MACAUBA OIL AS AN ALTERNATIVE FEEDSTOCK FOR BIODIESEL: CHARACTERIZATION AND CONVERSION TO BIODIESEL BY THE SUPERCRITICAL METHOD

Helmut J. Navarro-Díaz*[1], Samantha L. Gonzalez[1], Bruno Irigaray[2], Ignacio Vieitez[2], Iván Jachmanián[2], Bruno A. M. Carciofi[1], José Vladimir de Oliveira[1]

[1] EQA/UFSC, Departamento de Engenharia Química e Engenharia de Alimentos
Universidade Federal de Santa Catarina
Florianópolis, Santa Catarina, Brasil

[2] Laboratorio de Grasas y Aceites, Departamento de Ciencia y Tecnología de Alimentos, Facultad de Química
Universidad de la República
Montevideo, Uruguay

Email: helmutnavarro@gmail.com

Abstract. Macauba palm (*Acrocomia aculeata*) is native from tropical areas of South-America and provides very high oil productivity (1500-5000 kg-oil/hectare/year). Macauba oil is non-edible and presents low production costs, thus the use of this oil as an alternative feedstock for biodiesel production is attractive due to economic and environmental reasons.

In this work, different samples of Brazilian macauba pulp oil obtained by pressing were characterized and the ester yield achieved using a catalyst-free continuous process under supercritical alcohols was determined.

Oils analysis showed that the major fatty acid was oleic acid (49.6-72.7%); the amount of FFA was very high (37.4-65.4%); samples contained glycerides (7.4-16.5% TAG, 14.2-16.8% DAG and 1.0-3.4% MAG); and moisture by Karl-Fisher was 1.0%. Due to the extremely high content of FFA this kind of feedstock cannot be converted using conventional alkali-catalyzed transesterification, but the supercritical method is known to show high efficiencies when applied to acid raw materials. Therefore, oil was processed in a continuous reactor using supercritical methanol or ethanol and the effects of temperature, pressure, oil to alcohol molar ratio, water concentration and flow rate on process efficiency were evaluated.

The higher ester content achieved in reactions with supercritical methanol was 78.5% while with supercritical ethanol was 69.6%, due to the presence of non-convertible impurities in the feeding oil, hence corresponding to actual conversions of 98.0% and 86.9%, respectively.

Results demonstrate that macauba oil might be a potential alternative for biodiesel production, though purification steps should be taken into account to achieve biodiesel specifications. Process economics are shown.

Keywords: Macauba oil, biodiesel production, supercritical method, catalyst-free continuous process.

1. Introduction

Macauba (*Acrocomia aculeata*) is a palm native from South American tropical forests. An important amount of oil is obtained from the coconuts of this palm, its productivity yields between 1500-5000 kg of oil per hectare per year, which is the second largest productivity after palm oil (*Elaeis guineensis*). The oil content in the pulp of the coconut varies from 30 to 78% with a mean value of 65%. The oil content in the seeds varies from 35 to 69% with a mean value of 48%. Macauba oil is non-edible and presents low production costs, thus the use of this oil as an alternative feedstock for biodiesel production is attractive due to economic and environmental reasons [1-5].

Production of biodiesel has gained increased attention because of global environmental concerns and the fact that alternative renewable energy sources comprise nowadays a matter of great interest. Biodiesel is defined as mono-alkyl esters of long chain fatty acids derived from vegetable oil or animal fats, a clean-burning biofuel that can be produced entirely from renewable sources [6]. Vegetable oils have been considered to date the most attractive renewable source for biodiesel production due to its environmental benefits [7].

Currently, large scale production of biodiesel is performed through alkali-catalyzed transesterification of vegetable oils in the presence of a short chain alcohol to form fatty acid esters and glycerol [8, 9]. Such conventional production technique presents negative effects on the transesterification reaction caused by the presence of free fatty acids (FFA) or water in the feedstock [10-13].

The non-catalytic transesterification of vegetable oils in supercritical alcohols, so-called supercritical method, has received growing interest because the quality of the products generated and environmental benefits [14-18]. With such technique high yield of esters can be achieved and has been proved to be more tolerant to the presence of high contents of water and FFA, allowing the use of various types of vegetable oils, even waste oils [19-24] and animal fats [25], for which alkaline-catalyst transesterification is unsuitable [26, 27]. The use of cheaper feedstock for biodiesel production is a key point towards economic competitiveness of this biofuel. With the supercritical method waste oils, raw vegetable oils and rectified alcohol can be used for biodiesel production. The extent of these reactions needs to be more studied along with the appropriated purification steps to determine technical and economical process viability [28].

