



DEACIDIFICATION OF MACAUBA PULP OIL (*Acrocomia aculeata*) CATALYZED BY CATIONIC RESIN

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ABSTRACT: The traditional route of biodiesel production is based on the transesterification reaction, in which the main requirement is the use of low acidity raw material. It is known that the cost of raw material, such as soybean oil, has the largest contribution to the final price of biodiesel. Brazil has a huge potential for the use of others oleaginous plants, such as Macauba. However, the extractive way of harvest generates a raw material of high acidity. The objective of this study is to use a commercial cationic exchange resin as heterogeneous and reusable catalyst to esterify the free fatty acids content, reducing the acidity and making the Macauba oil suitable to transesterification process. The resin Purolite CTR275DR was evaluated in this study as esterification heterogeneous catalyst. The initial acidity of pulp oil was reduced from 40.8% to than 2.2% w/w, demonstrating the potential of the resin in the esterification of free fatty acids.

KEYWORDS: *Acrocomia aculeata*; esterification; cationic resin.

1. INTRODUCTION

The classic process for biodiesel production is based on a reaction called transesterification, in which a vegetable oil or animal fat, consisting mainly of triacylglycerols, reacts with alcohol (methanol, ethanol or other short-chain alcohol) in the presence of a catalyst generating molecules of biodiesel and glycerol (Knothe et al., 2005). For economic and technical reasons, it is used a homogeneous alkaline catalyst, usually sodium hydroxide or sodium methoxide (Miao et al., 2009).

Despite of the technical simplicity, there are restrictions in using alkali homogeneous catalyst, such as the use of low acidity raw material, up to 0.5% w/w of

oleic acid, and low water content. The reaction with oils with acidity levels up to 5% w/w also can be catalyzed by alkalis. However, a larger amount of catalyst should be added to compensate the formation of soap, a salt produced in the reaction of free fatty acid with the alkali, as shown in Figure 1. Furthermore, the high amount of soap formed during the reaction will affect the step of purification of the biodiesel, as it inhibits the phase separation between the products of the transesterification reaction, biodiesel and glycerol (Van Gerpen, 2005).

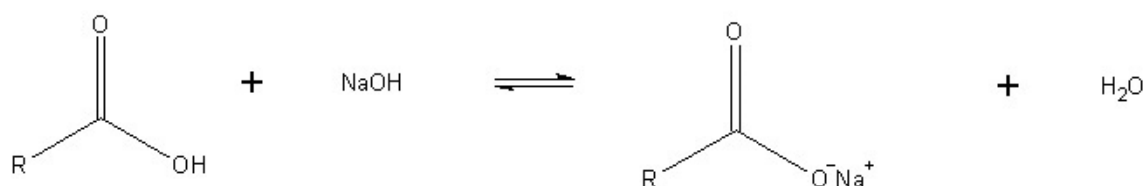


Figure 1 - Saponification reaction of free fatty acid with sodium hydroxide (Miao et al., 2009).

Macauba is a native perennial tree, largely found in Minas Gerais State and other regions in Brazil, with high oil productivity (4000-5000 kg/ha). However, the extractive way of harvest generates a raw material of high acidity, thus not suitable for biodiesel producing by conventional processes (Costa et al., 2009).

The acid catalysis is an alternative to solve the high acidity raw material problem. The acid catalyst does not introduce metal ions in the reaction system, preventing the saponification reaction. In parallel to transesterification, the acid catalyst promotes the esterification of free fatty acids, according to the reaction represented in Figure 2 (Jacobson et al., 2008). However, the transesterification reaction catalyzed by an acid catalyst, such as sulfuric acid, requires higher temperatures, lower speed reactions and excesses of alcohol reactant. Therefore, the acid catalysis is used only for the esterification of free fatty acids, as pretreatment step (Sharma and Singh, 2009).

