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Full Length Article

Efficiency of heterogeneous catalysts in interesterification reaction from macaw oil (*Acrocomia aculeata*) and methyl acetate

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HIGHLIGHTS

- Heterogeneous catalysts were evaluated in interesterification reaction from macaw oil.
- All investigated catalysts were active in the reaction.
- Alumina and niobium phosphate were the most suitable catalysts.
- Reusing results indicate that alumina performed better than niobium phosphate.

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ABSTRACT

Heterogeneous catalysts (niobium phosphate, niobium oxide, γ-alumina and zeolite HY) have been evaluated in interesterification reaction of macaw oil with methyl acetate, to produce fatty acid methyl esters (FAME) and triacetin. The reaction was conducted with a methyl acetate to oil molar ratio of 30:1, 5 wt% of catalyst and 250 °C. All the catalysts, except zeolite HY, exhibited good catalytic activity, and the most suitable were γ-alumina and niobium phosphate, that reached a FAME and triacetin content of 51.60 wt% and 53.55%, respectively, in 2 h, which considering the maximum oil convertibility of 61.6 wt%, corresponds to 83.77 wt% and 86.93 wt% of conversion efficiency, respectively. The effect of reaction time was studied for these catalysts and it was observed that for γ-alumina one hour of reaction was enough to reach 52.49 wt% of FAME and triacetin yield, corresponding to 85.21 wt% of conversion efficiency. On the other hand, in reaction with niobium phosphate two hours and a half were required to achieve 52.90 wt% of FAME and triacetin yield, corresponding to 85.87 wt% of conversion efficiency. γ-alumina could be reused for at least 5 cycles without great activity loss, while niobium phosphate presented significant activity loss from the first to the second cycle.

1. Introduction

Biodiesel, commonly referred as alkyl esters of fatty acids, could be produced from vegetable oils, animal fats or waste oil [1]. Physicochemically similar to diesel, biodiesel is the focus of new research in recent years due to the depletion of fossil fuel reserves, the increasing on energy demand [2] and the concern with the greenhouse gases concentration increase in the atmosphere [3].

Conventionally produced by triglycerides transesterification with alcohols (mainly methanol) in the presence of basic catalysts, this technology is sensitive to free fatty acids (FFA) content in the feedstock. FFA consume the basic catalyst, reducing the reaction rate and making the separation of fatty acids methyl esters (FAME) and glycerol more difficult [4]. Another disadvantage of this method is the glycerol production, which requires subsequent separation and purification steps. Besides, this by-product is undervalued in the world market due to its excessive supply, derived from biodiesel production [5].

In this context, a patent proposed by Saka suggested the replacement of methanol used in the transesterification for methyl acetate in a reaction called interesterification [6]. This reaction produces triacetin as a byproduct, which has higher added value, is soluble in biodiesel and is considered an additive, improving its characteristics [7]. Additionally, FFA in vegetable oil also reacts with methyl acetate through an esterification reaction, producing FAME and acetic acid. Catalytic action of acetic acid was studied

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by Campanelli et al. whom suggest edit has a moderate catalytic effect in biodiesel production and it reduces the triacetin thermal degradation [5].

Interesterification reaction has been studied using mostly raw materials with low FFA content in the presence of basic homogeneous catalysts [8–10], enzymes [11,12] and without catalyst at supercritical conditions [1,5,13,14]. Homogeneous catalysts are reagent soluble, difficult to separate at the end of the process, unlike heterogeneous, that can easily be recovered and reused [15]. Although enzymes can also be reused, they are expensive and require specific conditions for reaction [8]. The use of supercritical fluids has been studied in the interesterification reaction, however, besides requiring high energy spending, high temperatures and pressure applied can cause degradation of biodiesel [14,16,17]. This way, chemical heterogeneous interesterification arises as an alternative for reducing operating costs. Chemical catalysts are cheaper than enzymes and they are less sensitive to reaction conditions [8]. From the knowledge of the authors, interesterification reaction using heterogeneous catalyst has not been widely investigated. Some studies have been focused on ester interchange reaction of triglycerides to improve fat and oils properties, as reported by Xie and Chen[15] which studied the heterogeneous interesterification of edible oils using potassium-doped alumina to obtain zero *trans* fats. Related to biodiesel production, just a few studies were conducted using alkali methoxides, that are partially soluble due to alcohol absence as reactant, changing reaction mixture from polar to non-polar [8,9,18]. Besides that, all of them studied reactions using oils with low FFA content.

In conventional biodiesel production, two key factors affect the final cost: raw materials and processing (multi-stage) costs. The use of heterogeneous catalysts in interesterification reaction would decrease the expense on catalyst separation step and purification stages of glycerol. In order to minimize raw materials costs waste oils, animal fats and non-edible oils could be used [19]. In this context, macaw (*Acrocomia aculeata*) is a potential source of raw material for biodiesel production [20]. Native plant of tropical America and abundant in the Brazilian cerrado, the macaw has an annual production capacity of 6.2 tons of oil per hectare, much higher than soybean, for example, which produces 500 l of oil per hectare [21,22]. The high acidity and the presence of water, as a crude oil, suggests the interesterification of this oil using heterogeneous acid catalyst to be a suitable method to obtain biodiesel with low cost production and high yield.

