Transesterification of Brazilian Vegetable Oils with Methanol over Ion-Exchange Resins

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ABSTRACT: The transesterification of several Brazilian vegetable oils with methanol was carried out at 60°C in the presence of several ion-exchange resins having different structures. The vegetable oils used were from Babassu coconut, corn, palm, palm kernel, and soybean. The effect of the methanol/oil mole ratio and the influences of the structure of the ion-exchange resin and the type of vegetable oil used on the catalytic activity of the ion-exchange resins were investigated. The resins used were Amberlyst 15, Amberlyst 31, Amberlyst 35, and Amberlyst 36. Amberlyst 15 produced the best results for the transesterification of vegetable oils. The methyl ester yield is higher for palm kernel oil and Babassu coconut oil than for soybean oil, probably owing to their higher content of shorter-chain FA. Therefore, it was shown that the catalytic activity of the resin depends on the FA composition of the vegetable oil employed.

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KEY WORDS: Acid catalysis, fatty acid methyl esters, ion-exchange resins, methanolysis, transesterification, vegetable oils.

Vegetable oils are a renewable energy source. However, the direct use of vegetable oils in diesel engines is problematic owing to their high viscosity and low volatility (1). Many different procedures have been considered to reduce the high viscosity of vegetable oils. Transesterification with methanol is a possible choice, since many physical characteristics of FAME are similar to those of diesel fuel (1). Moreover, FAME are raw materials for the production of fatty alcohols and can be used as lubricants, additives for diesel fuels, printer's ink solvents, emulsifiers, or stabilization agents in cosmetics, detergents, plasticizers, perfumery, and flavor chemicals and as precursors to pharmaceuticals, agrochemicals, and other fine chemicals (2).

In transesterification of vegetable oils, TG molecules are converted into fatty esters and glycerol. The overall transesterification reaction can be represented by Equation 1.

$$\text{Triglyceride (TG)} \xrightleftharpoons{\text{catalyst}} 3\ \text{RCO}_2\text{R}' + \text{glycerol} \qquad [1]$$

Transesterification consists of a sequence of consecutive reversible reactions wherein the TG is successively transformed into DG, MG, and finally into glycerol and fatty alkyl esters. The stoichiometry of this reaction thus requires 3 mol of alcohol per 1 mol of TG to give 3 mol of fatty alkyl ester and 1 mol of glycerol (1,3). However, in practice, a higher alcohol/TG mole ratio is used to increase ester production. Although the esters are the desired products of the reactions, glycerol recovery is also important for economic reasons owing to its numerous applications in different industrial processes (2,3).

The alcohols used most frequently are methanol and ethanol. Several parameters, including the type of catalyst (alkaline or acid), alcohol/vegetable oil mole ratio, temperature, and purity of the reactants (main contaminants are water and FFA), have an influence on the transesterification reaction (1,3). Homogeneous acid catalysts can be used to catalyze the transesterification reaction; the most commonly used ones are strong mineral acids or *p*-toluene sulfonic acid, mainly owing to their low cost and when it is necessary to carry out a prior esterification of FFA present in vegetable oil (4,5). The disadvantage in using homogeneous catalysts is their miscibility in the reaction medium, which causes separation problems. Moreover, at higher acid catalyst concentrations, equipment corrosion and secondary reactions can occur. Hence, the use of heterogeneous catalysts such as zeolites and ion-exchange resins have clear advantages since they are noncorrosive and are easy to separate from the reaction mixture; furthermore, no washing of the ester is required, presenting fewer disposal problems (6–8).

Ion exchange resins are convenient catalysts for etherification, esterification, and transesterification reactions ,and a large number of applications have been reported in the literature (9,10). Symmetrical dicarboxylic acids with 4–14 carbon atoms gave selective corresponding monoesters in high yields in esterification reactions catalyzed by strongly acidic ion-exchange resins (11). The cationic acid resins are active at low temperatures and, owing to their molecular sieve action, produce few by-products and may be highly selective (12).

