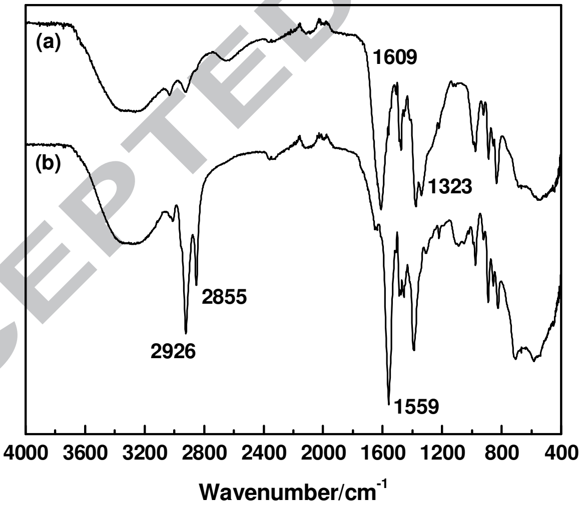

(a)
1609
(b)
1323
2855
2926
1559
4000 3600 3200 2800 2400 2000 1600 1200 800 400
Wavenumber/cm^{-1}

Fig. 3

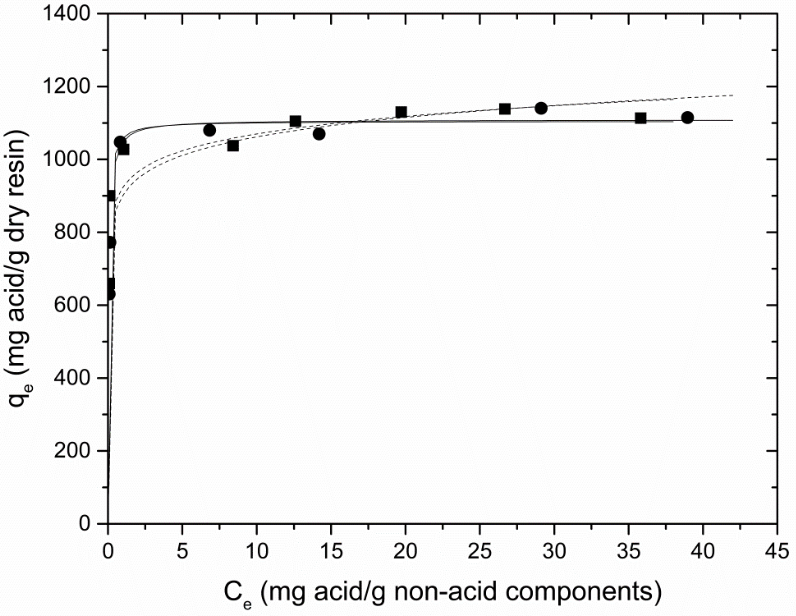

1400
1200
1000
800
600
400
200
0
0
5
10
15
20
25
30
35
40
45
q_e (mg acid/g dry resin)
C_e (mg acid/g non-acid components)

Fig. 4

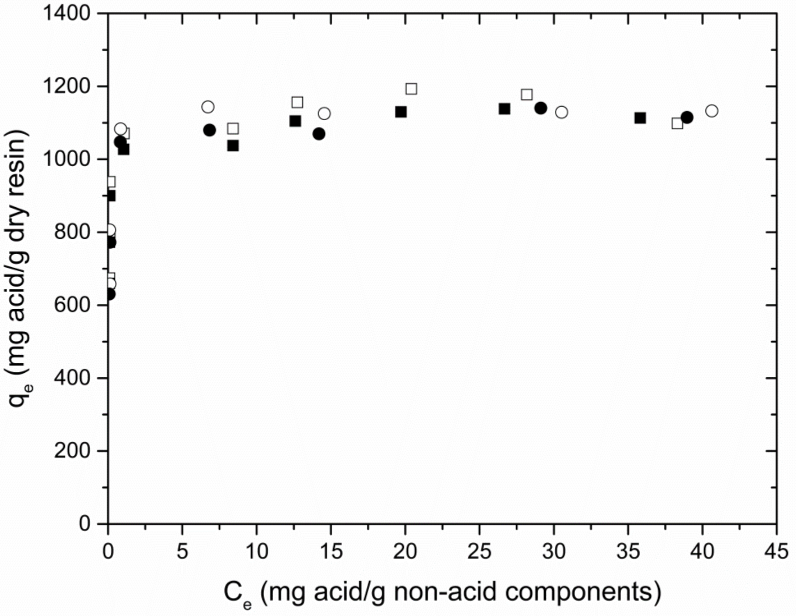

1400
1200
1000
800
600
400
200
0
0
5
10
15
20
25
30
35
40
45
q_e (mg acid/g dry resin)
C_e (mg acid/g non-acid components)

