



Activity of heterogeneous catalysts in the methyl and ethyl transesterification of soybean oil

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Abstract

The aim of this study was to evaluate the synthesis of methyl and ethyl esters of soybean using two different types of heterogeneous catalysts: mesoporous molecular sieve [CTA+]Si-MCM-41 and KF-clay. Reaction conditions using methanol were temperature of 80°C with molar ratio of 1:12 to oil/alcohol, and 1:9 to [CTA+]Si-MCM-41 and KF-clay, respectively. Reaction times ranged from 1 to 2 hours. With the application of ethanol, the catalyst mass was maintained and some conditions were changed, such as temperature at 100°C, molar ratio of 1:15 and 1:12, and reaction time of 4 hours. Catalysts were characterized by means of (BET) N₂ physisorption, X-ray diffraction (XRD) and scanning electron microscopy (SEM). Conversions of ethyl esters were lower than those of methyl esters. With catalysts [CTA+]Si-MCM-41 and KF-clay, conversions of 6.4 and 63.3% by using ethanol as well as conversions of 91.0 and 95.2% with methanol were obtained.

Key words: Ethanol, methanol, potassium fluoride.

Introduction

The world's leading energy generation today comes from fossil sources, but even though there is high dependence on these sources, the consistent development of some countries, based on the desire for energy independence and alternatives that tend to minimize the generation of greenhouse gases (GHGs), boost the study and development of renewable fuels ¹. One of the alternative fuels obtained from biomass is biodiesel, which stands out worldwide as part of the Brazilian commercial large-scale production, and presents high investment in the sector as well as wide variety of raw materials, such as vegetable oils and animal fats ².

Brazil currently has a biodiesel manufacturing capacity of around 7.40 million m³/year. The production in 2012 amounted to 2.71 million m³, whereas in 2011 it reached 2.67 million m³. With the new regulation for biodiesel in Brazil, in which the mixture will rise from 5% to 7%, the country is able to ensure biodiesel supply just by utilizing its unused capacity ³.

Biodiesel consists of alkyl esters of long chain carboxylic acids. Its synthesis can happen by various means, including the process of transesterification of vegetable oil, which is the one used more often, due to its ease of application and availability of raw materials. The transesterification reaction aims to reduce the viscosity of vegetable oils and increase volatility, generating glycerin as a byproduct when under stoichiometric conditions ^{4,5}.

The production of these esters consists of the reaction of alcohol

with lipid sources and the application of a catalyst. Methanol and basic homogeneous catalysis are the most used in the reaction of transesterification due to technical and economic reasons, but this alcohol presents some drawbacks, such as its high toxicity. Its synthesis is based on non-renewable sources, and Brazil is not self-sufficient in its production ⁶.

An alternative route to the production of methyl esters is the ethyl route process. Ethanol presents some favorable features when compared to methanol because it is nontoxic and is obtained from renewable sources. Brazil is considered one of the largest ethanol producers in the world, thus, its employment in biodiesel production processes can be feasible ⁷.

Transesterification with basic homogeneous catalysis is most often used process due to its low cost and the ability to allow the use of lower temperatures and pressures, providing lower energy expenditure ⁸. Although basic transesterification has these advantages, there are some drawbacks, such as the production of undesired compounds, impossibility of reusing the catalyst and difficulty in purifying biodiesel and glycerin ⁹. Thus, the search for a process that provides better yield has been intensified. An option to replace homogeneous catalysts is heterogeneous catalysis, which provides a more pure biodiesel; the catalyst can be recovered and reused, and it also contributes to less waste production during the stage of biodiesel purification ¹⁰.

Mesoporous MCM-41 molecular sieves are the most used

catalysts and are characterized by high surface area, large pore diameter and considerable thermal and hydrothermal stabilities and have unidirectional pores. The use of such materials for biodiesel production has been studied in reactions which can involve high molecular weight molecules, such as triglycerides¹¹. A study on the synthesis of biodiesel from sunflower oil using heterogeneous catalyst NbMCM-41 8% showed 84% conversion¹². Georgogianni *et al.*⁹ used Mg/MCM-41 and verified that the yield of the reaction corresponded to 19% and 85% at periods of 5 and 24 hours, respectively.

Furthermore, clays have also received attention due to their environmental friendliness, low cost, selectivity, and thermal and recycling. One of the studied treatments is impregnation with potassium fluoride (KF) in the clay. It is assumed that fluoride ions bind to silicon ions present in the clay, resulting in a Si-F bond¹³. Alves *et al.*¹⁴ obtained a conversion of 99.7% when using smectite with KF treatment in the reaction involving soybean oil with methanol at 42°C and reaction time of 1 hour.