In the present paper, the effects of the structure of different ion-exchange resins and vegetable oil composition on the catalytic activity of the resins were investigated in the transesterification reaction. Several types of Brazilian vegetable oils including Babassu coconut, corn, palm, palm kernel, and soybean were studied in transesterification with methanol.

EXPERIMENTAL PROCEDURES

Materials. Commercial soybean oil (Liza, Rio de Janeiro, RJ, Brazil), corn oil (Salada, Rio de Janeiro, RJ, Brazil), Babassu

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coconut oil (VETEC, Rio de Janeiro, RJ, Brazil), palm kernel oil (Agropalma, Bélem, Pará, Brazil) and palm oil (Agropalma) were used without further purification. Methanol, THF, hexane, and H_2SO_4 were commercial-grade products purchased from VETEC.

The beads of sulfonated styrene-divinylbenzene (DVB) copolymers (Amberlyst 15, Amberlyst 31, Amberlyst 35, and Amberlyst 36) were obtained in the acid form from Rohm and Haas (São Paulo, Brazil). Prior to use, Amberlyst 15, Amberlyst 35, and Amberlyst 36 resins were dried at 105°C under vacuum for 12 h, and Amberlyst 31 was swelled in methanol for 12 h before use.

Characterization. The surface areas and pore volume of the cation-exchange resins were determined from nitrogen adsorption isotherms at the normal boiling temperature of liquid nitrogen following the BET method (Brunauer–Emmett–Teller) (13). The adsorption isotherms were obtained in a Micromeritics ASAP (Accelerated Surface Area and Porosimetry), model 2010. The cation-exchange capacity was determined by converting weighed resin samples from the H^+ form to the Na^+ form with 1 M NaCl and titrating the liberated H^+ with standard 0.1 N NaOH (14).

Analysis of the vegetable oils. The FFA present in the vegetable oils were determined by titration with standard NaOH (15). We found 0.74 mg KOH/g oil for Babassu oil, 0.50 mg KOH/g for corn oil, 0.31 mg KOH/g for palm oil, 0.21 mg KOH/g for palm kernel oil, and 1.74 mg KOH/g for soybean oil.

The FA composition of the oils was determined through chromatographic analysis of the transmethylated oils. A methanol/oil molar ratio of 10:1, with potassium carbonate as catalyst, was used, and the reaction time was 1 h at the boiling temperature of methanol. The products were analyzed by GC by using an HP-5890 gas chromatograph series II coupled with an HP-5972 mass spectrometer equipped with a 30 m DB-5 capillary column (Varian, Raritan, NJ), with helium as the carrier gas (2 mL/min). The GC injector temperature was 260°C, and the oven temperature was programmed from 60 to 250°C at 8°C/min.

Reaction procedure. All experiments were performed in a 100-mL two-necked flask equipped with a reflux condenser and magnetic stirrer. The reactions were carried out using different alcohol/oil molar ratios (120:1, 300:1, 400:1, 600:1, or 800:1) and 1 g of resin in the presence of a co-solvent (THF). The mixture was refluxed at the b.p. of the alcohol, and 0.2-µL samples were removed periodically from the reaction mixtures over a period of 8 h.

Isolation and analysis of products. The samples were washed with water, and the organic phase (esters) was extracted with hexane, dried with magnesium sulfate, and, after removal of solvent, submitted to ^{1}H NMR (Bruker Avance DPX-200 spectrometry) analysis in $CDCl_3$, using tetramethylsilane as the internal standard. The conversion of the oils to a mixture of methyl esters was determined as described in the literature (16,17).

RESULTS AND DISCUSSION

Properties of ion-exchange resins. The properties of the treated sulfonated poly (styrene-co-divinylbenzene) resins used are listed in Table 1. Amberlyst 15, Amberlyst 3,5 and Amberlyst 36 are macroporous resins and have an average pore diameter of 200–257 Å, surface area of 35–45 m^2/g, and an ion-exchange capacity of 4.7–5.4 meq H^+/g dry resin. Amberlyst 31 resin is a gel type resin.

