

Transesterification of Soybean Oil for Biodiesel Production Using Hydrotalcite as Basic Catalyst

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Biodiesel, a mixture of fatty acid (methyl) esters (FAME), is a renewable fuel produced from the homogeneous catalytic transesterification of vegetable oils and animal fats, using basic hydroxides as catalysts.

Advantages such as product separation, catalyst reuse and favorable reaction conditions, inherent in the heterogeneous catalytic transesterification process, have led to the development of various solid catalysts to carry out this reaction.

The hydrotalcite has been considered of great interest in the transesterification reaction due to its strong basicity, high surface area and pore volume. It consists of a natural anionic clay containing carbonate anions intercalated between lamellar double hydroxide, magnesium and aluminum. The lamellar double hydroxides, although not abundant in nature, can be synthesized in the laboratory at a relatively low cost. Thus, this study investigated the transesterification of soybean oil to produce biodiesel using methanol and Mg/Al hydrotalcite as a basic catalyst solid.

In this work, hydrotalcite was synthesized using the co-precipitation method with Mg/Al molar ratio of 3.0 and calcined at 450 °C (723 K), under Ar flow, for 6 h. The obtained solid was characterized by X-ray powder diffraction and temperature-programmed desorption of CO₂ (CO₂-TPD). The reactions of transesterification were carried out at atmospheric pressure and at 64 °C (337 K) in a jacketed reactor coupled to a condenser, under magnetic stirring, by varying the molar ratio methanol/oil and the reaction time. The obtained ester phase was characterized by viscosity and gas chromatography.

The best condition was achieved with a methanol/oil molar ratio of 20:1, 5.0 % catalyst (w/wt), for 10 h, which resulted in the highest FAME conversion of 94.8 %. The result was showed that the proposed solid catalyst is a promising for the production of biodiesel via heterogeneous catalytic transesterification under milder reaction conditions.

1. Introduction

Biodiesel is a renewable clean bio-fuel, which is defined chemically as a mixture of methyl esters with long-chain fatty acids (FAME). Typically, it is produced from the homogeneous catalytic transesterification of vegetable oils and animal fats with alcohol, using basic hydroxides as catalysts (da Silva, 2011). Usually, methanol is the preferred alcohol for the production of biodiesel due to its low cost and industrial availability (Leung et al., 2010).

The homogeneous process leads to higher yields, especially if the content of free fatty acids (FFAs) in the used feedstock is less than 1 %, when compared to the heterogeneous catalytic transesterification (Karmakar et al., 2010). Nevertheless, the homogeneous process presents some disadvantages in its application, such as expensive separation of the homogeneous catalyst from the reaction mixture; generation of large amounts of wastewater during the separation and purification of the product and

formation of soap due to the reaction of the alcohol with the FFA's present in the reaction medium (Sharma and Singh, 2010).

Therefore, advantages like product separation, the most favorable reuse of the catalyst and reaction conditions, inherent in heterogeneous catalytic transesterification process, have led to the development of different heterogeneous solid catalyst (Borges and Díaz, 2012).

Metal oxides represent a group of heterogeneous basic catalysts most widely studied in the literature. Among them there are the calcium oxide, magnesium oxide, strontium oxide, mixed oxides and hydrotalcite (Borges and Díaz, 2012). The Mg-Al hydrotalcites have been considered of great interest in the transesterification reaction, due to the fact that they are resistant to the presence of water and FFA, show high activities and give no place to leaching (Santacesaria et al., 2012).

Hydrotalcite is a clay mineral containing carbonate anions intercalated between lamellar double hydroxide, magnesium and aluminum. These compounds may be represented by the following general formula: $M_{(1-x)}^{2+}M_x^{3+}(\text{OH})_2(\text{A}^{n-})_{x/n} \cdot y\text{H}_2\text{O}$, where M^{2+} and M^{3+} represent divalent and trivalent metal cations, respectively, and A^{n-} represents an intercalated anion with charge n (Wang and Jehng, 2011). Hydrotalcites have an ideal formula of $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ (Guerreiro et al., 2011). The activation of hydrotalcite by thermal treatments removes the interlayer carbonate, forming the Mg-Al mixed oxides with high specific surface areas and excellent basic properties (Guerreiro et al., 2011).