The aim of this work was to study the performance of different heterogeneous catalysts in interesterification of macaw oil with methyl acetate, to produce FAME and triacetin. The influence of the reaction time in the methyl ester content and the reusability of the most suitable catalyst were also studied.

2. Materials and methods

2.1. Materials

Alumina was synthesized using aluminum nitrate nonahydrate (98%) and sodium hydroxide (98.5%) purchased from Sigma-Aldrich, Brazil. Zeolite Y in acid form was synthesized using extracted silica from rice husk donated by Induber (Santa Maria, Brazil) and pseudo bohemite synthesized with aluminum nitrate nonahydrate (98%) and sodium hydroxide (98.5%) purchased from Sigma-Aldrich, Brazil. Niobium oxide and niobium phosphate were kindly donated by Brazilian Company of Metallurgy and Mining (CBMM – Brazil). Crude macaw oil was purchased from Cocal Brazil Company (Cocal, Brazil), and kept in a cool and dry place, protected from light, and filtered before use to remove beads coming from extraction process. Methyl acetate (99%) used as solvent in the interesterification reaction was purchased from Sigma-Aldrich, Brazil. Heptane (99%), methyl heptadecanoate (internal standard) and standard references for FAME analysis which include methyl palmitate, methyl oleate, methyl linoleate and methyl linolenate were also obtained from Sigma Aldrich, Brazil.

2.2. Macaw oil characterization

Chemical composition of major fatty acids was determined by conversion of fatty acids to methyl esters as described by Hartman and Lago [23] and analyzed in a gas chromatograph Shimadzu GCMS-2010, equipped with a flame ionization detector (FID) and RTX-Wax capillary column (30 m × 0.25 mm × 0.25 μm). The temperature program was set to 60 °C and then held for 2 min, the column was heated to 200 °C at a rate of 10 °C min^{-1}, then it was heated again up to 240 °C and held for 7 min. Helium gas was used as carrier gas at flow rate of 1.53 $mlmin^{-1}$, with a split ratio of 1:60. Injector and detector temperatures were set at 250 °C. The fatty acids were identified by comparing the retention times of the sample peaks with those of FAME standards. Water content was quantified by Karl-Fischer titration and acid value was determined by titration according to AOCS Cd 3d-63 method.

Since crude vegetable oils could contain compounds not-convertible to alkyl esters, the maximum theoretical ester content in the final product may not correspond to 100 wt%. Determination of the maximum conversion to esters is defined as "Convertibility" [24]. All the fatty acids from macaw oil were converted to their corresponding alkyl esters according to Hartman and Lago [23] and analyzed in a Shimadzu gas chromatograph GCMS-2010 in the same conditions of fatty acid composition analysis. The convertibility was determined from the area percentage obtained from analysis using methyl heptadecanoate peak as internal standard. To evaluate the real efficiency of the process, conversion efficiency could be calculate according to Eq. (1) [24].

$$convertion\ efficiency\ (wt\%) = \frac{alkyl\ ester\ yield}{convertibility} \times 100 \quad (1)$$

2.3. Catalyst preparation

Alumina (Al_2O_3) was synthesized by sol-gel process, from hydrolysis of aluminum nitrate nonahydrate, followed by addition of sodium hydroxide to produce aluminum hydroxide in the precipitate form [25]. The resulting gel was dried for 20 h at 100 °C, and calcined at 500 °C, with heating rate of 2 °C per minute for 2 h, to obtain transition form γ-Al_2O_3. The Y zeolite in sodium form (NaY) was obtained by standard synthesis from IZA (International Zeolite Association). As silicon source extracted silica from rice husk ash was used and, as aluminum source, pseudo boehmite. The NaY crystals, dried in an oven at 110 °C for 12 h, were subjected to an ion exchange procedure with ammonium chloride solution to obtain Y zeolite in acid form (HY). The resulting solid was calcined at 550 °C with a heating rate of 5 °C per minute for 6 h. The niobium oxide (Nb_2O_5) and the niobium phosphate ($NbOPO_4$) donated were calcined at 300 °C at a heating rate of 10 °C per minute for 2 h [26].

2.4. Catalyst characterization

The crystal structures were identified by X-ray diffraction (XRD) using Rigaku diffractometer (Miniflex 300) with Cu Kα radiation (λ = 1.54051 Å) and power supply with 30 kV and 10 mA. The scan was made between the angles 2–80° for γ-Al_2O_3, 2–50° for zeolites HY, 5–70° to $NbOPO_4$ and 10–70° for Nb_2O_5, with step of 0.03° for 1 s. Textural properties were determined by nitrogen adsorption-