Composition of vegetable oils. Of the vegetable oils used in this work, soybean oil has the highest concentration of FFA (1.74 mg KOH/g oil). The FA composition of the vegetable oils studied is listed in Table 2. The main constituent of Babassu coconut and palm kernel oils is the saturated lauric acid (12:0). Corn and soybean oils have the highest content of the di-unsaturated FA, linoleic acid (18:2), and palm oil contains mainly the saturated FA palmitic acid (16:0) and the monounsaturated FA oleic acid (18:1).

Effect of reactant mole ratio. One of the most important variables affecting the ester yields is the alcohol to vegetable oil mole ratio used. The stoichiometry of this reaction is 3 mol of alcohol per mol of TG to yield 3 mol of fatty ester and 1 mol of glycerol. Other workers have used molar ratios up to 100:1 particularly in acid-catalyzed reactions (3). In this work, the effect of a 100:1 molar ratio on ester yield was studied, mainly because of the large dependence on yield. The results obtained from the transesterification reaction of Babassu coconut oil with methanol, in which the mole ratio was varied from 120:1 to 800:1 (methanol/TG), using the same amount of Amberlyst 15 resin (1 g) (reaction followed for 6 h), are shown in Figure 1. For mole ratios of 300:1, 400:1, 600:1, and 800:1, the conversion to esters after 6 h of reaction time are similar; and for mole ratios lower

TABLE 1
Physical Properties of Cation-Exchange Resins

Physical property	Amberlyst 15	Amberlyst 35	Amberlyst 36	Amberlyst 31
Shape	Beads	Beads	Beads	Beads
Surface area (m^2/g)	43.5	35.7	35	—
Porosity (cm^3/g)	0.33	0.29	0.30	—
Average pore diameter (Å)	231	257	200	—
Exchange capacity (meq H^+/g dry resin)	4.7	5.2	5.4	4.8
Temperature stability (°C)	110	140	150	120
Crosslinking degree (%)	20	—	12	4

TABLE 2
Chemical Composition of Vegetable Oils

	FA composition (%)							
Vegetable oil	8:0	10:0	12:0	14:0	16:0	18:0	18:1	18:2
Babassu	1.4	3.7	51.5	18.4	8.9	2.5	12.2	1.6
Corn	—	—	—	—	12.5	0.5	29.1	57.7
Palm	—	—	—	0.4	51.1	1.8	44.8	1.6
Palm kernel	1.4	2	55.4	13.5	8.1	1.3	15.5	2.5
Soybean	—	—	—	—	12.7	4.6	32.7	50

than 300:1, a smaller conversion is observed. Consequently, mole ratios higher that 300:1 did not significantly increase ester yields. Therefore, it does not seem useful to use ratios (alcohol/vegetable oils) higher than 300:1 since the extra alcohol use would not be compensated for by an increase in ester yield.

Effect of different macroporous resins. For comparing the catalytic activity of the different macroporous cation-exchange resins with yield of the transesterification reaction, Babassu coconut oil, methanol (using a 300:1 alcohol/oil molar ratio and 1 g of resin), and the macroporous resins Amberlyst 15, Amberlyst 35, and Amberlyst 36 were used. The results are shown in Figure 2. Although the difference in the hydrogen ion capacities of Amberlyst 15, Amberlyst 35, and Amberlyst 36 is minimal, Amberlyst 15 had higher activity than the others. The catalytic activities of the different macroporous resins were also compared with the performance of H_2SO_4 in the transesterification reaction of Babassu coconut and soybean oils with methanol (using a 300:1 mole ratio) (Table 3).