This study aimed to evaluate the synthesis of alkyl esters using two different alcohols (methanol and ethanol) and heterogeneous catalysts [CTA⁺]Si-MCM-41 and KF-clay, assessing the conversion of methyl and ethyl transesterification, the action of potassium fluoride and leaching of the catalysts along the reaction.

Materials and Methods

Synthesis of catalysts

MCM-41 molecular sieve: For the preparation of MCM-41 mesoporous molecular sieve, we adopted the method of Grün *et al.*¹⁵. The reagents used were CTMABr (Sigma) - 99% (director agent) NH₄OH - 29% Fmaia (mineralizing agent) TEOS - 98% Acros Organics (tetraethyl orthosilicate) as a source of silica, absolute EtOH - 96% (ethyl alcohol) as co-solvent of TEOS and ultra-purified water. The CTMABr was dissolved in water and added to a solution of ethyl alcohol/NH₄OH. This mixture was subjected to agitation for 15 min at 30°C. Subsequently, the TEOS was added to the reaction medium where it remained for 2 hours under stirring. The gel formed was filtered and washed with 400 ml of water and dried at 60°C for 24 hours.

KF-clay: Bentonite clay was subjected to drying in an oven at 110°C for 24 hours. After the drying step, the sample underwent treatment with inorganic salt (KF - 98% Synth). Initially, we prepared a suspension of 15% (m/v) of the sieve calcined in a 1.5 M KF solution, which remained under constant stirring at a reflux system at 80°C for 30 min. The suspension was subjected to water removal, which consists in keeping it in a hot plate under stirring. After water removal, the sample underwent complete electric oven drying at 110°C for 24 hours. The sample was subsequently deagglomerated.

Catalysts characterization: In this work, N₂ physisorption analyses were performed by the methods of Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD) and scanning electron microscopy (SEM).

Surface area by the BET method: Equipment used for the determination of the surface area of the catalysts involved in this work consisted of Quantachrome Corporation's Nova-2000.

X-ray diffraction (XRD): In order to analyze the MCM-41 mesoporous molecular sieve, we used a Rigaku Geigerflex diffractometer (radiation of Cu K α 45kV-25mA) with scanning of 1.5° < 2 θ < 40°, and speed of 1°/min. As for the KF-clay heterogeneous catalyst, analysis was performed in Siemens Kristalloflex equipment, in the range of 4° < 2 θ < 40° with K α radiation of copper (λ = 1.54056 nm, 40 kV, 40 mA), nickel filter and speed of 0.5°/min.

Scanning electron microscopy (SEM): To perform these analyses we used a FEI Quanta 440 scanning electron microscope. Samples were suspended in methanol and deposited in a sample holder and subsequently dried and metallized with a thin layer of gold on the surface. The images were obtained with zoom between 5000 X and 50000 X.

Production of esters: Regarding the transesterification reactions, reagents used were refined soybean oil, obtained from the local market, methyl alcohol (99.8%) and ethyl alcohol (99.5%). All reagents were used without pretreatment.

The reactions of ester production in this work were performed by methyl ethyl routes. Initially, catalysts were placed in an oven at 110°C for 12 hours for drying. The next step consisted in preparing the reaction mixture.

For the reactions of methyl transesterification with MCM-41 mesoporous molecular sieves and KF-clay, the reaction medium had oil/alcohol molar ratio of 1:12 and 1:9, catalyst mass corresponded to 5% and 15%, respectively (Table 1), maintaining a constant temperature of 80°C and reaction times of 1 to 2 hours. As for the ethyl transesterification, oil/alcohol molar ratio was 1:15 and 1:12 for the molecular sieve [CTA⁺]Si-MCM-41 and KF-clay, respectively, with temperature at 100°C and reaction time of 4 hours.

Table 1. Condition of the reaction medium in the production of methyl and ethyl esters.

Catalyst	Catalyst %	Oil/Alcohol molar ratio	t (h)	T (°C)	Type of alcohol
MCM-41	4	1:12	1 and 2	80	Methanol
	4	1:15	4	100	Ethanol
KF-clay	15	1:9	1 and 2	80	Methanol
	15	1:12	4	100	Ethanol

The whole procedure of ester production was conducted in a reactor of stainless steel with 50 cm³ with record of autogenous pressure. Upon completion of the reaction, the catalyst was separated from the mixture by vacuum filtration. Then the reaction mixture was centrifuged for 15 min at 3,000 rpm to facilitate the separation of ester and glycerin. The esters obtained were treated with anhydrous sodium sulfate for moisture removal. Subsequently, the excess alcohol was removed by evaporation.

