



New heterogeneous catalyst for the esterification of fatty acid produced by surface aromatization/sulfonation of oilseed cake



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HIGHLIGHTS

- Simple sulfonation of biodiesel waste cake in mild conditions produces a new and active heterogeneous acid catalyst.
- The catalytic activity is comparable to H₂SO₄ and the catalyst can be reused several times.
- The catalyst combines a carbon-sulfonic acid surface with a very hydrophilic cellulose surface responsible for water removal.

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ABSTRACT

In this work, an efficient heterogeneous acid catalyst for the esterification of oleic acid was prepared directly from oilseed cake by a simple sulfonation with concentrated H₂SO₄. Characterization by SEM/EDS, IR, Raman, TG, TG/MS, potentiometric titration showed that treatment with H₂SO₄ for 1, 2 and 4 h at 120 °C partially dehydrates the cake to form a carbon/cellulose composite which is sulfonated to produce strong –SO₃H acidic sites. These surface sites were active for the esterification of oleic acid with yields ca. 84%, 88% and 94% in the presence of 5, 10 and 20 wt% catalyst, respectively. These results are comparable to 98% yield obtained with 1 wt% H₂SO₄ and higher than 75% observed for a high surface area (880 m² g⁻¹) sulfonated activated carbon with similar number of –SO₃H active groups. These results are discussed in terms of two effects: (i) the number of sulfonic surface acidic groups and (ii) the presence of a hydrophilic cellulosic fraction in the catalyst that adsorbs/traps water formed in the reaction shifting the esterification equilibrium and improving the yield.

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1. Introduction

The transesterification reaction to produce biodiesel in the presence of basic homogeneous catalysts, e.g. KOH, NaOH or methoxides, has been extensively investigated in the last decade [1–4]. It is well established that this alkaline catalyzed transesterification is strongly affected by the presence of free fatty acids [4,5]. The presence of these acids in concentrations higher than ca. 2% can hinder the reaction and form surface active molecules with significant complications in the purification step due to the formation of stable emulsions [6].

An alternative route to deal with acidic oils is typically a previous esterification in the presence of H₂SO₄ as catalyst [7]. However, sulfuric acid is corrosive and cannot be recovered [8,9]. In this respect, the development of an active acid heterogeneous catalyst to produce biodiesel using acidic oils is of considerable interest. Heterogeneous catalysts can be easily removed and reused avoiding the washing step which simplifies the process [10–13].

Different types of acidic materials, such as zeolites [14–16]; mesoporous silica [17–19], resins [20,21], oxides, e.g. zinc, titanium, strontium oxides [22–24], zirconia [25–28], supported carbon nanotubes [29] and minerals such as a mordenite, kaolins, halloysite [30–32] have been investigated as catalyst for the esterification reaction. Also promising carbon based acid catalysts have been prepared by pyrolysis followed by sulfonation with sulfuric acid, using different precursors such as carbohydrates, lignin [33,34], sugar cane bagasse [35], fibers [36], biochar [37], resin

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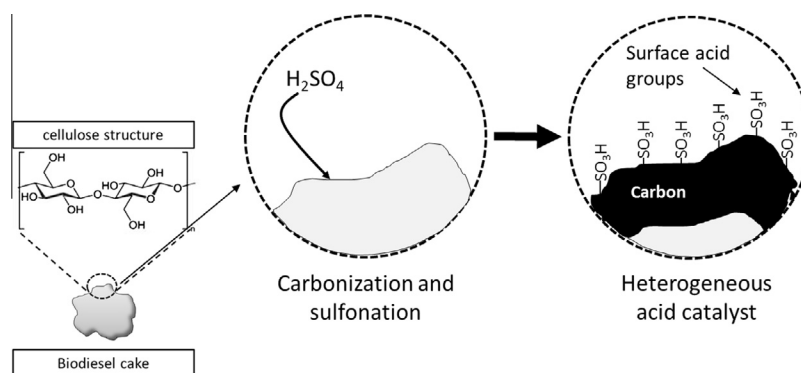


Fig. 1. Representation of the partial aromatization/sulfonation reaction of the biodiesel cake to produce the composite acid catalyst.

[38], bean vermicelli [39], de-oiled canola [40], polymers [41], D-glucose and sulfonated ordered mesoporous carbons [42–46]. These catalysts have shown great potential to replace the traditional homogeneous H_2SO_4 catalysis.

In this work, we present a new and simple reaction procedure to prepare an active heterogeneous catalyst from oilseed cake, a biodiesel byproduct. Biodiesel cakes are solid materials obtained after oil extraction by mechanical pressing, consisting mainly of lignocellulosic fibers. The high concentrations of lignocellulosic material, deficiency of proteins and the presence of some toxic compounds strongly limit the use of some biodiesel cakes in feed blends for ruminant animals [47,48]. The active acid catalyst can be produced by the direct reaction of the cake with sulfuric acid according to the simplified scheme shown in Fig. 1.

