



Sulfonated poly(divinylbenzene) and poly(styrene-divinylbenzene) as catalysts for esterification of fatty acids



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ABSTRACT

Commercial ion-exchange resins (Amberlyst 35 and Amberlyst 36) and a resin synthesized in the laboratory, sulfonated poly(divinylbenzene) were evaluated as catalysts in the esterification of fatty acids (palmitic and oleic) with alcohols (methanol, ethanol and butanol). The study was developed in order to obtain a high rate of fatty acid conversion. The esterification reactions with fatty acids and methanol presented satisfactory conversion to methyl esters achieving a final conversion over 90% in both palmitic and oleic acid. A sample of waste vegetable oils with a high acid content from the residue of the palm oil and soybean oil refining industry were evaluated in the esterification with methanol. The best results were achieved with the new sulfonic resin, poly(divinylbenzene), which was synthesized in the laboratory and has proved efficient for the reaction in the study. Maximum biodiesel production was achieved from a fatty acid residue of the soybean oil refining industry and methanol (93%) which showed conversions very close to those obtained from their respective fatty acids.

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1. Introduction

Biodiesel, monoalkyl esters of fatty acids from a renewable lipid feedstock, are the best substitutes for diesel because they do not demand any modification in a diesel engine and have a high energy yield [1,2]. Besides, lipid feedstocks such as vegetable oil or animal fat are renewable, biodegradable and environmentally friendly properties and do not contain sulphur [1–3]. The basic homogeneous catalytic process for biodiesel production in the industry use refined vegetable oil. In this process the catalysts is not reused, involves the use of large amounts of water for neutralization, and the large amount of waste obtained increase the cost of the process. However new solid basic catalysis such as lithium orthosilicate and LiAlO₂ have been reported for the transesterification of refined oil with good yields [4–6].

The reaction of esterification of carboxylic acids with alcohols is a well known class of reactions in liquid phase and of considerable industrial interest due to the great practical importance of organic

esters. Recently, the esterification of fatty acids catalyzed by acid has attracted great interest because esters with long carbon chains can also be used as biofuels [2,7,8]. In the esterification process for biodiesel production it's possible used a not refined raw material, vegetable oil with high amount of free fatty acids or fatty acids from refined vegetable oil.

Generally, the esterification of fatty acids with alcohols is produced commercially by using liquid acid catalysts such as sulfuric acid, hydrochloric acid or organic acids such as *p*-toluenesulfonic acid. Homogeneous catalysts, though effective, lead to serious contamination problems, since they are toxic, corrosive and produce by-products, which are difficult to separate from the reaction medium, resulting in higher production costs. The removal, handling and disposal of corrosive waste has motivated a large number of studies concerning the development and application of heterogeneous catalyst systems for biodiesel production [1–15]. The solid acids used for the production of biodiesel have been the organic ion-exchange resins such as Amberlyst 15 [16–18], sulfonated zirconia [16,19–22], zeolites [23,24], ZnO/SBA-15 [25] and heteropoliacids supported on silica (HPA/silica) [26]. The use of these acid catalysts to obtain high conversion of triglycerides to biodiesel demands high reaction temperatures or a high

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triglyceride/methanol molar ratio. However, ion-exchange resins may be considered an exception because they catalyze both esterification and transesterification of free fatty acids (FFA) in oils with a high FFA contents, under mild conditions [11]. The esterification of carboxylic acids by solid acid catalysts is very important, considering the low cost of feedstocks with high concentration of FFA. Moreover, it is expected that a good solid acid catalyst can simultaneously carry out esterification of FFA and transesterification of vegetable oils [2,7,11].

There are some studies in the literature about the esterification of fatty acids with alcohols and ion exchange resins. The commercial resins Amberlyst 15, Amberlyst 35, Amberlyst 16 and Dowex HCR-W2 were evaluated in the esterification of free fatty acids in waste cooking oil with methanol at 60 °C using a 20/1 molar ratio of methanol/oil. The authors found that the resin Amberlyst 15 presented the best results and the conversion of the oil in methyl esters was 45.7% [27]. Commercial ion-exchange resins were evaluated in the esterification of acidified oils generated from waste frying oils. The best conversion (90%) was achieved using 18 wt% catalyst, a 3/1 molar ratio of methanol/oil, 66 °C and 3 h [28]. The reaction of crude palm oil containing a higher percentage of free fatty acids catalyzed by different acid-functionalized materials was investigated. The resins Amberlyst 36 and the Nafion-SiO₂ composite (SAC-13) both gave low yields of fatty acid methyl esters [29]. The production of 70% of fatty acids methyl ester from *Jatropha Cucas* oils using Amberlyst 15 was achieved with a 12/1 molar ratio of methanol/oil, 5 wt% of the catalyst, 160 °C and 6 h [30]. Styrene-divinylbenzene -SO₃H resins with different cross-linking degrees (CLD) were synthesized and evaluated in biodiesel production. The macroporous resins with high CLD were more mechanically durable and showed higher activities than those with low CLD [31]. Amberlyst 15 was investigated in the esterification and transesterification reactions of waste cooking oil with methanol. The conversion of 78% was achieved using a 12/1 molar ratio of alcohol/oil, 3 wt% catalyst, 65 °C and 9 h of reaction [32]. The methanolysis of refined soybean oil catalyzed by polydivinylbenzene-SO₃H was evaluated. The conversion in methyl ester was 97% after 8 h and superior to commercial resins [33]. The catalytic activity of mesoporous polydivinylbenzene-SO₃H in the esterification of lauric acid with ethanol was superior to Amberlyst 15 and the conversion was 99% and 75.2% respectively. The superior performance of the mesoporous polydivinylbenzene-SO₃H can be attributed to their large surface area that is favorable to access the catalytic sites and the mesoporosity that facilitates the mass transfer [34].