Fig. 5

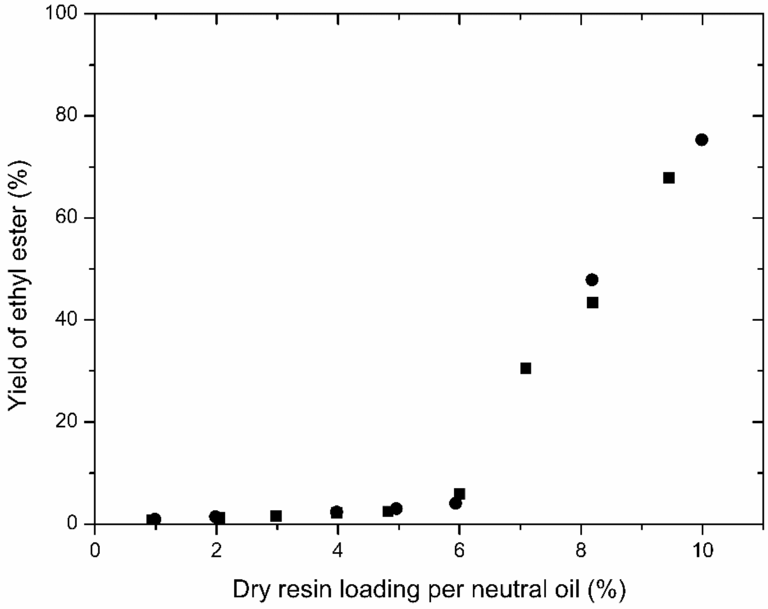

Yield of ethyl ester (%)
Dry resin loading per neutral oil (%)
0
20
40
60
80
100
0
2
4
6
8
10