Quantification in esters: Approximately 300 mg of sample was collected after the purification of the mixture of esters, added to a 10 mL volumetric flask and the volume was completed with n-heptane. Then 100 μ L of this solution was transferred to a 1 mL flask along with 100 μ L solution of methyl heptadecanoate (internal standard) at a concentration of about 13,000 mg/L. The balloon volume was again complete with n-heptane.

Then 2 μ L of solution was injected in duplicate into the Agilent

7890A gas chromatograph with flame ionization detector, ZB-WAX (Zebron) capillary column (30 m x 0.25 mm x 0.25 mm), split injection, 1:50, and column temperature of 160-230°C at a rate of 4°C/min. Samples were maintained at the final temperature for 3 min. Carrier gas was helium, at 1.5 mL/min; injector temperature 250°C. The conversion of esters was determined according to EN 14 103 (2001) using equation 1.

$$\text{Conversion (\%)} = \left(\frac{\sum A - A_{PI}}{A_{PI}} \frac{C_{PI}}{C_{\text{sample}}} \right) \times 100 \quad (\text{Equation 1})$$

where $\sum A$ = sum of the areas corresponding to ester peaks (C14:0 to C24:0) and internal standard (C17:0), A_{PI} = internal standard area (C17:0 – methyl heptadecanoate), C_{PI} = concentration of the internal standard in the sample injected (mg/L), and C_{sample} = concentration of the sample injected (mg/L).

Determination of catalytic activity of KF, in natural clay and KF-clay: KF-clay and in natural clay were tested in the transesterification reaction with methanol and ethanol (Table 2). The reaction conditions were as follows: with methanol, the oil/alcohol molar ratio was 1: 9 whereas with ethanol 1:12, with reaction time of 1 and 4 hours, and temperature of 80 to 100°C, respectively.

Table 2. KF loads used in catalytic assessment.

Samples	Alcohol	Oil/Alcohol molar ratio	t (h)	KF load (g)
In natura clay	Methanol	1:9	1	0
	Ethanol	1:12	4	
KF-clay	Methanol	1:9	1	1.17
	Ethanol	1:12	4	
KF	Methanol	1:9	1	2.45
	Ethanol	1:12	4	

Catalyst leaching test: Initially, 1.39 g of each catalyst was weighed and placed in a quantitative filter paper, which was closed with several folds. Then, the samples were kept in a system of reflux in Soxhlet with 150 mL of methanol or ethanol for a period of 10 hours. At the end of reflux, samples were dried at 100°C for 48 hours. After this period, samples were weighed again for the assessment of catalyst mass loss.

Results and Discussion

Catalyst characterization: Textural properties such as specific surface area, pore volume and pore diameter influence the activity performed by catalysts. The [CTA⁺]Si-MCM-41 mesoporous molecular sieve was characterized with a surface area of 36.834 m².g⁻¹, pore volume of 0.03362 cm³.g⁻¹, and pore diameter of 19.64 Å which is in the size range of mesoporous materials, within 2 to 50nm.

Surface area of the in natural clay corresponded to 44.219 m².g⁻¹. After saline treatment there was a reduction to 4.940 m².g⁻¹. This reduction was expected once that KF impregnation into clay tends to fill empty spaces.

X-ray diffraction of mesoporous molecular sieve MCM-41 presents three different peaks. Peak 100 is most intense. The other two are less intense with reflections at 110 and 200 (Fig. 1). These peaks are characteristic of MCM-41 as a consequence of its hexagonal order. The degree of order of the material can be verified by this analysis.

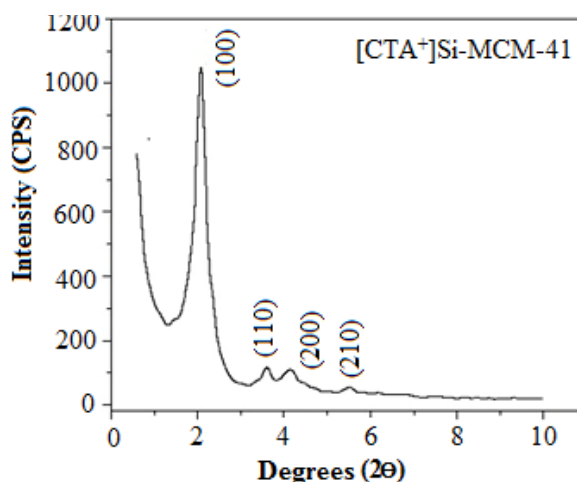


Figure 1. XRD analysis of mesoporous molecular sieve [CTA⁺]Si-MCM-41.

