Esterification of fatty acids using acid-activated Brazilian smectite natural clay as a catalyst

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A B S T R A C T

This work reports the use of an acid-activated Brazilian smectite natural clay-based catalyst in the esterification of fatty acids at atmospheric pressure and without a co-solvent. Conversion levels of 99%, 98%, 93% and 80% were reached for caprylic, lauric, stearic and oleic methyl esters, respectively, using 1:3 fatty acid/methanol molar ratio, heating bath at 100 °C after 4 h. A conversion level of 89% was achieved for methyl esters from a fatty acid residue of the palm oil refining industry in the same reaction condition. The acid-activated clay provided better performance than the commercial catalyst **K-10**. The effects of catalyst amount, temperature, fatty acid/alcohol molar ratio and time were investigated. The heating activation of the catalyst immediately before the catalytic test increased the conversion from 94% to 99% using 1:1.5 stearic acid/methanol molar ratio, heating bath at 100 °C after 4 h. The catalyst was reused five times. The conversion decreases less than 5% in the first three reuses. The smectite natural clay and the catalyst were characterized by X-ray fluorescence, X-ray diffraction, *n*-butylamine thermodesorption, nitrogen adsorption analysis, thermogravimetric analysis and differential thermal analysis.

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1. Introduction

The increasing demand for biodiesel has stimulated the development of new technologies and new catalysts. The industrial production of biodiesel is performed by a transesterification process using mainly hydroxide or methoxide as a catalyst [1]. The problem involved in this process is the formation of soap. Because of this, there are studies involved in the development of new catalysts. Most of them are focused on the development of heterogeneous catalysts [2–9]. The homogeneous alkaline catalysis provides high yields in a short time and mild reaction condition, so find a promising heterogeneous catalyst is not an easy task. There are also parallel efforts to optimize the homogeneous alkaline catalytic process. Some examples include economics in terms of process conditions, studies involved in continuous process design as well as scale-up [10–12].

Although vegetable oils are the major feedstock for the production of biodiesel, there are other fatty acid sources that have been studied, such as used cooking oils, sewage sludge and animal fats [13]. Some feedstocks have high concentrations of free fatty acids (FFA), reaching levels up to 15 wt%. This characteristic makes them inappropriate for the conventional direct base-catalyzed transesterification route to biodiesel due to soap formation. An integrated process enables the use of these materials by the combination of acid-catalyzed FFA esterification followed by base-catalyzed triacylglyceride transesterification. Despite the additional cost of production, the process is being increasingly applied to produce biodiesel from high-FFA feedstock [14].

Biodiesel can also be produced from the direct esterification of FFA feedstocks. Low-grade starting materials, such as waste from vegetable oil refining industries, can be used. To achieve a satisfactory ester conversion, it is necessary to remove the water produced or use a stoichiometric excess of alcohol. Sulfuric acid is the most widely used catalyst in esterification reactions. It is very active and has an important dehydrating effect. By contrast, it is corrosive, presents problems of storage and control and, in particular conditions, can react with the double bond present in unsaturated fatty acids [15].

Nowadays, there is intensive research of new catalysts for the esterification of fatty acids that allow milder reaction conditions and that can be reused. In an integrated process, the intermediate step of neutralizing the acid catalyst increases the volume of waste.

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The use of a heterogeneous catalyst may result in additional steps or units, but still could simplify the process, since it could be removed by filtration, without neutralization, and the product could be immediately submitted to the transesterification reaction.

There are several studies in the literature for the esterification of fatty acids with short-chain alcohols and using different heterogeneous catalysts [16–30]. Regarding the use of clay as a catalyst in the esterification of fatty acids, Kantam, Bhaskar and Choudary used Fe^{3+}-montmorillonite in the esterification of stearic acid with methanol. A conversion rate of 98% was obtained after 5 h of reaction, using a Dean–Stark apparatus and toluene as a solvent [31]. Neji, Trabelsi and Frikha investigated the use of commercial montmorillonite-based catalysts (KSF, KSF/0, KP10 and K10) in the esterification of stearic, oleic and palmitic acids with short-chain alcohols [32]. The reactions were carried out in a semi-continuous reactor at 150 °C with continuous removal of water. The best catalytic activities (>90% after 3 h) were obtained with the KSF/0 catalyst. Nascimento et al. prepared catalysts for the esterification of oleic acid with methanol from two Amazon kaolins and two standard kaolins. After 4 h, a conversion rate of more than 90% was achieved using an acid/alcohol molar ratio of 1:60 at 130 °C [33]. Ghiaci, Aghabarari and Gil showed that a modified bentonite with 1-benzyl-1H-benzimidazole-based Brønsted acidic ionic liquids was able to catalyze the esterification of oleic acid to its methyl ester in 6 h with yields of more than 92% [34]. Zatta, Gardolinski and Wypych studied the esterification of lauric acid with methanol using raw halloysite as a catalyst. A conversion level of 95% was achieved at 160 °C for 2 h in a pressurized steel reactor [35]. The esterification of oleic acid with methanol catalyzed over sulfuric acid-activated pillar bentonite clay was performed by Jeenpadiphat and Tungasmita [36]. The use of a 1:9 molar ratio of oleic acid/methanol at 60 °C for 3 h reached 100% of yield. In 2012, we used acid-activated Brazilian clay-based catalysts in the esterification of different carboxylic acids and alcohols, including lauric acid and methanol. After 3 h, a conversion rate of 87% in methyl laurate was achieved using a carboxylic acid/alcohol molar ratio of 1:3, atmospheric pressure and heating bath at 100 °C [37]. Recently, Aghabarari and Dorostkar studied the esterification of oleic acid with ethanol using bentonite modified with ionic liquids as a catalyst [38]. A conversion rate greater than 93% was observed after 6.5 h at 60 °C using an oleic acid/ethanol molar ratio of 1:2.