Fig. 6

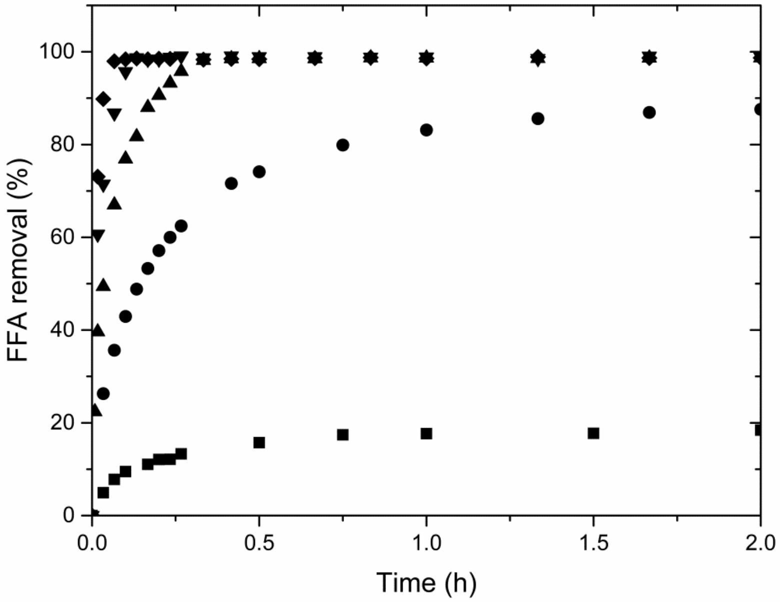

FFA removal (%)
Time (h)
0
20
40
60
80
100
0.0
0.5
1.0
1.5
2.0

Fig. 7

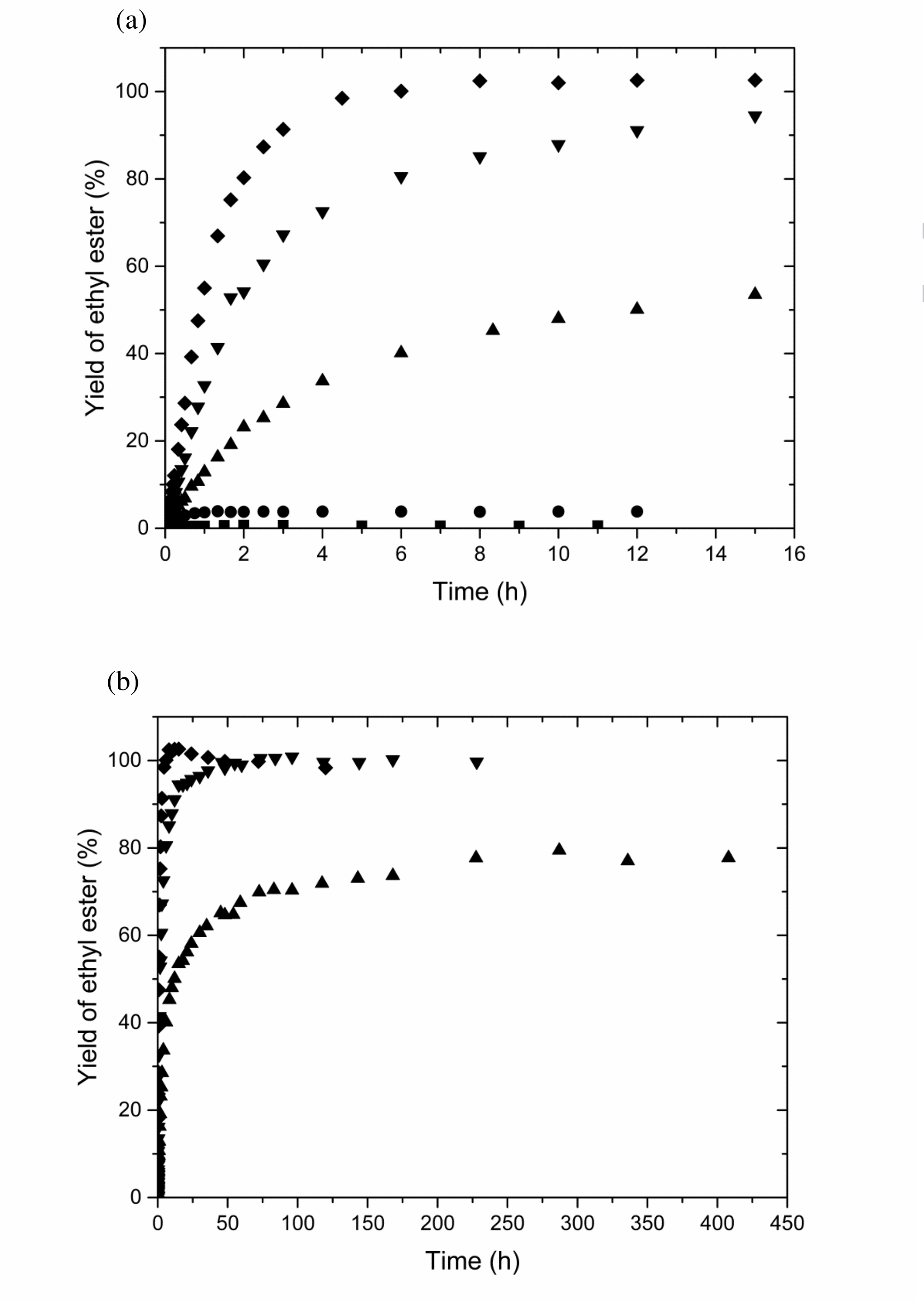

(a)
Yield of ethyl ester (%)
0
20
40
60
80
100
Time (h)
0
2
4
6
8
10
12
14
16
(b)
Yield of ethyl ester (%)
0
20
40
60
80
100
Time (h)
0
50
100
150
200
250
300
350
400
450