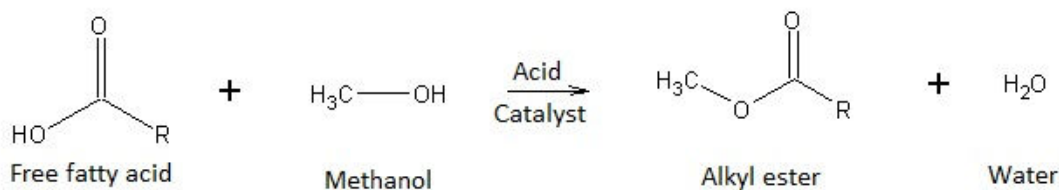


Figure 2 - Esterification reaction of the free fatty acids (Schuchardt et al., 1998).

After the esterification step, it is necessary to remove the homogeneous acid catalyst from the reaction medium. The acid neutralization using an alkali is the commonly used process, increasing the effluent generation. Therefore, in order to minimize this environmental problem, cationic resins have been studied as acid catalysts to promote the esterification reaction of free fatty acids content (Bianchi et al., 2009).

The cationic resins are cross-linked polymer matrices that have cation exchangers groups in its structure such as sulfonic acids. Porous resins with high heat resistance have been widely used as catalysts. The major advantages of its use are the easy removal from reaction medium and the reusability and the regeneration capacities (Bianchi et al., 2009). In general, commercially available cationic resins used as catalysts for esterification are composed of copolymers of styrene and divinylbenzene with sulfonic acid groups bonded to benzene as active sites. The catalytic activity is strongly dependent on the expansion property, since this property controls the access of reagents to active sites (Feng et al., 2010).

Esterification reactions catalyzed by the cationic resins Amberlite IR 120 H and Amberjet 1200 H were described in literature and the acidity of a sample of karanja oil (*Pongamia pinnata*) was reduced from 11 mg KOH / g to less than 2 mg KOH / g in reactions conducted at 60 °C, with the molar ratio of methanol to oil of 6:1 and 0.8% w/w of resin in 25 minutes (Bala et al., 2012).

Samples of lard with the addition of 5% to 7% w/w of oleic acid were esterified in the presence of the commercially available cationic resins Amberlysts 15d, 36d, 39W, 46W and 70w (macroporous cation exchange resin with -SO₃H as the active site) achieving conversions greater than 90%. The reactions were performed at 65 °C, catalyst/lard ratio of 10% by weight (Bianchi et al., 2009).

In the present study, commercial cationic resin Purolite CT275DR was tested as

catalyst for the esterification of free fatty acids contained in an Macauba oil, extracted from the pulp of the fruit of Macauba palm tree, with acidity of 40.8% w/w of oleic acid.

The alcohol used in this study was the ethanol since it is abundant in Brazil, produced from renewable source, by the fermentation of the juice obtained by sugarcane plantation. Methanol was only used for process comparisons purposes.

2. MATERIAL AND METHODS

The Macauba pulp oil with acidity of 40.8% w/w was supplied by the Macauba Laboratory installed on the Chemical Engineering Department of the Federal University of Minas Gerais. The alcohols used for esterification were the ethanol 99.3% and the methanol 99.8%. The cationic resin evaluated as catalyst was the CT275DR manufactured by Purolite Ion Exchange Resins, a cation exchange resin with sulfonic groups, with the polymer matrix of styrene and divinylbenzene, supplied in dry form, with less than 3% of moisture. The characteristics of the resin informed by the supplier are presented in Table 1.

Table 1 - Cationic resin used as catalyst in the present work.

Properties	CT275DR
Manufacturer	Purolite
Nature	Cationic
Type	Porous
Cross-link density (%)	-
Particle size (mm)	0.65 – 0.90
Density (g/dm ³)	1200
Exchange capacity (meq/m ³)	6.2 x 10 ³
Operating temperature (°C)	145 (H ⁺)

A rotary evaporator (FISATOM), whose vertical condenser and condensate collecting flask were replaced by a Liebig condenser with water circulation, was used as

a reactor. A rotation of 80 rpm was adopted in all tests to promote the stirring of reactants, catalyst and products. The rotary reactor is represented schematically in Figure 3. The reactor system was maintained in a bath with a controlled temperature. After the reaction, the resins were removed by vacuum filtration, the alcohol was recovered by vacuum distillation and phase separation was promoted by centrifugation. In all reactions conducted in this study, it was used 15 g of Macauba oil with 866 g/mol, value based on the typical fatty acid profile (Bora and Rocha, 2004).