The main purpose of the present work is to develop a comparative study of commercial resins (Amberlyst 36 and Amberlyst 35) and a resin synthesized in the laboratory, sulfonated polydivinylbenzene (polyDVB-SO₃H), for esterification reactions of fatty acids (palmitic acid and oleic acid) and Brazilian free fatty acid feedstocks (soybean and palm) with alcohols under solvent-free conditions.

2. Materials and methods

2.1. Materials

The reagents used in the present study were oleic acid (Vetec), palmitic acid (Vetec), methanol, ethanol, butanol (Vetec), hexane (Vetec), *p*-toluenesulfonic acid (Aldrich). Fatty acid residue of the soybean oil and palm refining industry were kindly supplied by Miracema-Nuodex and Agropalma respectively. None of them were submitted to any previous treatment. The commercial resins employed Amberlyst 36 (A-36) and Amberlyst 35 (A-35) were supplied by Rohm and Haas and dried at 105 °C under vacuum for 12 h before use. The synthesized resin, a sulfonated

polydivinylbenzene (polyDVB-SO₃H), named FS, was obtained in two steps. First, aqueous suspension polymerization of divinylbenzene was performed to yield spherical beads. Toluene was used as a pore forming agent in a volumetric ratio of 1:1 to DVB. In a second step, the polymer beads were sulfonated by a mixture of concentrated H₂SO₄ and 1,2-dichloroethane. The polymerization and sulphonation details were described in an earlier work [33,35]. Textural properties of FS resin were determined by nitrogen adsorption of the normal boiling point of liquid nitrogen at 77 K in a volumetric apparatus ASAP 2010 (Micromeritics). The exchange capacity was determined as described in the literature [35]. The chemical modification of polydivinylbenzene by the sulphonation reaction was evaluated by Fourier transform infrared spectroscopy (FTIR). KBr pellets of the polymer and the sulphonation product were analyzed in the 4000–400 cm⁻¹ region with a 4 cm⁻¹ resolution and 16 scans (Fig. 1). The bands at 1350 cm⁻¹ and 1342 cm⁻¹, due to the asymmetric and symmetric stretching vibrations of the -SO₂ group, and at 3400 cm⁻¹, due to the -OH stretch, confirm the presence of the sulphonic acid group and the success of the polymer sulphonation.

The physical properties of resins used in this work are shown in Table 1. The results presented in Table 1 show that sulfonic catalysts based on poly (divinylbenzene) showed high specific surface area and were superior to the commercial resins Amberlyst-35 and Amberlyst-36. The commercial resins present superior exchange capacity compared to the synthesized resin.

2.2. Esterification reaction

A mixture of fatty acid, alcohol and catalyst was added to a two-necked flask equipped with a reflux condenser. The reactions were performed at the temperature of the mixture reflux, under magnetic stirring, for 6 h. Aliquots were taken at pre-determined times and were subsequently extracted with hexane/water and analyzed by ¹H NMR spectra.

The separation of alkyl esters produced from esterification was performed by transferring the reaction mixture to a separation funnel, to which water and hexane were added. The organic layer was separated and washed with water to remove the alcohol. The organic phase was then treated with anhydrous sodium sulfate, filtered and after the solvent was removed. The product was analyzed by ¹H NMR.

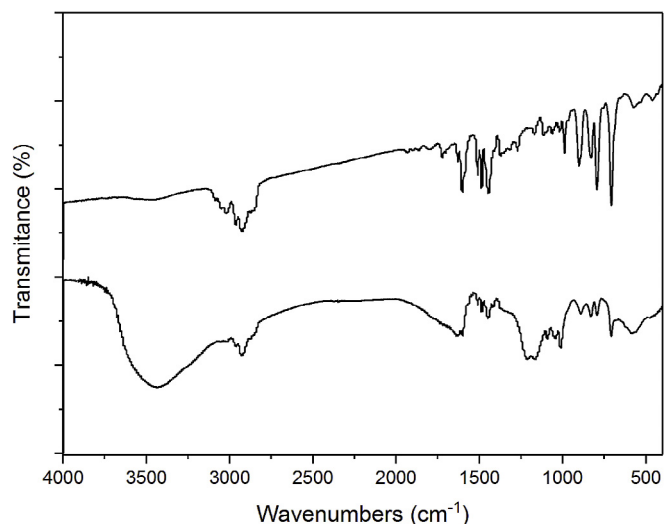


Fig. 1. FTIR spectra of the precursor copolymer (upper) and the polydivinylbenzene sulfonated (bottom).

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