Fig. 8

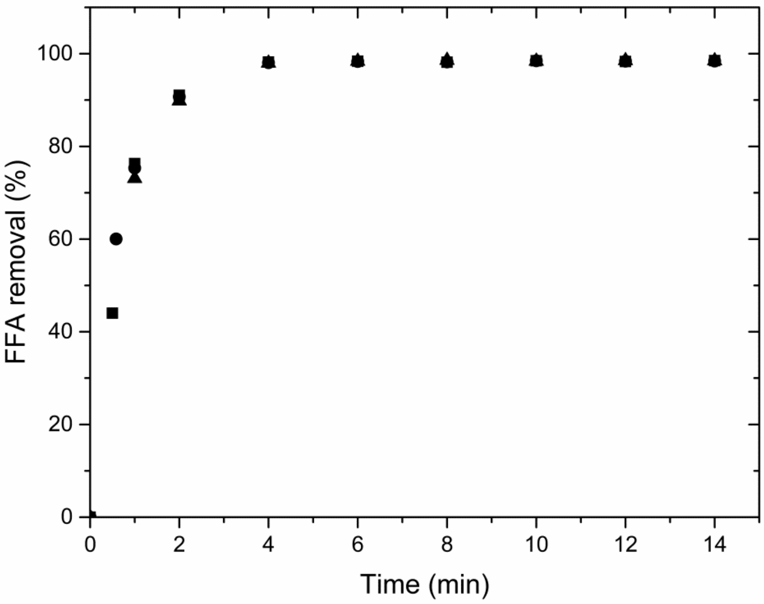

FFA removal (%)
0
20
40
60
80
100
0
2
4
6
8
10
12
14
Time (min)

Fig. 9

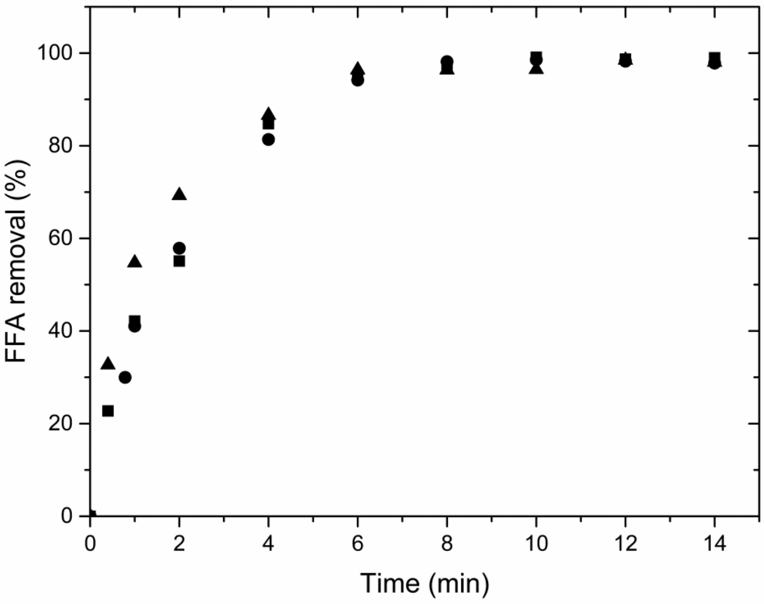

FFA removal (%)
0
20
40
60
80
100
0
2
4
6
8
10
12
14
Time (min)

Fig. 10

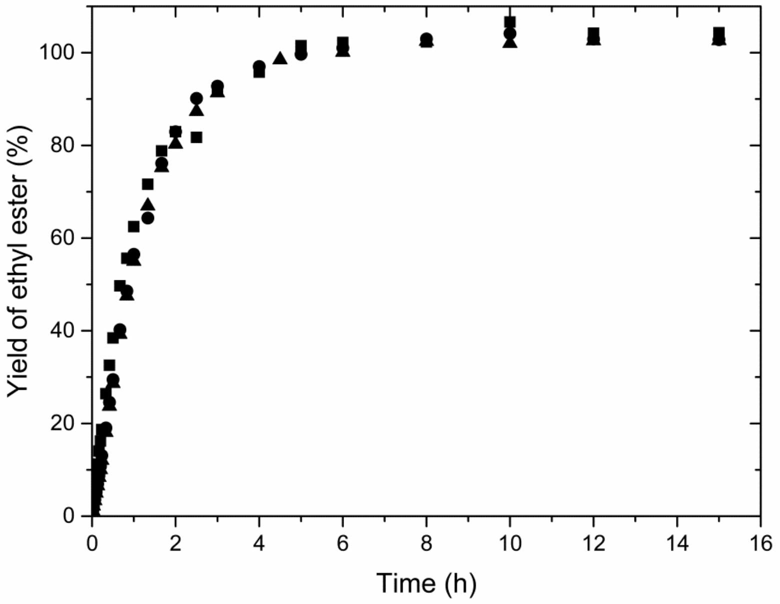

Yield of ethyl ester (%)
0
20
40
60
80
100
0
2
4
6
8
10
12
14
16
Time (h)

