CHEMICAL ENGINEERING TRANSACTIONS
VOL. 65, 2018
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet
Guest Editors: Eliseo Ranzi, Mario Costa

ISBN978-88-95608- 62-4; **ISSN** 2283-9216

Esterification of Crude "Macaúba" Oil *(Acrocomia aculeata)* Using Amberlyst 15 as a Heterogeneous Catalyst Performed in Reactor Parr

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The "macaúba" (*Acrocomia aculeata*) is a Brazilian palm tree that represents a promising alternative for the production of biodiesel. The kernel and the almond of the fruits are rich in oil. Its oil has interesting physicochemical characteristics for the production of biodiesel. It consists mainly of triacylglycerols and small amounts of mono and diacylglycerols, and it has a high content of unsaturated fatty acids, mainly oleic acid. However, it has a high content of free fatty acids which prevents reactions with basic catalysis for biodiesel production. The use of solid catalysts to improve the biodiesel production processes is considered as a promising alternative in this case. In addition, the solid catalysts have the highest reaction rate when compared to acid catalysts. The aim of this study was to obtain ethyl esters of crude oil from *A. aculeate* with high acid value (45.3 mg KOH g^{-1}), using heterogeneous catalyst, with low reaction temperature. The reactions were done in an under-pressurized Parr 4843 reactor. For the reaction, the factorial design is 2 elevated to 2 and response surface methodology was used. The variables studied were: temperature (T), molar ratio (MR) (ethanol:oil) and catalyst Amberlyst 15 (C, wt%). The response was obtained into yield (%) of ethyl esters and conversion (%) of free fatty acid, which were quantified by gas chromatography (GC). The response surface indicated the reaction at temperature 80-100 °C, molar ratio ethanol:oil 9.0:1 and catalyst 9-11 wt% presented an yield in 32.8% of fatty acid ethyl esters (FAEE) and 72.0% of conversion, with 48.8 of selectivity index. The Amberlyst 15 catalyst showed little selectivity for yield in terms of FAEE, but a greater conversion of free fatty acids (FFAs) to the respective ethyl esters occurred. The surface response graph indicated that the reaction medium at temperature 60-70 °C, ethanol:oil 8.0:1-9.0:1 and catalyst 2-4% wt provided 83.8% of FFA conversion. This result is expected for oils with high FFA content, since conversion occurs at lower temperatures, while good yields occur at elevated temperatures.

1. Introduction

The conventional production of commercial biodiesel is based on the use of edible energy crops such as soybean oil, canola, coconut, palm and sunflower oil. However, it is necessary to find new raw materials which are not competitive with food production crops (Ma and Hanna, 1999; Lim et al., 2010, Pirola et al., 2014). "Macaúba" (*Acrocomia aculeata*) is a Brazilian palm tree with high oil productivity that can reach six ton per hectare per year (Nucci et al., 2008, Silva and Andrade, 2011). It is mainly composed of triacylglycerols and small amounts of mono- and diacylglycerols and it has a high content of unsaturated fatty acids (76.2%), mainly oleic acid (52-55%) (Pires et al., 2013, Souza et al., 2016). It is essential that the acidity levels of the oil vary from 0.5 to 2.0 (wt%) for conventional biodiesel production processes (Wang, 2006). In the case of oils with FFA more than 6 (wt%), it is not possible to use basic catalysis for biodiesel production (Lotero, 2005). Acid heterogeneous catalysts can simultaneously perform esterification of FFAs and transesterification of triacylglycerides (Helwani et al., 2009, Tesser et al., 2010, Raia et al., 2017). The main advantages related to the use of solid acid catalysts for biodiesel production are the fact that they are insensitive to the high content

of FFAs present in the oil (Kulkarni and Dalai, 2006, Jitputti et al., 2006). The most commonly used solid catalysts for the esterification reactions are ion exchangers, such as Amberlyst 15, which are synthetic, solid polymeric compounds. In addition, it is important to note that the use of resins with a high ion exchange capacity and low water solubility can offer several advantages for the process (Jeffery et al., 1992, Yadav and Thathagar 2002, Helwani et al., 2009). Therefore, the aim of this work was to obtain under-pressure Fatty Acid Ethyl Esters (FAEE) from macaúba oil with a high content of free fatty acids without previous treatment, using a heterogeneous catalyst Amberlyst 15, using an experimental design 2^2.