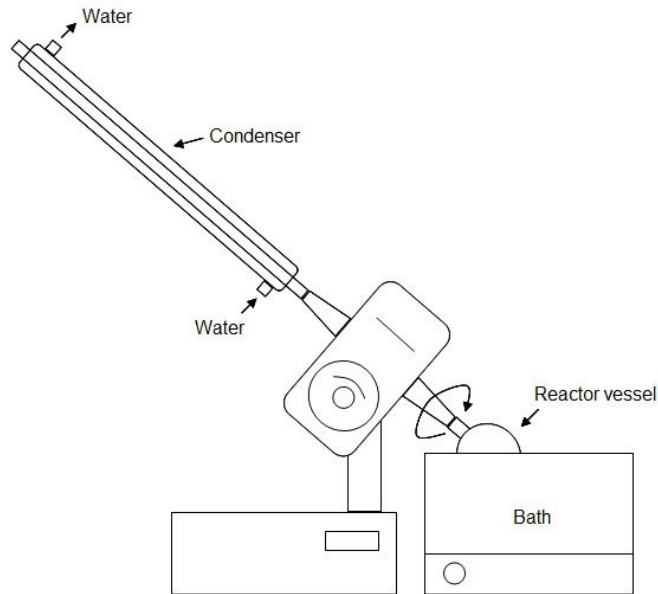


Figure 3 - Schematic representation of the rotary reactor, used in this study.

The free fatty acids conversion into alkyl esters was evaluated by gas chromatography (GC) and acid-base titration. The consumption of free fatty acids can be measured by titration while the production of alkyl esters can be measured by GC analysis. Both tests can be used directly as a conversion efficiency parameter. The acidity is measured through acid-base titration, according to methodology AOCS Cd3d-63.10. For the acid-base titration, it was used 25 ml of a solvent consisting of ethanol 99.5% and ethyl ether 99.5% in volume ratio of 2:1. Potassium hydroxide (KOH) 0.1 mol/L was used as the titrant, and phenolphthalein solution 1% as the indicator.

The content of alkyl esters by gas chromatography (GC) is the key feature in the evaluation of the reagent conversion. The test was performed on Perkin Elmer Clarus

600, according to EN/ISO 14103. The consumption of free fatty acids was monitored by acid-base titration with sodium hydroxide solution 0.1 mol/L as titrant and phenolphthalein, as indicator.

The deacidification tests followed a design of experiments with three factors, molar ratio alcohol:oil, reaction time and temperature, and two levels, using values based on preliminary tests, without replicate. The design of experiments is shown in Table 2, reactions E01 to E08. The amount of resin used in all tests was 20% w/w of the total weight of reagents and catalyst, according to preliminary studies performed in our laboratory. Under the same conditions of reaction E08, new reactions have been proposed for evaluating the use of methanol, E09 and E10.

The reaction with highest conversion was used to determine the kinetic model of the esterification reaction. To determine the kinetic model a sample was collected every hour to measure the conversion of free fatty acids into alkyl esters. This evaluation was performed by determination of the acid number by acid-base titration, and the concentration of ethanol was determined indirectly through the evaporation loss. The Macauba oil used has initial acidity of about 19.8% by weight of oleic acid.

Table 2 - Esterification experiments using Macauba pulp oil with an initial acidity of 40.8% w/w catalyzed by the resin CT275DR.

Reaction	Alcohol	Molar ratio alcohol:oil	Time (hours)	Temp. (°C)
E01	Ethanol	10	6	60
E02	Ethanol	10	6	90
E03	Ethanol	20	6	60
E04	Ethanol	10	8	90
E05	Ethanol	10	8	60
E06	Ethanol	20	6	90
E07	Ethanol	20	8	60
E08	Ethanol	20	8	90
E09	Methanol	20	8	90
E10	Methanol	20	8	60

3. RESULTS AND DISCUSSION

The results of the esterification experiments described in Table 2 are presented in Table 3.