The Association for the Advancement of Cost Engineering International (AACEI) indicates the suitability of cost of manufacturing (COM) for business plans. COM can be defined as the weighted sum of five factors according to Equation 1, where, FCI: fixed cost of investment, COL: cost of operating labor, CRM: cost of raw material, CWT: cost of waste treatment, and CUT: cost of utilities [29].

$$COM = 0.304\,FCI + 2.73\,COL + 1.23\,(CRM + CWT + CUT) \quad (1)$$

As in the case of other industrial process, the main proportion of total biodiesel COM corresponds to CRM, from which the oil cost is the major contributor. For conventional catalyzed biodiesel production, the oil expenses can easily overcome 80% contribution to COM [30]. Meanwhile, with the supercritical method using waste vegetable oils, the contribution rise above 70% of biodiesel COM [31].

In this work, different samples of Brazilian macauba pulp oil obtained by pressing were characterized and the ester yield achieved using a catalyst-free continuous process under supercritical alcohols was determined.

2. Materials and Methods

2.1. Materials

Samples of macauba oil were obtained from processing units of macauba coconut from the state of Minas Gerais in Brazil. The oils were obtained by pressing followed by filtration to separate impurities. Four different macauba pulp raw oils were analyzed together with one sample of unrefined oil from the seed. Identification of oil samples is presented on Table 1.

Methanol and ethanol were purchased from Merck with a purity of 99.9%. Other solvents, standards and reagents used in derivatization step, necessary for the analysis, were purchased from Sigma-Aldrich.

Table 1. Identification of macauba unrefined oils

Sample	Description	Harvest year
Pulp 1	Macauba pulp oil	2010
Pulp 2	Macauba pulp oil	2011
Pulp 3	Macauba pulp oil	2011
Pulp 4	Macauba pulp oil	2012
Seed 1	Macauba seed oil	2012

2.2. Oil characterization

Several analyses were performed for the characterization of the macauba oil. The chemical groups were qualitative determined by Thin Layer Chromatography (TLC). Peroxide index was determined by titration

according to method AOCS Cd 8-53. Moisture was determined by Karl Fisher titration, according to method AOCS Ca 2e-84, using a DL 50, Mettler-Toledo titrator. The acid value was determined by titration according to method AOCS Cd 3d-63.

Distribution of Triacylglycerides (TAG), diacylglycerides (DAG) and Monoacylglycerides (MAG) were determined according to method UNE-EN 14105. GC analysis was made on a Shimadzu GC-14B equipment with capillary column Optima-1 TG (Machery-Naguel 10m x 0.32mm x 0.1μm) was employed. The carrier gas was Nitrogen and column head pressure was 70kPa. The temperature was programmed as indicated by the norm.

The fatty acid composition of the oil was determined by Gas Chromatography (GC) analysis after esterification by hot methylation. Shimadzu GC-14B equipment with FID and capillary column SGE BPX70 was used. The temperature program was set to heat from 160ºC to 230ºC at rate of 4ºC/min and then holding for 10 min. Helium was used as the carrier gas.

Determination of maximum ester conversion of macauba oil was made by GC. Proceeding was similar as described above but using fatty acid C17:0 as internal standard for quantification of esters produced. The method was validated with refined sunflower and soybean oils achieving 99% ester conversion.

2.3. Reactions

The equipment used for the reactions was the same reported in a previous work [32]. The tubular reactor has a volume of 70 mL. All reactions were conducted in continuous mode and ester samples were collected after reaching the steady state. No catalyst was used. Reactions were conducted in supercritical methanol and supercritical ethanol to produced fatty acid methyl esters (FAME) and fatty acid ethyl esters (FAEE), respectively.

The process parameters studied were the reaction temperature (300, 325, 350 and 375ºC), the reaction pressure (100, 150 and 200 bar), the oil:alcohol molar ratio (1:20, 1:30 and 1:40), the water addition with respect to alcohol weight (0, 5 and 10wt%) and the flow rate of reaction mixture measured at the entrance of the reactor (1.0; 1.5; 2.0; 2.5 and 3.0 mL/min).

