

## Ethanolysis of Soybean Oil Using Mesoporous Molecular Sieves

Solange A. Quintella<sup>1</sup>, Davi C. Salmin<sup>1</sup>, Antonio S. Araújo<sup>2</sup>, Monica C.G. Albuquerque<sup>1</sup>,  
Célio L. Cavalcante Jr.<sup>1,\*</sup>

<sup>1</sup> Universidade Federal do Ceará, Fortaleza, Brazil

<sup>2</sup> Universidade Federal do Rio Grande do Norte, Natal, Brazil

\* Corresponding author. Tel: +55 85 3366-9611, Fax: +55 85 3366-9611, E-mail: celio@ufc.br

**Abstract:** This study evaluates the use of nanostructured materials as catalyst in biodiesel production from soybean oil using ethanol as transesterificant agent. Ethanol can be environmentally advantageous over methanol (more frequently used as reagent in biodiesel production) because it can be obtained from renewable sources whilst methanol is usually derived from mineral sources. The catalyst (La<sub>50</sub>SBA-15) has lanthanum oxide as active phase which was inserted by isomorphous substitution into the SBA-15 network. The LaSBA-15 mesoporous molecular sieves were synthesized using pluronic (P123) dissolved in aqueous HCl solution with tetraethyl orthosilicate and a given amount of hydrated lanthanum chloride (Si:La = 50) at 333K. The reaction was performed using the molar ratio soybean oil:ethanol of 1:20 at inert atmosphere (N<sub>2</sub>) at 343K with 1wt% of catalyst mass relative to total oil mass added to the reaction mixture. The reaction was evaluated for ethyl ester conversion after 3h and 6h. The ethyl esters content was measured using low frequency <sup>1</sup>HNMR spectroscopy (200MHz). A conversion of soybean oil in ethyl esters (biodiesel) of 80% after reaction time of 6h was obtained. The La<sub>50</sub>SBA-15 heterogeneous catalyst showed good performance in the ethanolysis of soybean oil, comparing well with previous reports for methanolysis of soybean oil.

**Keywords:** Biodiesel, ethanolysis, heterogeneous catalysis, La<sub>50</sub>SBA-15.

### 1. Introduction

Biodiesel can be defined as a fuel composed of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. The most common process for biodiesel production consists in a transesterification reaction in which a triglycerides source (vegetable oil or animal fat) reacts to a short chain alcohol (usually methanol) in catalyst presence [1-3]. Since ethanol is largely obtained in Brazil from renewable sources (mostly sugarcane) it might be advantageous to replace methanol in the transesterification reaction for biodiesel production [4].

The transesterification reaction may be catalyzed by acids, bases or enzymes [5]. Industrially, basic homogeneous catalysts such as potassium hydroxide and sodium hydroxide are often used in biodiesel production, because they display high reactivity, low cost and mild reaction conditions. However, as usually observed in homogeneous catalyst systems, they require downstream separation of the catalyst and byproducts, thus increasing the process complexity and cost [6-9]. Therefore process development for biodiesel production from heterogeneous catalysts has been largely studied in recent years [5,6,10-12]. Albuquerque et al. [11] studied calcium oxide catalytic properties supported on several mesoporous SBA-15 silica in transesterification of castor and sunflower oil with methanol. Yan et al. [6] studied the use of calcium oxide modified with lanthanum in the transesterification reaction with methanol. The mixture CaO-La<sub>2</sub>O<sub>3</sub> showed higher catalytic activity than when using pure calcium oxide or pure lanthanum oxide. Yan et al. [7] also studied the use of ZnO-La<sub>2</sub>O<sub>3</sub> as heterogeneous catalyst in the transesterification of unrefined or waste oil with methanol with noticeable strong interaction between zinc and lanthanum species. The catalyst sample with a 3:1 zinc lanthanum molar ratio displayed higher activity compared to pure metal oxides. Sun et al. [13] studied the properties of ZrO<sub>2</sub> impregnated with La<sub>2</sub>O<sub>3</sub> as a catalyst in sunflower oil transesterification with methanol. The best methyl ester conversion was found when using a catalyst concentration of 21wt.% La<sub>2</sub>O<sub>3</sub> on ZrO<sub>2</sub>.