Table 3 - Fatty acid alkyl esters content obtained by Gas chromatograph (GC) and acidity determined by acid-base titration.

Reaction	GC	Acidity
	% w/w	% w/w
Oil	-	40.8
E01	13.9	29.2
E02	46.5	4.1
E03	16.1	27.3
E04	51.7	3.3
E05	16.6	25.4
E06	38.6	7.5
E07	23.0	24.1
E08	51.7	2.2
E09	51.4	2.5
E10	28.2	12.0

The highest conversion was achieved in the most extreme condition tested, corresponding to the reaction E08, which is comparable to the result obtained by reacting E04, with the same conditions of temperature and reaction time, but with a lower molar ratio alcohol:oil. Hence, among the parameters tested, the bath temperature presented the greatest influence on the response and the molar ratio presented the smallest influence. Figure 4 presents the results of the esterification reactions graphically.

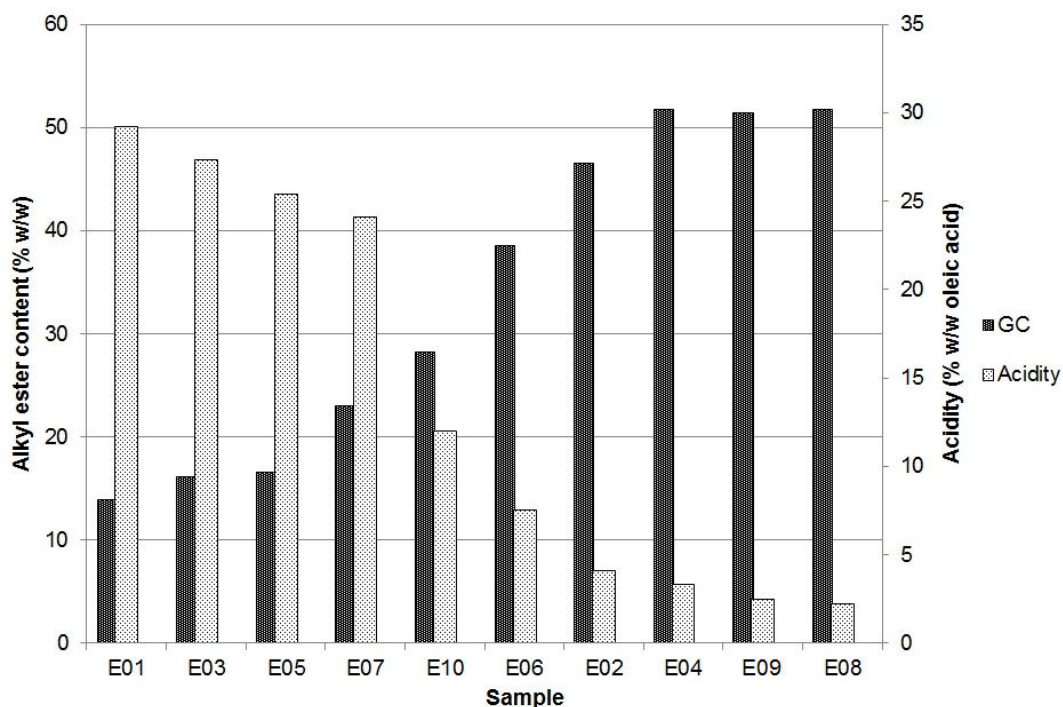


Figure 4 - Results of esterification reactions in order of decreasing acidity.

The comparison between ethanol and methanol tests at 60 °C, E07 and E10, indicates that the reaction with methanol reached better results than with ethanol, but both results provided low conversions. This large difference between the conversions requires more investigation. Considering the temperatures of 90 °C, E08 and E09, the results indicate satisfactory levels of acidity reduction with a slight advantage of ethanol on methanol performance. Considering the importance of producing biodiesel from renewable sources, this result is quite satisfactory.