Esters quantification was made according to method UNE-EN 14103/2001, which account only the esters of fatty acids from C14:0 to C24:0, using ester C17:0 as internal standard. The GC analysis was performed on a Shimadzu apparatus equipped with automatic injector, Split, FID and capillary column Rtx-Wax (30m x 0.25mm x 0.25μm). Temperature program starts at 120ºC holding for 1 min, heating at 15ºC/min until 180ºC and holding for 2 min, heating at 5ºC/min until 250ºC and holding for 2 min. Carrier gases were Nitrogen a synthetic ar.

3. Results and Discussion

Characterization of oils by TLC is shown in Figure 1. An important amount of free fatty acid (FFA) is noted in all samples tested.

In Table 2 are shown the composition in fatty acids of macauba oils studied. It's clearly observed that oleic acid (C18:1) is the major acid on all pulp oil samples. The seed oil, as expected, has a different profile with important amounts of short chain fatty acid like lauric acid (C12:0). As regulation for biodiesel accounts esters formed with fatty acids from C14:0 to C24:0, mixtures between pulp and seed oils are undesired. The fatty acid profile of pulp 2 sample suggests contamination with seed oil.

Results of oil characterization analyses are summarized in Table 3. TAG value was found inferior than expected (about 95%) and the acid value, that signifies FFA content, was very high. These values indicate hydrolysis of TAG into DAG, MAG and even FFA perhaps due to enzymes present in the fruit. All peroxide index values were below the maximum recommended by the Brazilian regulation, 15meq peroxide/kg [33].

For a mixture of esters of fatty acids be named as biodiesel it must has at least 96.5% of esters in mass [34]. Maximum ester conversion of unrefined macauba oils varied from 80 to 90% (Table 3), which can be caused by the amount of compounds non-convertible to esters present in these raw oils. Thus, since none of the maximum ester conversion reached the minimum value commanded, it can be predicted that appropriate purification steps after the reaction stage must be established.

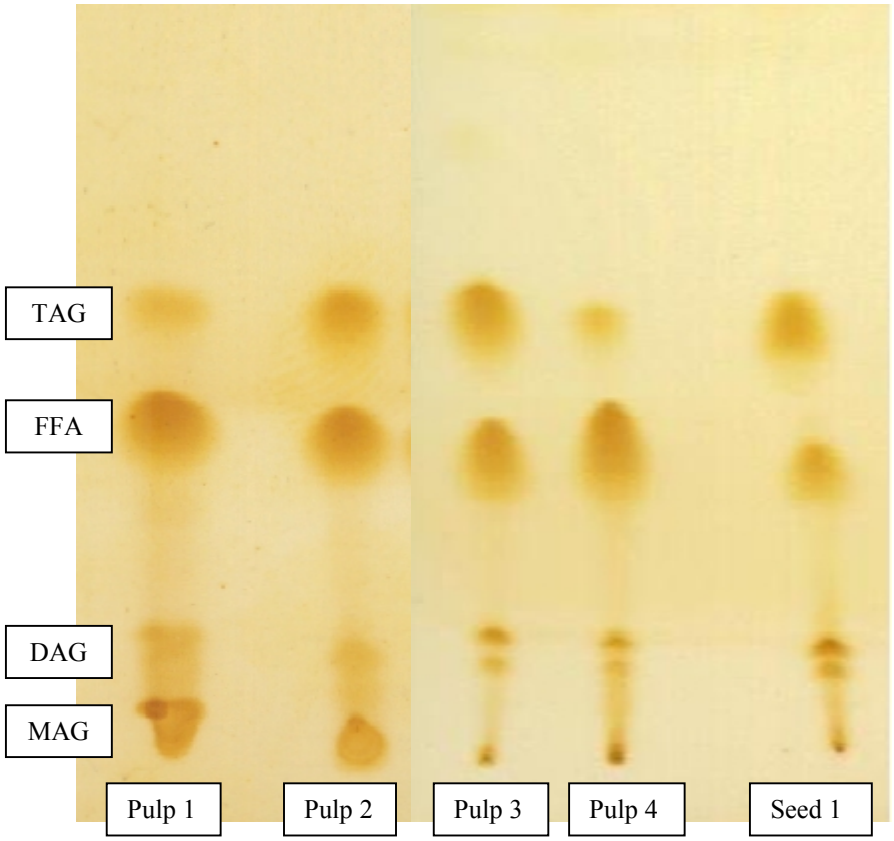

Figure 1. Chemical groups identify by TLC on macauba unrefined oils.