The reaction with concentrated sulfuric acid with the lignocellulosic waste seems to promote surface reactions likely based on dehydration with aromatization followed by sulfonation producing the acid catalytic sites. The synthesis, characterization and use of this heterogeneous acid catalyst for the esterification of oleic acid in bench and pilot/ultrasound scale are described below.

2. Material and methods

Different biodiesel cakes obtained after extraction of sunflower, castor, jatropha, curcas and macaw palm oil can be used as solid lignocellulosic precursor. In a typical procedure the biodiesel cake (1 g, ground to particles smaller than 2 mm and dried overnight at 80 °C) was mixed with concentrated H_2SO_4 (min 98%, 8 mL, Synth[®]), under stirring, at room temperature for 1 h (sample CK1rt) and at 120 ± 5 °C for 1, 2 and 4 h (samples CK1, CK2 and CK4, respectively). Due to the exothermicity of the reaction, the process should be well controlled in order to avoid overheating and dissipate possible hot spots generated on the precursor surface. Caution should be taken to control after the reaction the black solid was extensively washed with water (until reaching pH ~ 7) and dried at 80 °C for 12 h. Raman spectroscopy measurements were made using a Senterra Raman spectrometer from Bruker using a CCD detector, equipped with an optical microscope (OLYMPUS BX51) and a laser at 633 nm. Thermal analyses (TG/DTG) were performed in a Shimadzu 60H under nitrogen flow (100 mL min⁻¹) and heating rate of 10 °C min⁻¹ up to 900 °C. Scanning Electron Microscopy (SEM/EDS) results were obtained in a Quanta 200 – FEG – FEI 2006. FTIR spectra were obtained with KBr pellets in a Perkin Elmer FTIR GX instrument. Potentiometric titration was carried out in an automatic titrator Mettler 670 with a mixture of 25 mg of the sample dispersed in 0.01 mol/L of HCl and 0.1 mol/L of NaCl and titrated with 0.010 mol/L of NaOH solution. The thermogravimetric-mass spectrometry (TG–MS) analysis were performed in a NETZSCH TGA model STA 449 F3, coupled to a mass spectrometer

NETZSCH Aëolos model QMS 403C. About 20 mg of the sample was used an argon flow in the purge and protective lines, both at 20 mL/min, and with heating rate of 10 °C min⁻¹ up to 900 °C. Gaseous species released from the sample during the heating were drawn into an alumina tube fixed inside the furnace of the thermobalance close to the sample, connected to a capillary silica column heated at 300 °C. The gases were then directly sucked into the ionization chamber of the mass spectrometer.

The catalytic activity of the materials was tested in the esterification of pure oleic acid in a round bottom flask fitted with a reflux condenser at 60 °C for 2 h, with a ratio of 12:1 methyl alcohol:oleic acid and different catalyst concentrations (5, 10 or 20 wt%, with respect of oleic acid concentration). After the reaction the catalyst (ca. 1 g) was washed with ethanol (30 mL at room temperature) and dried at 80 °C for 4 h and tested in the reuse experiments. The conversion of methyl esters was analyzed by the Ca 5a-40/AOCS method and confirmed by ¹H NMR. (RMN Bruker Advance DPX 200). The signals used as references were of the methoxy groups in the methyl ester (3.7 ppm) and of the α -carbonyl methylene groups present in the oil and biodiesel (2.1 ppm) [49]. A calibration curve from the ¹H NMR spectra of oil/biodiesel mixtures using the 3.7 ppm and 2.3 ppm area ratio was obtained.

The catalytic activity of the materials was also investigated at a pilot plant scale using an ultrasound promoted reactor (see Supplementary Material – Fig. 1S) [50].

Commercially available activated carbon (from coconut shell, 880 m² g⁻¹, Sulfal) was used as a catalyst in a control reaction study. The activated carbon was sulfonated using the same conditions used for preparation of CK2 (sulfonation with concentrated H_2SO_4 for 2 h at 120 °C under stirring and washed with water (pH ~ 7) and dried at 80 °C for 12 h). The water absorption capacity of the CK2 material was determined by the “tea bag” method by weighing the water retained by the material [51].

3. Results and discussion

Biodiesel cakes from different sources, e.g. sunflower, castor, jatropha curcas and macaw palm are composed mainly of lignocellulosic fibers. In contact with sulfuric acid the lignocellulosic material becomes completely black suggesting a strong dehydration process to form polyaromatic/carbon on the surface. The reaction with H_2SO_4 was carried out at room temperature for 1 h (sample CK1rt) and at 120 °C for 1, 2 and 4 h (samples CK1, CK2 and CK4 respectively).

Raman analyses (Fig. 2) for all the obtained solids after reaction with sulfuric acid at 120 °C, showed two typical bands for carbonaceous materials: the D and the G band. The G band (at 1590 cm⁻¹) is typical for well-formed and organized graphitic structures whereas the D band (near 1350 cm⁻¹) indicates the presence of

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