2. Experimental

2.1 Obtaining ethyl esters

The macaúba (*Acrocomia aculeata*) pulp oil was acquired from the Association of Small-Scale Producers in the city of Riacho Dantas de Monte Carlos – Minas Gerais State, Brazil. The oil was stored at -4°C until its use in esterification reaction, and showed high acid value, 45.3±0.32 mg KOH g^{-1}. The physicochemical properties of the oil were previously reported by Souza et al.., 2016. Anhydrous ethanol 99.8% and the catalyst Amberlyst 15 resin (Dow Chemical) were used. To determine the optimal reaction conditions, response surface methodology was used to evaluate the FAEE yield and conversion as the response variable. The esterification reactions were carried out in a Parr 4843 reactor according to Souza et al.. (2016) using constant pressure at 70 psi and stirring velocity 700 rpm and reaction time of 4 h. Then, the reaction mixture was evaporated at 60°C under reduced pressure to eliminate the alcohol excess. Glycerol was then separated by decantation and the ethyl esters layer was then washed with water at 90°C. Three washes were performed, using 50 mL of water each. After decanting again, the ethyl esters were subjected to a rotary evaporator at 80°C under vacuum to remove moisture. Ethyl esters were quantified by GC as described below by comparisons of retention times with standards. Methyl tricosanoate (23:0) was used as internal standard. The FFA value was determined by the titrimetric method determined by Eq. (1) (Raia et al.., 2017). Titration procedure was used to calculate the conversion of oleic acid to the corresponding ester, using a 0.1 mg KOH g^{-1} standard solution, according to Eq. (2) (Park et al.., 2008a).

$$Free\ fatty\ acid\ (mg\ KOH\ g^{-1}) = \frac{V.f.5.61}{P} \quad (1)$$

$$Conversion\ (\%) = \frac{FFA_I - FFA_F}{FFA_I}.100 \quad (2)$$

,

where V is the volume of 0.1 mol L^{-1} NaOH (mL), *f* is the 0.1 mol L^{-1}. NaOH correction factor and P is the sample mass (g).

2.2 Chromatographic analysis

Ethyl esters were derivatized as previously described (Hartman and Lago, 1973) to improve volatility. Analyses were carried out according to the Ce 2-66 methodology (AOCS, 2004), as previously described (Souza et al.., 2016). Varian CP-3800 gas chromatograph (GC), equipped with a flame ionization detector (FID) containing a capillary column measuring 30 m x 0.25 mm (BP - X70 - SGE) was used. Helium was the carrier gas with a 1:10 split ratio for samples injection. Analysis was performed by setting the temperature of the column, starting at 110ºC, and heating up to 160ºC with an 8ºC.min^{-1} rate, and up to 230ºC with a 3.5ºC min^{-1} rate. The detector temperature was maintained at 220ºC and the injector temperature at 260ºC.

2.3 Experimental design

Three main variables (catalyst amount, temperature and ethanol:oil molar ratio) were studied (Souza et al.., 2016). Central composite rotational design (CCRD) planning methodology was employed (triplicate) for response surface studies, as shown in Table 1.

2.4 Statistical analysis

The statistical (ANOVA and non-linear regression model fit) and data response surface analyses were done using the software Statistica 7.1® (2005).

Table 1: Levels of central composite rotational design planning

Variables	Levels		
	-1	0	1
C – Catalyst (%)	2	6	10
T – Temperature (ºC)	60	80	100
MR – Molar ratio ethanol:oil (wt%)	3	6	9

3. Results

The experimental design DCCR 2^2, together with the surface response methodology, allowed 11 experiments with 3 replicates of the central point, obtaining the results of fatty acid ethyl esters yield (FAEE yield) in the solution and conversion of the free fatty acids to ethyl esters as shown in Table 2. The FAEE yield and conversion data were analysed by Statistica 7.1® software to obtain the regression model. ANOVA test was also performed and the response surfaces were obtained, in which the regression equation for FAEE yield (Equation 3) and conversion (Equation 4) was obtained.