Still, comparing the reactions E09 and E10, both performed with methanol with the same molar ratio, there is a considerable difference between acidity reductions. In E09, conducted at 90 °C, it was obtained a product with lower acidity and higher ester content. These results showed the importance of the bath temperatures in the conversion of free fatty acids.

The three parameters evaluated (molar ratio, bath temperature and reaction time) can potentially influence in acidity reduction. By increasing the alcohol content, the

equilibrium shifts toward the formation of products. The temperature contributes to reaction efficiency given the supplying the reactional medium with energy and increasing the miscibility between the reagents. Finally, the reaction time is relevant, as a kinetic parameter. Figure 5 presents the effect of the factor (molar ratio, reaction time and temperature) on acidity reduction. The greater the slope, the greater the influence of the factor in the efficiency of reaction. The bath temperature presented the greater influence on the response and the molar ratio the least influence. In addition, no interactions between factors was observed. Considering a 5% significance level, only the temperature influenced the response.

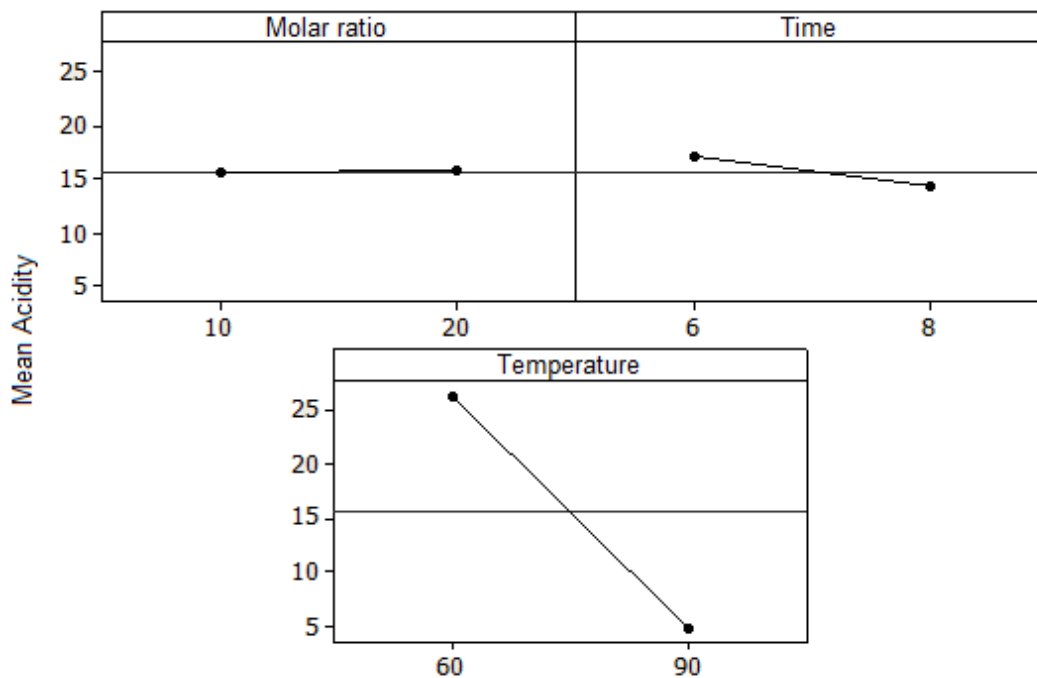


Figure 5 – Main effects in acidity.

The reaction E08 was repeated to determine its kinetic model. The reaction was conducted with a Macauba oil with initial acidity of 19.8% during 6 hours, with sampling every 1 hour. The Figure 6 presents the results of the acidity reduction in time. By means of the integral method of analysis of the reaction order, it was found that the batch presented a pseudo-second order behavior, as showed in Figures 7.