Table 2. Fatty acid composition of unrefined macauba oils

Fatty acid	Pulp 1 [%]	Pulp 2 [%]	Pulp 3 [%]	Pulp 4 [%]	Seed 1 [%]
C6:0	-	-	-	-	0,2
C8:0	-	-	0,2	0,3	3,1
C10:0	-	-	0,2	0,1	2,4
C12:0	0,7	13,3	1,7	1,0	24,6
C14:0	0,3	3,6	0,6	0,3	4,9
C16:0	22,2	16,1	15,6	12,0	8,4
C16:1	4,2	3,2	3,5	1,6	1,6
C18:0	1,9	2,2	1,6	2,3	2,6
C18:1	58,0	49,6	57,7	72,7	26,9
C18:2	9,7	8,7	16,5	5,5	24,8
C18:3	0,6	0,2	1,2	0,5	0,2
C20:0	-	-	0,1	0,2	0,3
C20:1	-	-	-	-	-
Total	97,5	96,7	98,9	96,5	100,0

Table 3. Characterization analyses of unrefined macauba oils

Analysis	Pulp 1	Pulp 2	Pulp 3	Pulp 4	Seed 1
Peroxide index [meq peroxide/kg]	4,4	-	0,4	0,8	5,8
Moisture [%]	0,9	1,0	-	-	-
Acid value [%]	56,3	45,1	37,4	65,4	21,7
MAG [%]	3,4	1,9	1,0	3,4	0,8
DAG [%]	14,8	16,8	15,1	14,2	24,2
TAG [%]	7,4	11,7	45,9	16,5	52,3
Maximum ester conversion [%]	80,1	88,8	91,6	82,7	87,2

The high acid value of macauba oil samples suggests that esters were produced via two major mechanisms, transesterification of glycerides and esterification of FFA. Also, it is expected that water produced by FFA esterification could hydrolyze glycerides among others reactions [19]. Which means that byproducts of all parallel reactions occurring in this process can affect ester production yield and kinetics, because of these situations the kinetic parameters are difficult to be estimated in order to propose a theoretical model for predict them.

Conversion reactions were assessed using the Pulp 1 macauba oil sample with methanol and with ethanol to produced, respectively, FAME and FAEE. When analyzed the influence of process parameters over the yield of esters, it was found that reaction temperature and incoming flow rate to reactor, which is related to reaction time, had the greater effects. Changes in the other parameters did not produce significant influence on ester production. In Figure 2 are presented the group of results that yielded higher FAME, which were achieved at the intermediate reaction conditions of all parameters but temperature. In the same manner, the higher ester yields from reactions of macauba oil in supercritical ethanol were obtained among the intermediate conditions; Figure 3 shows FAEE results at the same conditions presented in Figure 2. Such best results showed in Figure 2 and 3 would indicate that process parameters were optimized. Though, this last statement requires more study and confirmation, it is suitable as a first approach to understand the needs of the esters of fatty acids (biodiesel) production process using macauba oil as a feedstock via the supercritical method.

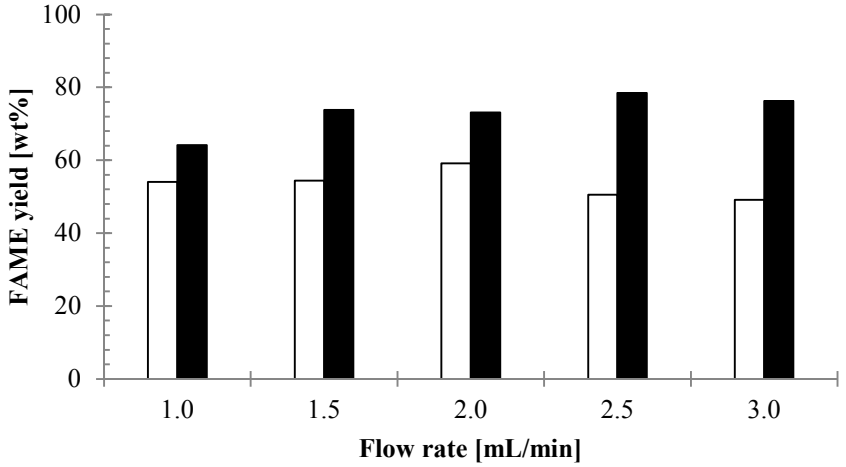

Figure 2. FAME yield from macauba unrefined oil via continuous esterification/transesterification reactions in supercritical methanol at 15 MPa, 1:30 oil:methanol molar ratio, 5 wt% water added to alcohol, 1.0 to 3.0 mL/min incoming flow rates to reactor and temperatures of 598 K (□) and 648 K (■).