Silva et al. (2010) investigated the methanolysis of soybean oil using Mg-Al hydrotalcites as heterogeneous catalyst and indicated the need for optimization of reaction conditions for transesterification to produce biodiesel using hydrotalcite. This is due to the fact that high temperatures are needed to obtain better yields. Thus, this study investigated the transesterification of soybean oil to biodiesel production using methanol and solid basic catalysts hydrotalcite-type Mg/Al in mild conditions of temperature and pressure.

2. Experimental

2.1 Hydrotalcite preparation

The hydrotalcite used in this work was synthesized by the co-precipitation method as described by Guerreiro et al. (2011). A solution containing 0.28 mol of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.09 mol of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was mixed with a second solution containing 0.84 mol of NaOH and 0.25 mol of Na_2CO_3 , at room temperature, under vigorous stirring. The mixture was maintained under stirring at 60 °C for 12h. The resulting sample was filtered and washed with deionized water until neutral pH. Then, the hydrotalcite was dried at 60 °C for 12h, followed by calcination under Ar flow at 450 °C for 6h, using a heating rate of 2 °C min^{-1} .

2.2 Hydrotalcite characterization

The characterization of the catalyst structure was obtained by powder X-ray diffraction (XRD). The patterns were obtained on a Shimadzu diffractometer model XRD600 with monochromatic radiation source of $\text{CuK}\alpha$ at 40 kV and filament current of 30 mA. Measurements were made with a diffraction angle 2θ from 5 to 85 ° with step of 0.02 ° at a speed of 1.2 ° min^{-1} .

The basic strength of the hydrotalcite synthesized was obtained by temperature-programmed-desorption (TPD) of CO_2 . The TPD was performed using a quadrupole mass spectrometer QMS-200 (BALZER). The sample (250 mg) was dried in Ar flow at 383 K (5 K min^{-1}) for 120 min. Then, the sample was cooled to room temperature, and the adsorption of CO_2 was carried out using a mixture of 10 % CO_2 /Ar in a flow of 30 mL min^{-1} , followed by purging with Ar. Finally, the sample was heated up to 1,023 K (5 K min^{-1}) using Ar as the carrier gas at a flow rate of 30 mL min^{-1} . Thus, the amount of desorbed CO_2 was calculated using a pulse of pure CO_2 (reference).

2.3 Transesterification reaction

The hydrotalcite was tested in transesterification reactions of commercial soybean oil with anhydrous methanol. The reactions were carried out at atmospheric pressure, in a batch jacketed reactor with a capacity of 50 mL, under magnetic stirring, connected to a condenser.

The experiments were carried out at a temperature of 64 °C (337 K) with 5 % (weight basis) of catalyst concentration varying the molar ratio (MR) methanol/ oil and reaction time as shown in Table 1.

After the reaction, the hydrotalcite was separated from the reaction medium by centrifugation at 8,000 rpm during 10 min and the final product was vacuum evaporated to remove the methanol excess. Then, the mixture was transferred to a decanting funnel for phase separation. After 24 h, the glycerol phase was separated and the ester phase (biodiesel) was collected. The quality of the obtained crude biodiesel, after

purification of the samples, was evaluated by measuring their viscosity and final content of fatty acids methyl esters (FAME).

Table 1: Transesterification reaction conditions

Experiment	Molar ratio (methanol:oil)	Reaction time (h)
1	10:1	5
2	20:1	5
3	10:1	10
4	20:1	10

The content of FAME was performed on a Shimadzu CG2010-AF Gas Chromatograph equipped with injector split/splitless and autoinjector AOC-20i coupled with a flame ionization detector (FID) and a 30 m × 0.25 mm × 0.25 μm capillary column specific for fatty acid separation, RTX-WAX. The carrier gas used was helium, in a split rate of 1:50. The analysis was performed with a column temperature program starting at 120 °C, heating up to 180 °C at 10 °C/min, after that heating up to 230 °C at 5 °C/min. The detector and injector temperatures were kept at 250 °C. The internal standard used was methyl heptadecanoate.

Biodiesel density and viscosity were determined according to the ASTM D1298 and D445, respectively. The viscosity of the final product was used as a parameter to show the occurrence of transesterification reaction. To determine the dynamic viscosity of the product a Brookfield rheometer (DV-III ULTRA) was used. The rheometer was coupled to a thermostatic bath, thereby measuring the viscosity at 40 °C. The viscosity values reported in this study are the mean values obtained for triplicate reading at a shear rate of 39.6 s⁻¹.