This study intends to investigate the use of La<sub>50</sub>SBA-15 in soybean oil transesterification using ethanol. The La<sub>50</sub>SBA-15 has lanthanum oxide as active phase inserted into SBA-15 framework by isomorphous substitution.

## 2. Materials and Methods

### 2.1. Catalyst Preparation and Characterization

The SBA-15 modified with lanthanum was synthesized by hydrothermal method using 4.0 g of Pluronic P123 (BASF Co.) as template, dissolved in 10.3 mL of aqueous HCl solution (VETEC, Brazil). Thereafter 10.3 mL of tetraethyl orthosilicate (Sigma-Aldrich) and a given amount of previously dissolved hydrated lanthanum chloride (VETEC, Brazil) were added (Si/La = 50), and the mixture stirred for 22 h at a temperature of 333 K. The resulting gel was placed into a Teflon container and submitted to hydrothermal treatment at a temperature of 373 K for 48 h. The solid was then filtered at room temperature, washed with a solution of HCl in ethanol 2 wt%, dried at 333 K for 1 h, and finally the solid was calcined at 823 K (heating rate=1 K/min). The samples, designated as La<sub>50</sub>SBA-15 (where 50 refers to the Si/La molar ratio) were characterized through X-ray diffraction (DRX), N<sub>2</sub> adsorption and desorption isotherms at 77 K, and scanning electron microscopy (SEM). Further details may be found in Quintella [14].

### 2.2. Reaction

The reaction experimental set-up consisted of a 100 mL round-bottomed flask with four outlets. A thermometer was attached to the first outlet for temperature control. The reflux condenser was inserted into the second one to minimize the ethanol loss through evaporation and the third received nitrogen flow providing inert atmosphere. The fourth outlet was used to introduce the catalyst and remove aliquots in order to monitor the reaction.

Initially the catalyst was activated at 1073 K, under inert atmosphere, during 1 hour in order to convert carbonates eventually formed by atmosphere contact into oxides since carbonates do not show catalytic activity [10]. In the transesterification reactor, 30.3 g of commercial soybean oil (Liza, Sao Paulo, Brazil) were added to 99.6% ethanol (J.T.Baker, Mexico). The molar ratio of soybean oil and ethanol used was 1:20. The reaction was carried out at inert atmosphere using 1000 rpm agitation. When the oil and alcohol mixture reached the desired temperature, 343 K, the catalyst was inserted to the reaction mixture using a catalyst/oil mass ratio of 0.01. Samples of 5 mL were taken after 3h and 6h, filtered under vacuum to extract the catalyst from the reaction mixture. To improve the phase separation in the reaction mixture, 99.5% dichloromethane (Cromolina, Diadema, Brazil) was added, and subsequently vaporized from the ester phase at 373 K.

The ethyl ester conversion was evaluated through hydrogen nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR) with 60 MHz frequency using Varian EM-360 equipment and CDCl<sub>3</sub> as solvent [15,16]. The <sup>1</sup>H NMR technique for ethyl esters determination is based on the analysis of three sets of signals: (A<sub>1</sub>) the hydrogen from the ester ethoxy carbons; (A<sub>2</sub>) the four methylene hydrogens from glycerol; (A<sub>3</sub>) the α-methylene carbonyl hydrogen present in all mono, di and triglycerides from both oil and fatty acid ethyl esters [17]. The conversion of soybean oil (EE) into biodiesel (ethyl esteres) was obtained from the <sup>1</sup>H NMR technique using Eq. (1).

$$EE(\%) = \frac{(A_1 - A_3)}{A_2} \times 100 \quad (1)$$

### 3. Results and Discussions

#### 3.1. Catalyst Characterization

The diffractograms of SBA-15 and La<sub>50</sub>SBA-15 are shown in Fig. 1. Three major peaks, referring to Miller index crystalline plans (100), (110) e (200), are characteristic of hexagonal symmetry p6mm (punctual planar group two-dimensional 6mm), common in mesoporous materials similar to SBA-15 [18-20]. It may be observed that the incorporation of lanthanum did not affect the hexagonal structure typical of SBA-15.