$$Y_{YIELD} = 23.300 + 8.491X_{RM} + 17.620X_T + 13.030X_C + 1.640X_{RM}X_T + 5.350X_{RM}X_C + 0.620X_TX_C \quad (3)$$

$$Y_{CONVERSION} = 66.193 + 28.137X_{RM} + 6.460X_T - 0.465X_C - 4.342X_{RM}X_T - 13.377X_{RM}X_C - 17.902X_TX_C \quad (4)$$

From the experimental data, the condition that showed highest FAEE yield was for all maximum X_{T1}, X_{C1}, X_{MR1} and for the conversion was two for minimum X_{T-1} and X_{C-1} and one for the maximum $XMR_{-1.68}$.
To test the fit of the model, the regression equation and the determination coefficient adjusted ($R^2_{adjusted}$) were evaluated. In this case, the coefficient of determination for FAEE yield was $R^2 = 0.9698$, while for conversion the coefficient of determination was $R^2 = 0.6673$.
Table 2 shows the analysis of variance (ANOVA) of the regression model and the significance of the terms for FAEE yield and conversion.

Table 2: ANOVA parameters for FAEE yield and conversion obtained from crude "macaúba" pulp oil.

FAEE Yield (wt %)				
Variation Source	DF	Sum of squares	Mean square	F_{calc}
Model	6	2338.02	389.67	97.39
Error	12	48.01	4.0008	
Total fixed	18	2386.03	$F_{0.05;\,6.12} = 2.996$	
Conversion (wt%)				
Model	6	5427.86	904.643	9.018
Error	12	1546.692	128.891	
Total fixed	18	6974.553	$F_{0.05;\,6.12} = 2.996$	

Souza et al., 2016 studied the esterification reaction of "macaúba" oil with a high acidity index, using acid catalyst, and reached a yield higher than 90% for ethyl esters at temperatures close to 120ºC. In the same way, it was also observed in this work that high temperatures favor the reactions with heterogeneous catalyst. However, it is important to point that during the process, produced water hinders the yield of FAEE (Park et al., 2010). Table 3 shows the DCCR experimental design for FAEE yields and conversion.
The Amberlyst-15 is a promising solid catalyst in the esterification/transesterification reaction of oils with high free fatty acid content, and presented great FFA conversion, consequently reducing the acid value of the oil (Park et al., 2008b). In this case, the catalyst showed small selectivity index for FAEE yield, but there was a greater conversion of free fatty acids (FFA) to ethyl esters of free fatty acids. 83.8% of the FFA of "macaúba" pulp oil was converted to the corresponding biodiesel.
The Pareto diagram (Figure 1A), showed p-values greater than 0.05, indicating that the variables temperature (T), molar ratio ethanol:oil (RM), catalyst (C) and the ratio-catalyst interaction are statistically significant variables at 95% confidence. It can also be observed that the variable that most influenced the reaction medium for the FAEE yield was the temperature. In addition to this, conversion was mostly influenced by the molar ratio (ethanol:oil) (Figure 1B).

Table 3: Matrix of the experimental planning and variables for analysis of the ethyl esters production from "macaúba" pulp oil

Run	Variables			Results		
	Temperature (ºC)	Catalyst (%)	MR ethanol:oil (wt%)	FAEE Yield (%)	Conversion (%)	IS
1	(1) 100	(1) 10.0	(1) 9.0:1	32.8	72.0	48.8
2	(1) 100	(1) 10.0	(-1) 4.0:1	31.1	44.3	45.1
3	(-1) 60	(1) 10.0	(1) 9.0:1	13.0	71.4	14.9
4	(-1) 60	(1) 10.0	(-1) 4.0:1	17.0	67.9	20.4
5	(1) 100	(-1) 2.0	(1) 9.0:1	27.9	87.3	38.6
6	(1) 100	(-1) 2.0	(-1) 4.0:1	25.3	65.8	33.8
7	(-1) 60	(-1) 2.0	(1) 9.0:1	14.5	83.8	16.9
8	(-1) 60	(-1) 2.0	(-1) 4.0:1	7.90	20.6	8.57
9	(0) 80	(0) 6.0	(0) 6.0:1	18.1	75.6	22.1
10	(0) 80	(0) 6.0	(0) 6.0:1	15.9	71.1	18.9
11	(0) 80	(0) 6.0	(0) 6.0:1	19.9	76.4	24.8