3. Results and Discussion

3.1 Catalyst characterization

The diffractogram of the hydrotalcite synthesized and used in this work is shown in Figure 1. It is typical of the hydrotalcite with Mg / Al = 3.0 calcined at 450 °C (337 K) for 6 h. After calcination, the characteristic lamellar structure disappears and XRD patterns show the presence of only MgO-like phase, which was observed by Silva et al. (2010) and Di Serio et al. (2012). This same diffraction pattern is shown in the work of Yang et al. (2002) who did a study of the structural changes that occur in hydrotalcites Mg/Al when subjected to thermal treatments.

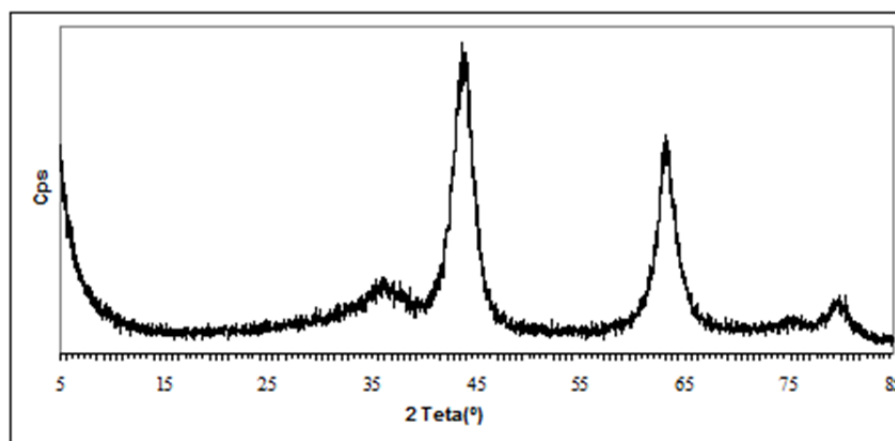


Figure 1: X-ray diffractogram of the Mg/Al = 3 hydrotalcite after calcination at 450 °C (337 K)

CO₂-TPD was also performed to investigate the basicity of the synthesized hydrotalcite. The result is displayed in the Figure 2. The TPD profile obtained is similar to the profiles of other publications in the literature (Bergada et al., 2007).

According to Di Serio (2012) the material obtained can be characterized qualitatively by dividing the profile of CO₂ desorption in three ranges of temperature (room temperature < 200 °C; 200 °C – 450 °C and > 450 °C) and associating them with the forces effects acting on the structures. In this spectrum it can be identify

the presence of basic active sites under the influence of low and medium binding forces / interaction forces. Di Serio et al. (2012) attribute the existence of strong sites due to the presence of isolated anions O^{2-} or the occurrence of decarbonation. The highest intensity peak that appears during the TPD, in the intermediate temperature range, indicates the presence of basic sites of moderate intensity. The low intensity peak that appears at the temperature region below 200 °C (473.15 K) it is attributed to the CO_2 physisorbed. It is found that the sites of moderate basicity are the most numerous sites in the sample of hydrotalcite synthesized.

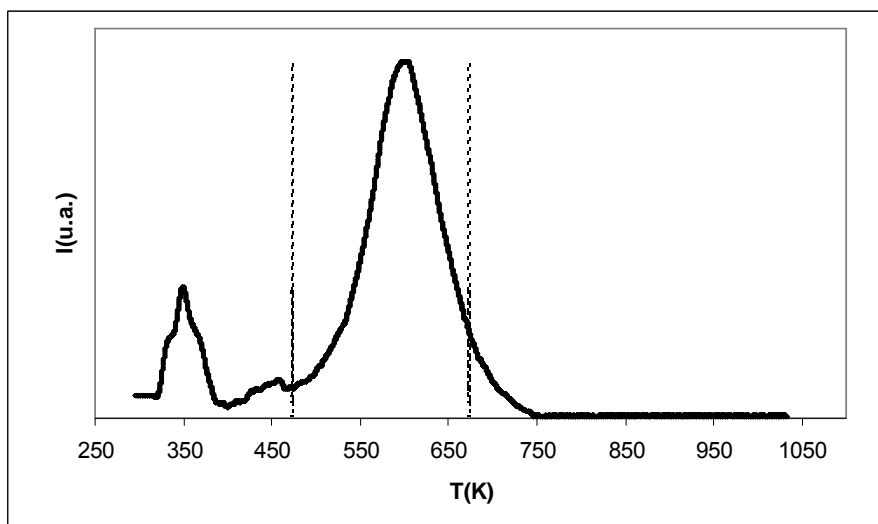


Figure 2: CO_2 – TPD profile for the Mg/Al = 3 hydrotalcite after calcination at 450 °C (337 K)