This work reports the esterification of fatty acids using acid-activated Brazilian smectite natural clay as a catalyst, at atmospheric pressure and without a co-solvent. The objective is to evaluate the potential use of a low-cost and friendly solid catalyst for the production of biodiesel based on the direct esterification of FFA. The acid treatment is very simple, and the acid-activated clay was tested in the esterification of different fatty acids, including a FFA industrial residue used as feedstock for the production of biodiesel in Brazil. The effect of the main variables was studied, and high conversions were observed using very mild reaction conditions. The reuse of the catalyst was also investigated. These results are a new contribution to the knowledge on the use of clays as catalysts in the esterification of fatty acid.

2. Materials and methods

2.1. Materials

The smectite natural clay was from the Boa Vista district, Paraíba, Brazil. Sulphuric acid (95–99%), lauric acid (99%), oleic acid (P.A.), sodium sulphate (99%), ethanol (99.8%), propanol (99.5%) and butanol (99.4%) were purchased from Vetec (Brazil). Ethyl acetate (>99%) and methanol (>99%) were from Tedia (Brazil), and caprylic acid (>98%) was from Merck (USA). Stearic acid (95%), methyl

stearate (>99%), ethyl stearate (>99%), methyl oleate (>99%), methyl laurate (>99%) and methyl caprylate (>99%) were from Aldrich (USA). The FFA industrial residue was kindly donated by the palm oil refining industry, and its fatty acid composition was determined by gas chromatography-mass spectrometry. It is composed by 46% palmitic acid, 39% oleic acid, 8% linoleic acid, 6% stearic acid and 1% myristic acid (% of area in the chromatogram).

2.2. Catalyst preparation

The natural clay was used as received, without any previous treatment to eliminate organic materials, quartz, other materials or minerals. It was completely crushed and passed through a 0.250 mm sieve opening. The homogenised clay, called **SME$_{nat}$**, was acid-activated in a round-bottom flask connected to a reflux condenser. A 10% w/v suspension of clay in 4 mol L^{-1} sulphuric acid was stirred at 90 °C for 2 h [39]. The solid was filtered under reduced pressure and washed with distilled water until the washing water had the same pH of the first. The material was dried in an oven at 110 °C for 24 h and finally ground until passage through a 0.250 mm sieve opening again. The activated clay, called **SME$_{acid}$**, was kept in a desiccator.

2.3. Catalyst characterization

The chemical compositions of **SME$_{nat}$** and **SME$_{acid}$** were determined by X-ray fluorescence (XRF) using a Bruker spectrometer (AXS S4 Explorer) equipped with a Rhodium tube. The sample, previously dried, was fused with lithium tetraborate at 1100 °C at a ratio of 1:6 sample/lithium tetraborate.

The cation exchange capacity (CEC) of the natural clay was determined according to the procedure proposed by Jackson [40], and 1 g of **SME$_{nat}$** was exchanged with 1 mol L^{-1} potassium acetate solution through centrifugation. The suspension was washed with 95% ethanol, and the aqueous phase was discarded. Then, the K^+ ion was exchanged by NH_4^+ ion with a 1 mol L^{-1} ammonium acetate solution. The K^+ solutions were collected in a volumetric flask, and the volume was completed to 100.00 mL with ultrapure water. The procedure was performed in triplicate, and the amount of K^+ ion was determined by flame spectrometry, using a flame photometer Micronal B262.

X-ray diffraction (XRD) analysis was performed on a Bruker-AXS D5005 at 35 kV and 40 mA. A 2θ range from 5° to 80° was scanned at 0.02° s^{-1}.

The BET-specific surface area was measured by nitrogen adsorption data in a relative pressure range from 0.05 to 0.98, employing a Micromeritics A.S.A.P. 2010. The average distribution of pore sizes was calculated using the BJH method. The adsorption and desorption isotherms were obtained at −196 °C. Prior to each measurement, all samples were degassed at 120 °C for 5 h under vacuum.

The number of weak, moderate and strong acid sites was estimated by thermodesorption of n-butylamine. Each sample was heated to 120 °C at a rate of 10 °C min^{-1} under helium flow at 40 mL min^{-1}. After 30 min at 120 °C, the material was kept under helium flow saturated with n-butylamine for 10 min. Next, pure nitrogen percolated the sample during 20 min to remove any physisorbed n-butylamine molecules. Thermogravimetric results were obtained under nitrogen flow at 20 mL min^{-1} from 20 up to 800 °C at a rate of 10 °C min^{-1}, on a TGA-51 Shimadzu.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were done on a 2960 STD V.3.0.F TA instrument under air flow at 35 mL min^{-1}. The samples were analyzed from 25 to 1000 °C at a rate of 10 °C min^{-1}.