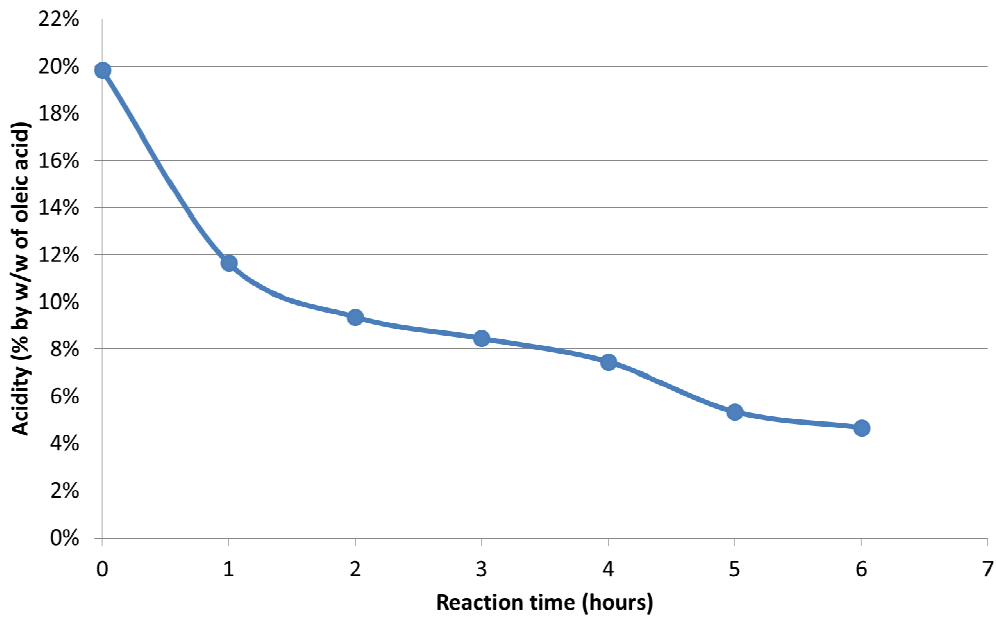


Figure 6 – Acidity reduction during 6 hours of esterification reaction.

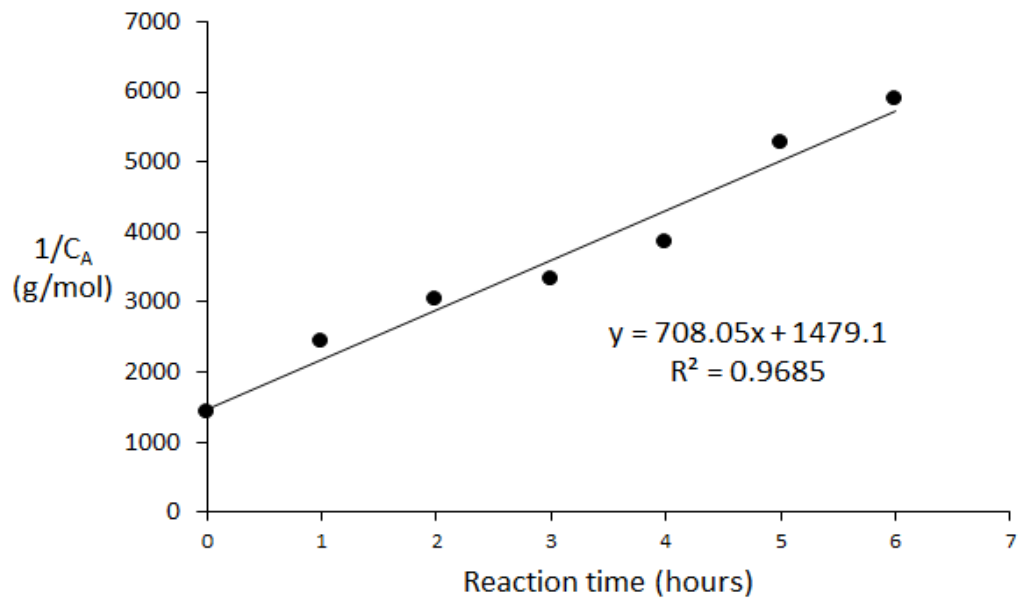


Figure 7 – Pseudo-second order reaction behavior concerning the free fatty acids content, C_A.