MR – Molar ratio ethanol:oil (wt%); IS = Selectivity Index (IS = FAEE Yield/Conversion)

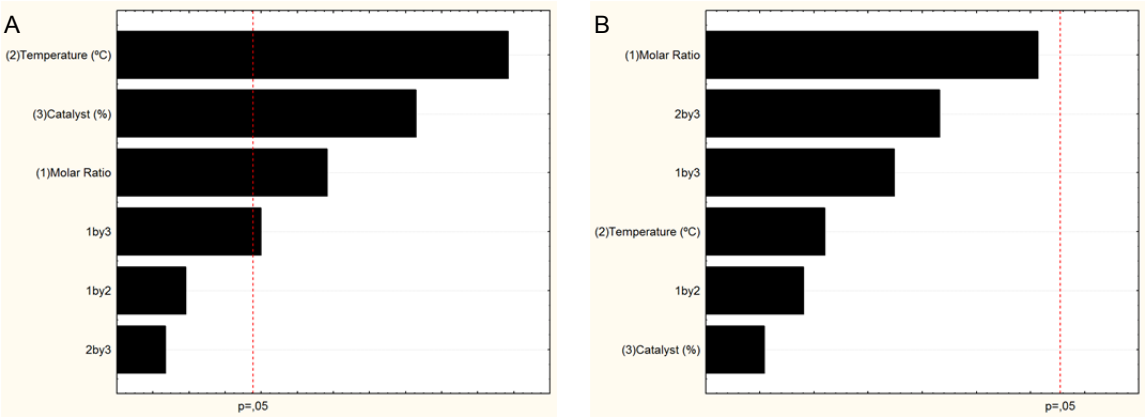

Figure 1: Pareto graph resulting from CCRD planning, for FAEE yield (A) and conversion (B)

The response surface graphs shown in Figures 2A and 2B represent the FAEE yield and conversion obtained as a function of temperature and ethanol:oil molar ratio. It was observed that the FAEE yield increases with the temperature, probably by the increase of the collisions between the molecules participating in the reaction. The better results were obtained for temperatures at 100°C and the molar ratio ethanol:oil above 7:1 (wt%). For the conversion, a response greater than 80% was observed at temperature at 55°C in the molar ratio higher than 7:1 (wt %).

Figures 2C and 2D show the FAEE yield and conversion as a function of the amount of catalyst and ethanol:oil molar ratio. A low FAEE yield was observed at the concentrations studied; the optimum region for the conversion was observing using molar ratio ethanol:oil of 8:1 and catalyst amount higher than 2.0%.

When analyzing Figures 2E and 2F, which in turn illustrates the FAEE yield and conversion as a function of temperature and catalyst amount, it can be seen that high temperature is necessary to achieve a higher FAEE yield. The best conditions were observed for catalyst at about 10% and temperature above 90°C. It was observed an inverse correlation between the amount of catalyst and temperature for conversion.