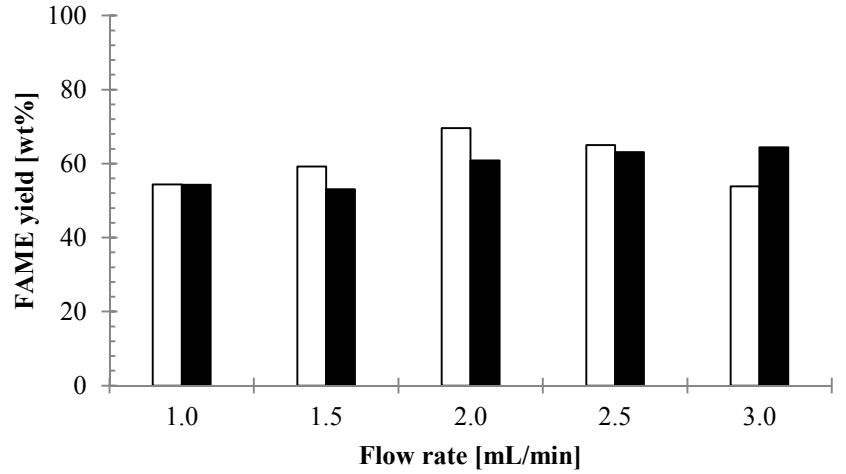

Figure 3. FAEE yield from macauba unrefined oil via continuous esterification/transesterification reactions in supercritical ethanol at 15 MPa, 1:30 oil:ethanol molar ratio, 5 wt% water added to alcohol, 1.0 to 3.0 mL/min incoming flow rates to reactor and temperatures of 598 K (□) and 648 K (■).

By comparing the ester yield results obtained at identical reaction conditions for both alcohols tested, it was observed, as a general rule, that reactions in supercritical methanol yielded more ester content than reactions in supercritical ethanol. The same tendency was seen for the highest ester value achieved for both alcohols, although the reaction conditions were different. The 78.5% FAME yield was attained at 648 K, 15 MPa, 1:30 oil:methanol molar ratio, 5wt% water added to alcohol and 2.5 mL/min flow rate. Meanwhile, the 69.6% FAEE yield was obtained at 598 K, 15 MPa, 1:30 oil:methanol molar ratio, 5wt% water added to alcohol and 2.0 mL/min flow rate. As maximum ester conversion of the Pulp 1 sample of unrefined macauba oil was found as high as 80.1%, it might be established that with the best reaction conditions the process efficiencies for FAME production was as high as 98.0% and for FAEE was 86.9%.

Proper purification steps are yet to be studied in order to set up the whole project for biodiesel production through the supercritical method in continuous mode using alternative non-edible feedstock as unrefined macauba oil. For this matter, purification stages, such as centrifugal separators, vacuum dryers and distillation columns, which are commonly used by current industry performing conventional reaction methods, could be chosen.

Analyzing the process economics, purification steps are going to have a significant contribution to biodiesel COM, because the final reaction mixture did not achieve the minimum ester content required (96.5%). Despite that fact, the CRM will still represent an important portion on total production cost. This is a very important issue to explore especially in a country like Brazil, where about 80% of biodiesel is produced from soybean oil and the actual price of crude macauba oil (US$ 600 to US$ 800 per ton) is lower than soybean oil (around US$ 1100 per ton).

The growing biodiesel production requires the use of new technologies and alternative raw materials to maintain the growing demand of this biofuel. The data presented in this paper is part of a more complete work that attempts to assist into the completion of the new production requirements.

4. Conclusions

The quality and composition homogeneity of unrefined macauba oil will depend on its provenance, extraction method and storage, although, similarities were found in the samples tested. The characterization analyses of this oil show that its use for biodiesel production without pretreatment stages can only be possible by the supercritical method operating in continuous mode. Some peculiarities of this oil, such high acid value and the content of non-convertible to ester compounds, prevent the treatment by conventional catalyzed methods without a previous conditioning of the feedstock.

The esters of fatty acids from macauba oil achieved higher yields when produced with supercritical methanol than with supercritical ethanol. However, minimum ester content was not reached, so purification steps are required. Benefits of macauba oil, such high productivity, non-edibility and low prices, arouse industrial interest for using this oil as an alternative feedstock to produce biodiesel.

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