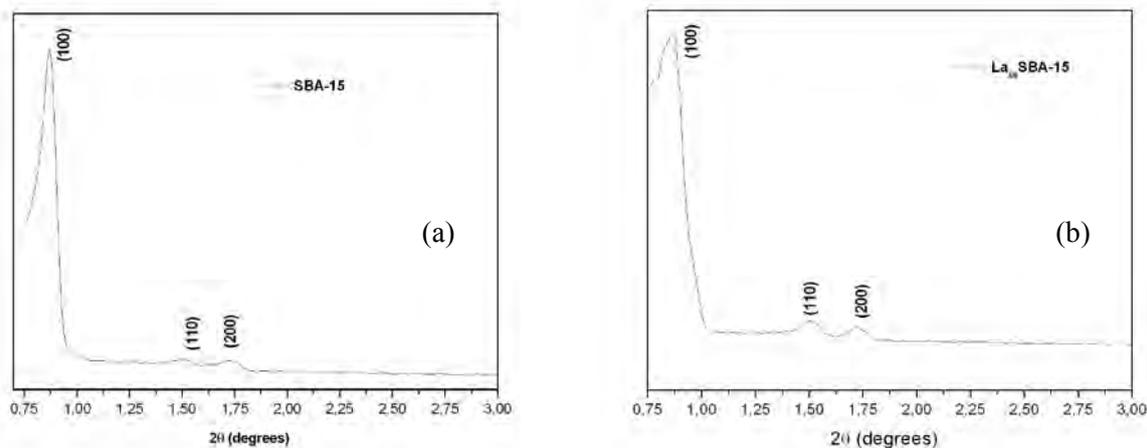


Fig. 1. X-Ray Diffractograms (a) SBA-15 ; (b) La<sub>50</sub>SBA-15.

The nitrogen adsorption and desorption isotherms for samples show a type IV shape (Brunauer classification) as characteristic for nanoporous materials (see Fig. 2). Table 1 summarizes the textural properties of both samples (SBA-15 and La<sub>50</sub>SBA-15).

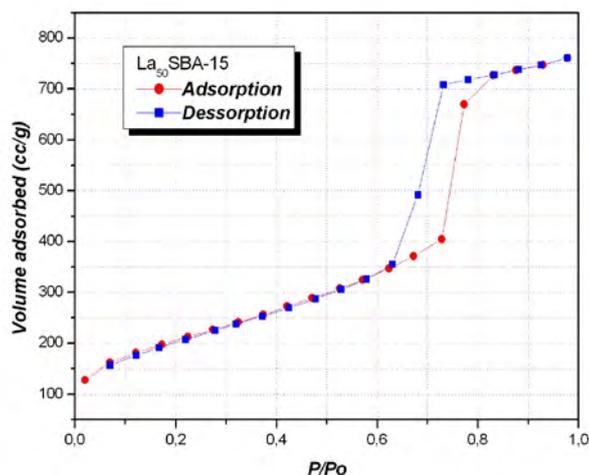
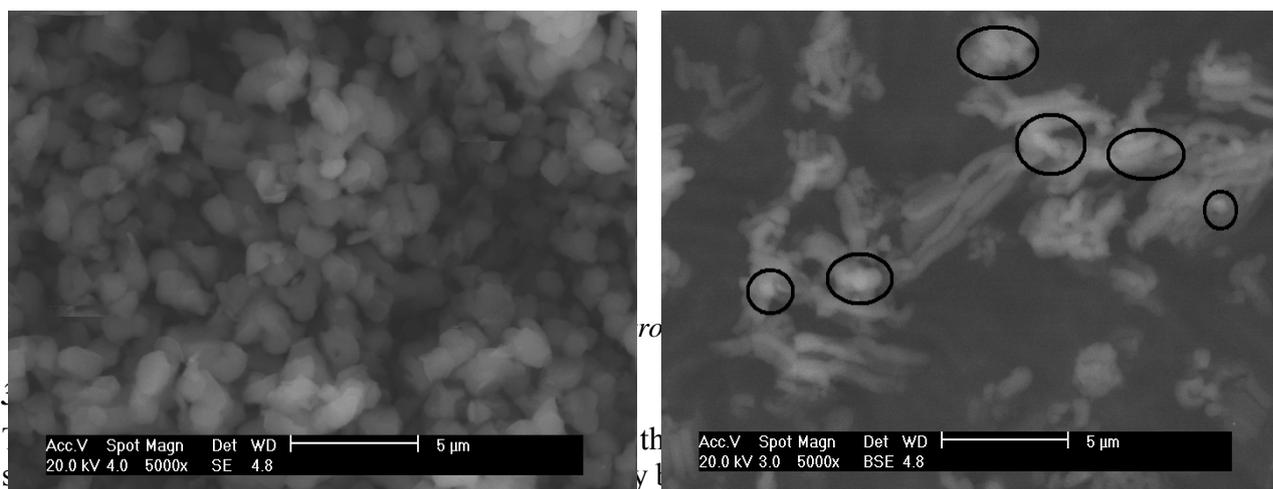


