

Esterification of free fatty acids in the presence of chitosan with sulfonic acid groups

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Introduction

Biodiesel is a clean fuel source, which is viewed as a viable alternative for dwindling petroleum-based diesel resources. Biodiesel is generally synthesized by the transesterification of natural oils, or fat of vegetable or animal origin [1], which is carried out by acid or base catalysis [2,3]. However, some of the natural oils or fats contain considerable amount of free fatty acids, which interfere with transesterification process and must be converted into their corresponding esters before reaction. Thus, esterification forms an essential step in the production of biodiesel. Esterifications are conventionally carried out homogeneously using mineral acids, which are however corrosive with the excess acid also requiring neutralization post-reaction, leaving large quantities of salts for subsequent environmental disposal. Heterogeneous catalysts are preferable, offering easy separation from the reactants and by filtration.

Poly(vinyl alcohol) and polystyrene functionalised with sulfonic acid were used as catalysts in the esterification of palmitic acid with methanol, at 60 °C. It was observed that the catalytic activity of PVA is higher than the obtained with the PS ones. The esterification of stearic and oleic acid with methanol was also studied using poly(vinyl alcohol) with sulfonic acid groups, as catalysts, at 60 °C [4].

Chitosan is a very abundant biopolymer obtained by the alkaline deacetylation of chitin (a polymer made up of acetylglucosamine units). Chitin is present in the exoskeletons of crustaceans and the cuticles of insects. In catalysis, the polymer can be used as a catalyst and as a support for the preparation of heterogeneous catalysts [5].

This work reports the esterification of palmitic acid, oleic acid and stearic acid with methanol over chitosan with sulfonic acid groups.

Experimental

Chitosan was obtained from Sigma–Aldrich Chemicals, USA. Chitosan (0.4 g) was dissolved in 50 ml of distilled water containing 2% of acetic acid with constant stirring for about 24 h at room temperature. After that, appropriate amount of sulfosuccinic acid (1 mmol) was added to chitosan solution, which was vigorously stirred at room temperature for 24 h. The homogeneous solutions were poured and cast on a Teflon plate. The cast polymers were allowed to dry at 60°C during 24 h. The dried chitosan matrix was heated at 100°C, during 2 h.

The catalytic experiments were carried out in a stirred batch reactor at 60° C. In a typical experiment, the reactor was loaded with 30 mL of methanol, 0.2 g of chitosan with sulfonic acid groups. Reactions were started by adding 8 mmol of fatty acid.

Results and Discussion

Figure 1 shows the FTIR spectra of chitosan (CH) and chitosan crosslinked with sulfosuccinic acid (CH-SO₃H). The absorption band at 1730-1735 cm⁻¹ in the spectrum of CH-SO₃H, usually assigned to the ester group (-CO-O-), suggests that the crosslinking with SSA was succeeded. The absorption band at 1255 cm⁻¹ in the spectrum of CH-SO₃H, which does not appear in the spectrum of CH, indicates the presence of the sulfonic acid group by the introduction of SSA.

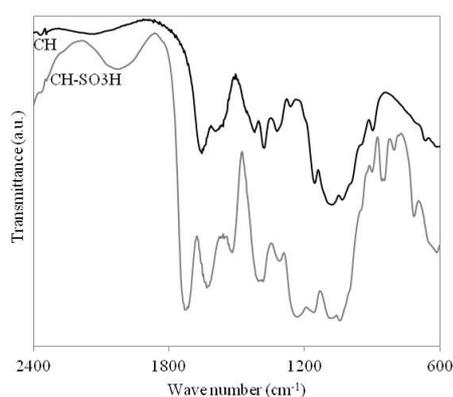


Figure 1. FTIR spectra of chitosan (CH) and chitosan crosslinked with sulfosuccinic acid (CH-SO₃H)

Figure 2 shows the initial catalytic activities of chitosan with sulfonic acid groups in esterification of palmitic acid, oleic acid and stearic acid calculated from the maximum slopes of ester kinetic curves. It was observed the catalytic activity of CH-SO₃H for the different substrates used in esterifications decreases slightly with the length chain of the fatty acids.

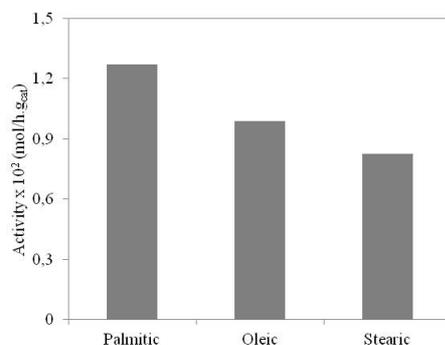


Figure 2. Esterification of FFA with methanol over CH-SO₃H at 60° C.

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