After the same reaction time (8 h) and using the same conditions, the yields obtained for all catalyst systems studied indicate that for the same vegetable oil, the acid resin catalysts gave higher conversions than H_2SO_4 (Table 3, entries 1, 2, 5, 6). Therefore, ion-exchange resins can be used successfully in the transesterification of Babassu oil. Table 3 also shows that the yields varied with vegetable oil. In comparing the Babassu and soybean oil FA contents (Table 3), it is clear that fatty ester yields are higher for the oils with higher content of short-chain FA.

Influence of the type of microstructure of the resin particle. Resins with two types of structure were studied: One had a gel structure (Amberlyst 31) and the other, a macroporous structure (Amberlyst 15). Experiments with soybean and Babassu coconut oils were carried out under identical conditions with both resins. Amberlyst 31 had a lower activity compared with Amberlyst 15, as suggested by the results in Figure 3, which indicates that the methyl ester yield depends on the structure of the resins. In the case of Amberlyst 31 (gel resin), the swelling of the resin in the solvent apparently is an important factor (18). On first contact with the hydrophobic fatty esters, a contraction of the gel matrix probably occurs that limits the accessibility of the reactant to the active sites. On the other hand, the active sites of Amberlyst 15 are located in the macroporous structure, where they are easily accessible to the reactants (18) and consequently produce better ester yields than the yields of the resins with the gel structure.

Influence of the hydrocarbon chain length of the FA. Since ester yields were best with Amberlyst 15, further experiments were conducted with this resin as the catalyst but using different vegetable oils with methanol under identical experimental conditions. The results, presented in Figure 4, clearly show that chain length of the FA group of the oil has an influence on the transesterification activity of the resin, with palm kernel and babassu coconut giving the best ester yields (*ca.* 80%) and oils with long-chain acyl groups giving yields of about 50%.

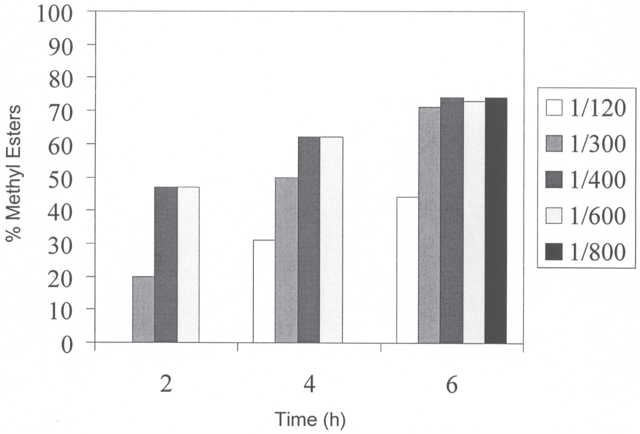

FIG.1. Results of transesterification reaction of the Babassu coconut oil with varied methanol/vegetable oil ratios (120:1–800:1), using Amberlyst 15 resin.

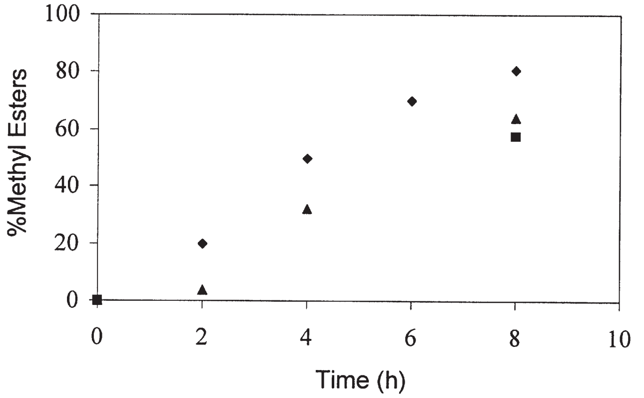

FIG. 2. Results of transesterification reaction of the Babassu coconut oil with different resins [molar ratio 300:1 (methanol/oil) at 60°C]. (◆) Amberlyst 15, (■) Amberlyst 35, (▲) Amberlyst 36.