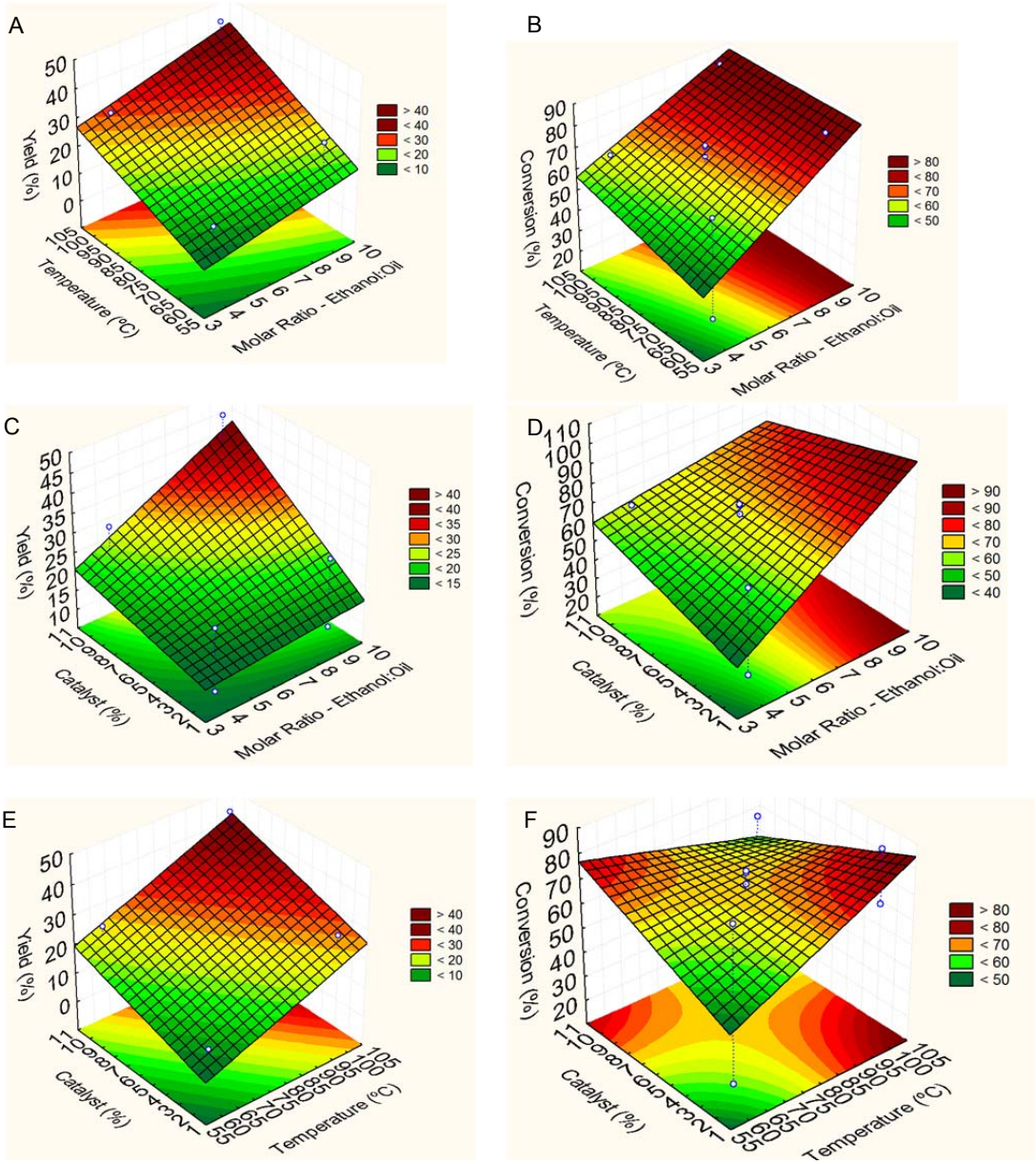

Figure 2: Response surface graphs of (A, B) temperature (°C) and molar ratio ethanol:oil (wt%); (C, D) catalyst (%) and molar ratio ethanol:oil (wt%); (E, F) catalyst (%) and temperature (°C) resulting from the DCCR factorial design that evaluates the effects of each variable for FAEE yield and conversion.

4. Conclusions

Experimental investigations showed that the catalyst Amberlyst 15 can be used for esterification and transesterification reactions of “macaúba” oil with high acid content. The catalyst promoted a greater conversion of free fatty acids (FFAs) to their respective ethyl esters. The surface response graph indicated that high reaction temperature improved the efficiency of the process. In the conditions studied, the use of the Amberlyst 15 resin catalyst showed to be promising for biodiesel production using the macaúba pulp oil, however more studies are necessary to improve the fatty acid ethyl esters (FAEE) yield.

Acknowledgments

The authors are thankful for the financial support and fellowships provided by CAPES (Coordenação de Aperfeiçoamento de Pessoal de Nível Superior).

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