Fig. 11

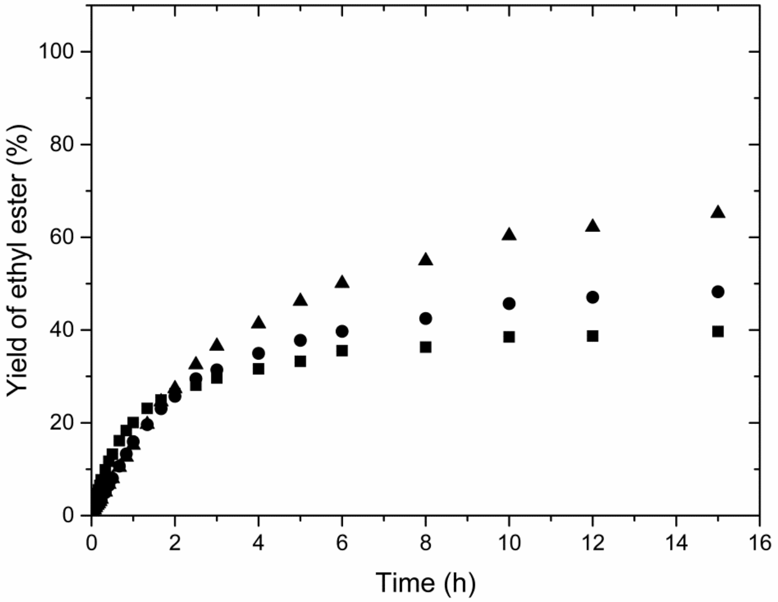

Yield of ethyl ester (%)
0
20
40
60
80
100
0
2
4
6
8
10
12
14
16
Time (h)

Fig. 12

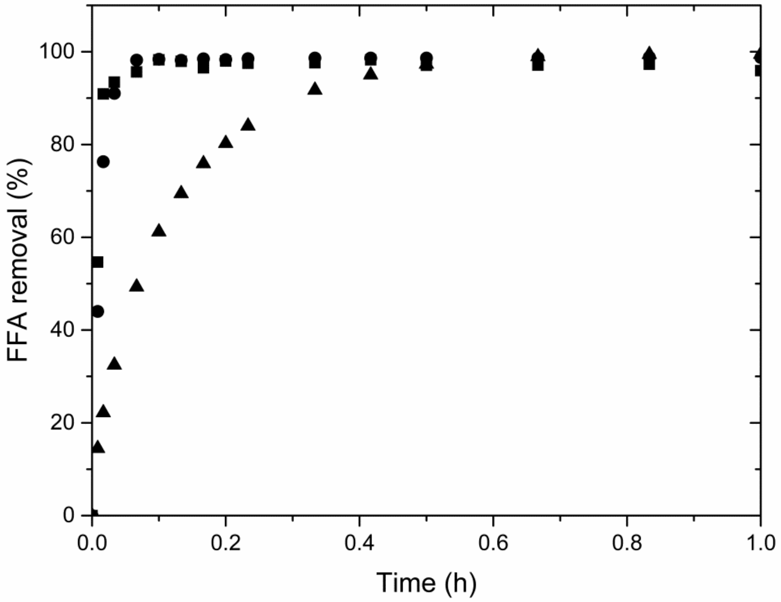

FFA removal (%)
0
20
40
60
80
100
0.0
0.2
0.4
0.6
0.8
1.0
Time (h)