Considering a pseudo-second order reaction, the rate constant, k , is given by the slope of $1/C_A$ vs. time. Hence, through the experimental data and the linear regressions, the rate constant is $708.05 \text{ g}\cdot\text{mol}^{-1}\cdot\text{h}^{-1}$. The kinetic model can be expressed as the following:

$$r_A = \left[708.05 \left(\frac{\text{g}}{\text{mol}\cdot\text{h}} \right) \right] C_A^2 \quad (1)$$

With r_A is expressed in $\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ and C_A in $\text{mol}\cdot\text{g}^{-1}$.

Concerning the reusability of the resin, the conversion of the free fatty acids remained close to the original value after five batches without washing or regeneration steps of the resin. The results indicate that there is no significant reduction of catalytic activity of the resin, which keeps efficient for all batches, as can be seen in Figure 8.

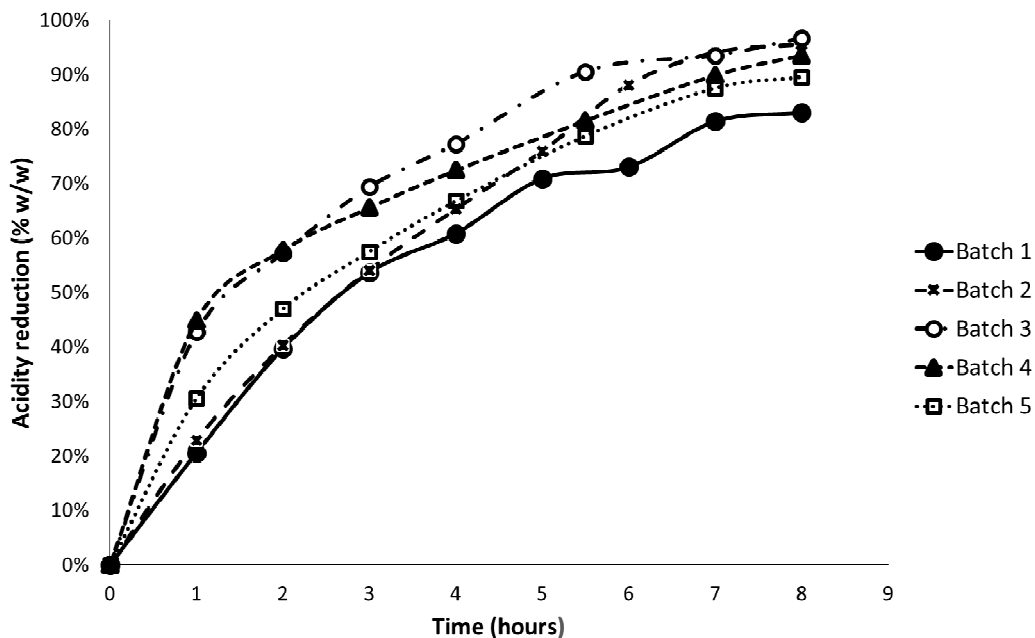


Figure 8 – Resin reusability evaluation (Rezende et al., 2015).

4. CONCLUSION

Esterification reactions catalyzed by cationic resin achieved satisfactory reduction in the oil acidity in a sample of Macauba pulp crude oil with initial acidity of 40.8% w/w. The largest reduction was achieved in the most extreme condition tested, the

molar ratio ethanol:oil of 20:1, bath temperature of 90 °C and reaction time of 8 hours, resulting in a final acidity of 2.2% w/w. It was observed that temperature is a key factor in the reaction efficiency.

Under the experimental conditions studied, samples with initial acidity of 19.8 %, the kinetic model showed second order behavior in the concentration of free fatty acids, considering the constant concentration of ethanol. The constant average rate was 708.05 g.mol⁻¹.h⁻¹. The five batches showed no significant drops in catalytic activity of the resin.

It was showed that the cation exchange resins can be an alternative with great potential as catalysts for the esterification of free fatty acids, which can be used as a pre-treatment of raw materials with high acidity in biodiesel production.

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