TABLE 3
Methanolysis of Babassu Oil and Soybean Catalyzed by Different Resins[a] and H_2SO_4[b]

Entry	Vegetable oil	Catalyst	Conversion (%)
1	Babassu	H_2SO_4[b]	44
2		A15	74
3		A35	72
4		A36	64
5	Soybean	H_2SO_4[b]	18
6		A15	56

[a] Reaction conditions: methanol/vegetable oil/resin mole ratio (300:1,1 g), 60°C after 8 h.
[b] Reaction conditions: methanol/vegetable oil 300:1, 3% H_2SO_4, 60°C.

Similar results were observed in the selective monotetrahydropyranylation of symmetrical diols when catalyzed by ion-exchange resins. An increased number of carbon atoms of the diols reduced the selectivity in monoether owing to the lower solubility of the diols in the water layer of the catalyst (19). Catalyst activity and selectivity were affected by FA chain length during esterification of glycerol with FA in the presence of ion exchange resins (18). Our results show that in the transesterification of vegetable oils with methanol, the longer the FA chain, the lower the conversion to methyl esters. As can be observed, the best results were obtained with palm kernel and Babassu coconut oils. The length of the hydrocarbon chain of the FA influences the conversion of the reaction. Palm kernel and babassu coconut oils presented the best results, probably because their main components are lauric acid (12:0). Presumably, the shorter hydrocarbon chain FA have greater access to the active sites on the polar resin phases. The other vegetable oils in this study are dominated by FA of chain lengths of C16 and C18, and these could produce a lower compatibility with the polar resin phases.

The transesterification reaction of vegetable oils may be promoted by using ion-exchange resins as catalyst. This is the first example of the use of ion-exchange resins as catalysts for methanolysis of Brazilian vegetable oils. The transesterification of vegetable oils with methanol catalyzed by ion-exchange resins depends on the FA composition of the vegetable oil. Vegetable oils with short-chain FA lead to higher yields of methyl esters, probably owing to a greater accessibility to the active sites in the polar resin phases.

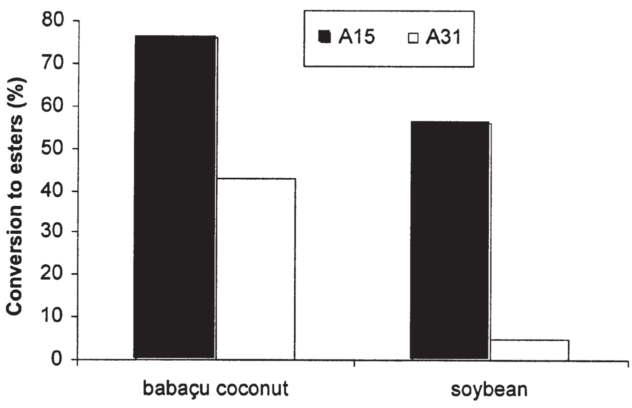

FIG. 3. Results of transesterification reaction of the Babassu (Babaçu) coconut and soybean oil using Amberlyst 15 and Amberlyst 31 resins (methanol/oil, 300:1, at 60°C, after, 8 h).

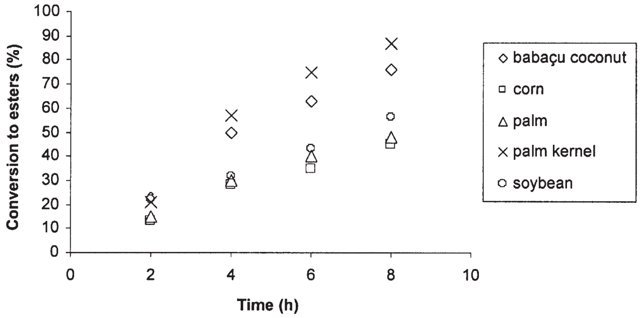

FIG. 4. Influence of type of vegetable oil fatty acyl chain length on ester yields in transesterification reactions catalyzed by Amberlyst 15 resin (methanol/oil, 300:1, at 60°C, after 8 h).

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