Fig. 2. N<sub>2</sub> adsorption

Table 1. Textural characteristics synthesized materials samples

Sample	a <sub>0</sub> (nm)	D <sub>p</sub> (nm)	V <sub>p</sub> (cm <sup>3</sup> g <sup>-1</sup> )	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )
SBA-15	11.88	4.33	0.95	931.3
La <sub>50</sub> SBA-15	11.88	7.29	1.09	735.2

The SEM micrographs for both samples are shown in Fig. 3. It may be observed that SBA-15 displays a non uniform morphology showing irregular spheres (Fig. 3a). For La<sub>50</sub>SBA-15 (Fig. 3b), it may be noted some regions with clearer areas than others, indicating the presence of another material, probably lanthanum, which had not been observed in Fig. 3a. The lanthanum addition to the support framework caused morphological changes indicated by the noticeable stick shapes.



glycerol methylenic hydrogen; four glycerol hydrogens; dimethylenic hydrogens; three CH<sub>2</sub> α-carboxylic groups; CH<sub>2</sub> carbon groups neighboring the unsaturated carbons; CH<sub>2</sub> carbons neighboring the saturated carbons; CH<sub>2</sub> carbons bonded to 2 saturated carbons atoms; and three terminal methyl groups.

The <sup>1</sup>H RMN spectrum of the ethyl ester product is shown in Fig. 5. The quartet signal relative to the OCH<sub>2</sub>- group hydrogen, which appears exclusively at the spectrum of the ethyl esters molecule, may be observed in the region of 3.8-4.2 ppm. Also, the triplet signal relative to α-CH<sub>2</sub>- groups, which may be found in both oil and ethyl esters, is seen in the region of 2.2-2.5 ppm.

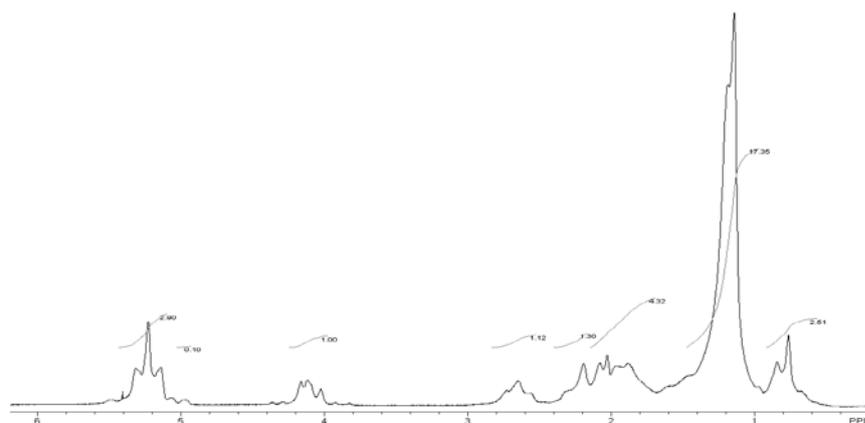


Fig. 4. <sup>1</sup>H NMR spectrum of pure soybean oil.