3.2 Transesterification reaction

Table 2 shows the ester yield (%FAME) and dynamic and kinematic viscosities (μ and η , respectively) of biodiesel samples analyzed after transesterification reactions of soybean oil with methanol using hydrotalcite (HT) as catalyst at experimental conditions described in Table 1. The ester content, expressed as a mass fraction in percent (%FAME), was calculated using the equation 1, according to the method EN 14103. The integration was carried out as from the methyl myristate (C14) peak up to that of the methyl ester in C24:1 taking all the peaks into consideration, including the minor ones.

$$C = \frac{(\sum A) - A_{EI}}{A_{EI}} \times \frac{C_{EI} \times V_{EI}}{m} \times 100\% \quad (1)$$

Where C is the ester content, $\sum A$ is the total peak area from the methyl ester in C₁₄ to that in C_{24:1}; A_{EI} is the peak area corresponding to methyl heptadecanoate; C_{EI} is the concentration, in mg/mL, of the methyl heptadecanoate solution; V_{EI} is the volume, in mL, of the methyl heptadecanoate solution and is the mass, in mg, of the sample.

The kinematic viscosity (μ) was estimated from the ratio of the dynamic viscosity (η), measured experimentally, and the density of biodiesel, which is equal to 880 kg m⁻³. The viscosity of the soybean oil, measured experimentally, used as a feedstock was 29.6 mPa s.

Table 2: Characterization of the biodiesel obtained using hydrotalcite as catalyst at 5 % (wt)

Experiment	% FAME	η (mPa s)	μ (mm ² /s)
1	42.4	3.7	4.2
2	93.2	4.0	4.6
3	92.6	5.2	5.9
4	94.8	4.0	4.6

The results demonstrated that the hydrotalcite is a promising catalyst for biodiesel production, considering that the viscosity of the oil was reduced to values within or very close to that recommended by the legislation. The purity of the final biodiesel product is an important issue, which in Brazil is specified by the

National Agency of Petroleum, Natural Gas and Biofuels (ANP), based on the American ASTM D6751 and European EN14214 standards, with some modifications to meet the Brazilian raw material requirements (Gomes et al., 2011). The norm EN 14214 establishes an acceptable range of viscosity from 3.5 to 5.0 mm²/s, while ASTM D6751 allows a somewhat broader range from 1.9 to 6.0 mm²/s and viscosity permitted by the resolution of ANP 07/08 is from 3.0 to 6.0 mm²/s (ANP, 2008).

The results of % FAME presented in Table 2 show that with the smallest amount of methanol required a reaction time over 5h to obtain acceptable yields. Increasing the molar ratio of methanol/oil, highest conversions were obtained even in a lowest reaction time. The highest conversion (94.8 %) was achieved with methanol/oil molar ratio of 20:1 at 10h. Silva et al. (2010) investigated the methanolysis of soybean oil using Mg-Al hydrotalcites calcined at 500 °C and obtained the highest yield of 90 % with methanol/oil molar ratio of 13:1, 5 % (wt%) of catalyst in harsher conditions (T = 230 °C and P = 34 atm) but with a reaction time of only 1 h.

The results reported in this paper are in agreement with that reported by Gomes et al. (2011) at similar condition of transesterification reaction. The authors employed MgAl hydrotalcites as solid heterogeneous catalysts for biodiesel production and found yields more than 90 % FAME, using different types of vegetal oils.

4. Conclusions

The hydrotalcite synthesized in this work showed satisfactory catalytic activity for biodiesel production by the reaction of soybean oil with methanol under mild conditions of temperature and pressure. These results reinforce the possibility of obtaining biodiesel from transesterification of soybean oil using hydrotalcite as catalyst. The obtained results showed that greater conversions are obtained carrying out the reaction at greater times (10h) or at greater methanol:oil molar ratios. The highest ester content (94.8%) was achieved applying a molar ratio of 20:1 (methanol:oil) and with a reaction time of 10 h.

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