Fig. 13

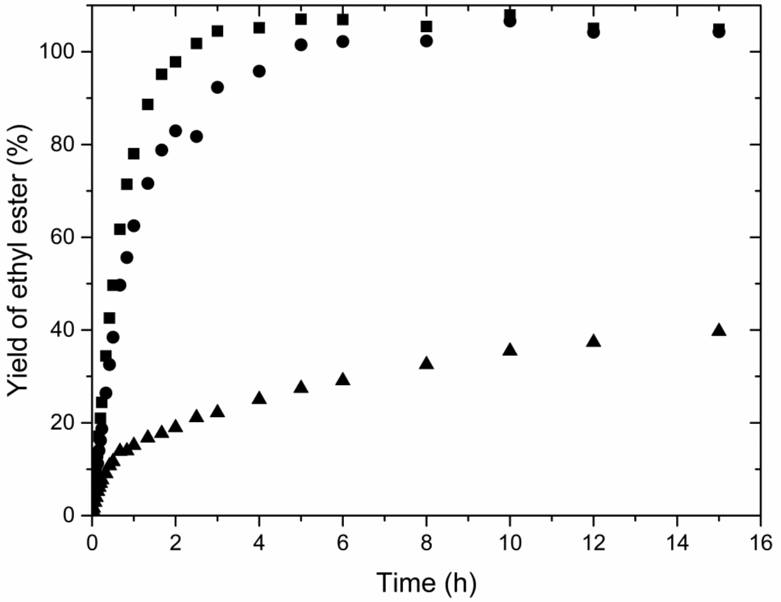

Yield of ethyl ester (%)
0
20
40
60
80
100
0
2
4
6
8
10
12
14
16
Time (h)

Fig. 14

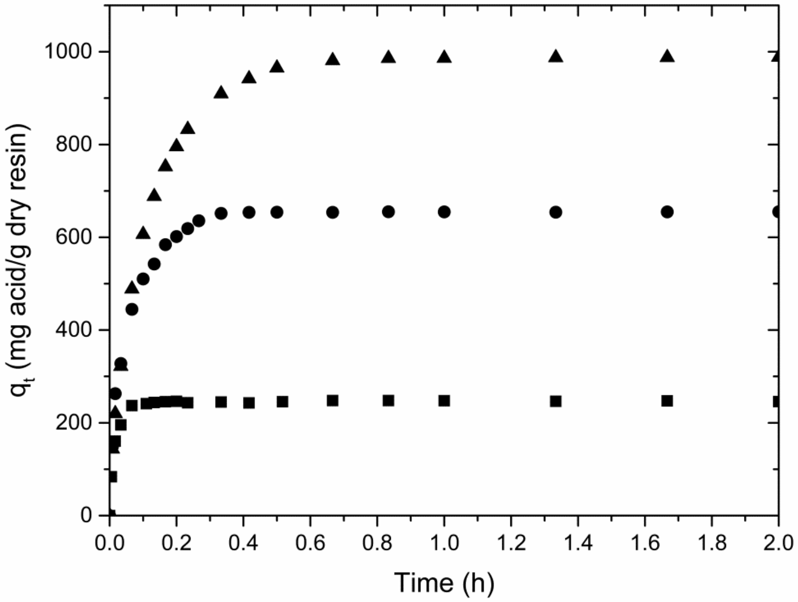

q$_t$ (mg acid/g dry resin)
0
200
400
600
800
1000
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
Time (h)