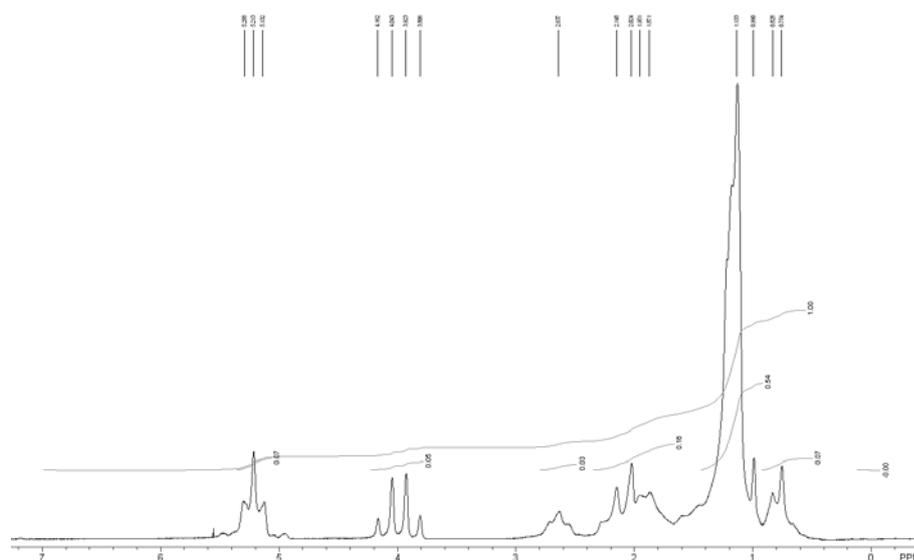


Fig. 5.  $^1\text{H}$  NMR spectrum of the ethyl ester after 6 hours of reaction.

The  $^1\text{H}$  RMN spectrum of the product after reaction time of 3 hs showed no conversion to ethyl ester. After 6 hs (Fig. 5), the calculated value of the conversion of soybean oil with ethanol using as catalyst in the transesterification reaction was 80% v/v, which is comparable to previously reported values (see Table 2). The classical homogenous process catalyzed by KOH is reported using ethanol as transesterificant agent with conversions as high as 96%v/v, however the downstream separation of the products (ester/glycerin phases) is rather difficult if compared to heterogeneous systems.

Other studies using heterogeneous catalysts with methanol, instead of ethanol, have been reported (also seen in Table 2). Those studies present somewhat higher values for conversion (as high as 98%v/v of methyl ester), however at more extreme operation conditions (temperature and time) and higher ratios of alcohol/oil and catalyst/oil.

Table 2. Comparison of conversion to biodiesel with previously reported values.

Oil/Alcohol	Alcohol/Oil molar ratio	Catalyst	Catalyst/oil mass ratio	Temp. (K)	Time (h)	Conv. (%v/v)	Ref.
Soybean/EtOH	20	LaSBA15	0.01	343	6	80.0	This study
Soybean/EtOH	18.8	homogeneous (KOH)	0.01	n.a.	4	96.0	22
Soybean/MeOH	21	$\text{Ca}_3\text{La}_1$	0.05	331	3	94.3	6
Waste/MeOH	36	$\text{ZnO-La}_2\text{O}_3$	0.023	473	2	95.0	7
Sunflower/MeOH	30	$\text{La}_2\text{O}_3/\text{ZrO}_2$	0.05	473	5	98.1	13

#### 4. Conclusions

The results of the transesterification reaction of soybean oil using  $\text{La}_{50}\text{SBA-15}$  as heterogeneous catalyst confirm the possibility of its use in the ethanolysis of soybean oil at milder operation conditions than previously reported studies with methanol. A conversion of 80.0%v/v could be obtained using oil/ethanol molar ratio of 1:20; catalyst/oil mass ratio of 0.01; temperature 343 K; inert atmosphere; and 6 hours of reaction.

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