Fig. 15

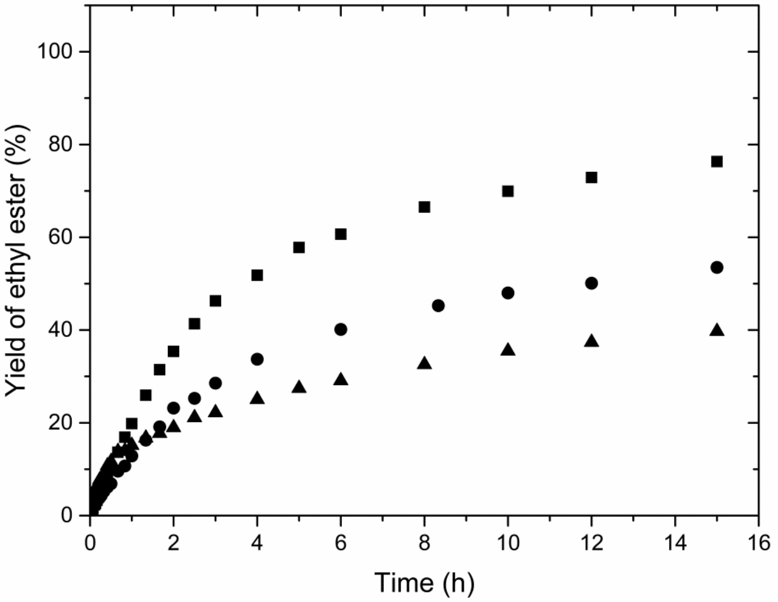
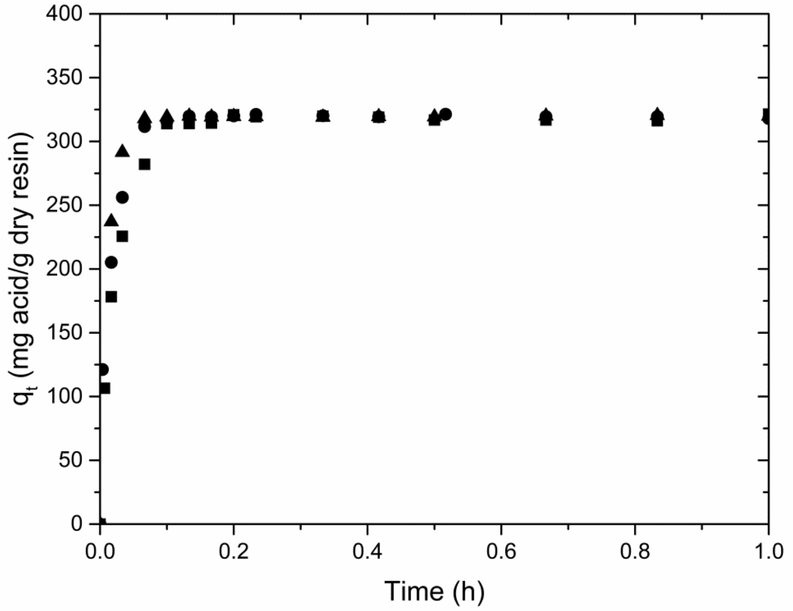
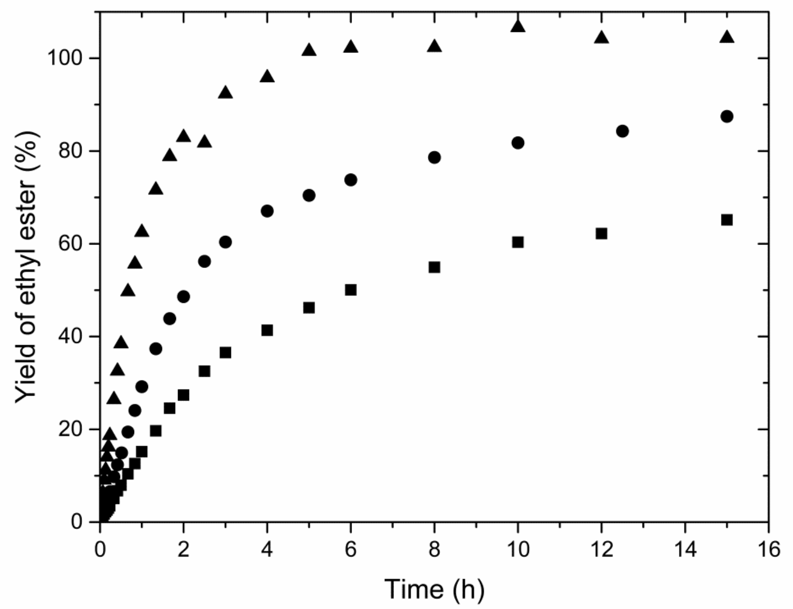

Yield of ethyl ester (%)
0
20
40
60
80
100
0
2
4
6
8
10
12
14
16
Time (h)

Fig. 16



q_t (mg acid/g dry resin)
0
50
100
150
200
250
300
350
400
0.0
0.2
0.4
0.6
0.8
1.0
Time (h)

Fig. 17



Yield of ethyl ester (%)
0
20
40
60
80
100
0
2
4
6
8
10
12
14
16
Time (h)

HIGHLIGHTS

- Deacidification in these systems can occur with high speed and efficiency.
- The adsorption of the FFAs disabled the active sites of the resin for catalysis.
- A satisfactory biodiesel production was possible with high resin loading.