Compounds such as montmorillonite (Na-Mg-Al-Si₄O₁₁), quartz (SiO₂) and albite (Na(AlSi₃O₈)) (a type of feldspar which is typical of bentonite clay) were identified in the in natural clay and KF-clay. On the impregnated sample, it is possible to observe two peaks attributed to a crystalline phase formed by Fe, F and K right above 30°C, that did not exist before treatment (Fig. 2).

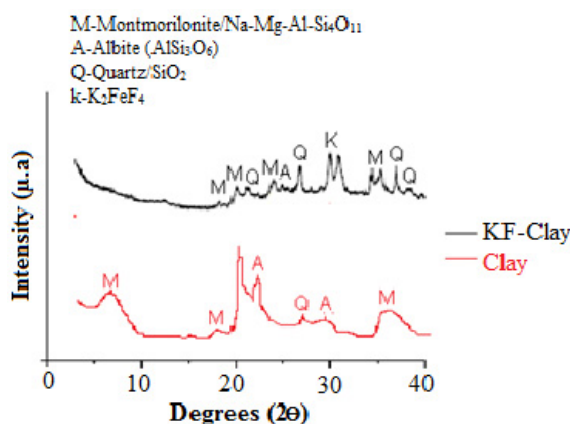


Figure 2. Diffractogram of in natura clay and heterogeneous KF-clay catalyst.

A homogenous distribution of particles can be seen on the analysis of the scanning electron microscopy. Particles present spherical aspect and size inferior to 1 μm, which are characteristics of a [CTA⁺]Si-MCM-41 (Fig. 3). After KF impregnation, there is more particle agglomeration, what causes a higher material roughness (Fig. 4).

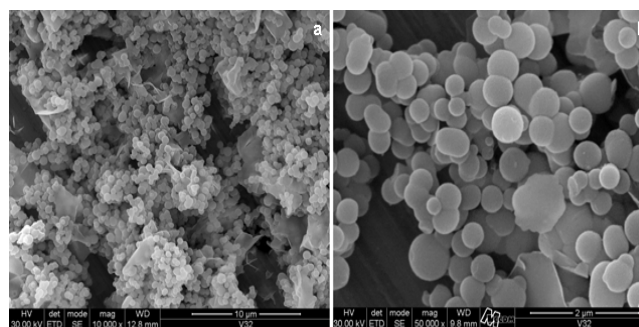


Figure 3. [CTA⁺]Si-MCM-41 micrograph (a) 10,000 x, (b) 50,000 x.

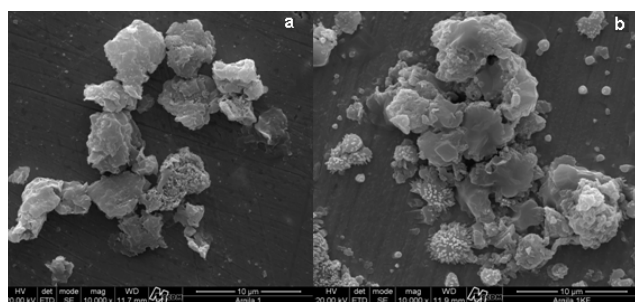


Figure 4. Micrograph (a) *in natura* clay and (b) KF-clay 10000 x.

Methyl and ethyl transesterification: Results show that even with the use of molecular sieve [CTA⁺]-Si-MCM-41 and KF-clay reaction time was one of the factors that most influenced the yield of methyl esters. Production was favored by longer reaction times, which increased conversion of both catalysts (Table 3).

Table 3. Methyl and ethyl transesterification by different heterogeneous catalysts. ([CTA⁺]-Si-MCM-41 and KF-clay).

Catalyst	Alcohol type	t (h)	Conversion (%)
[CTA ⁺]-Si-MCM-41	Methanol	1	81.2
	Methanol	2	91.0
	Ethanol	4	6.4
KF-clay	Methanol	1	85.2
	Methanol	2	95.2
	Ethanol	4	63.3

There are elevated concentrations of anions SiO⁻ on the surface of the mesoporous molecular sieve. Due to the presence of polar head in this material, catalytic activity derives from the SiO⁻ groups located in the entrance of the pores. Since the polar head cation CTA⁺ is a big molecule, the interaction with the anion SiO⁻ is small, leaving it available to catalytic activity¹⁶. During the reaction, the toughness to break molecules of triacylglyceride, diacylglycerid and monoacylglycerid encountered by ethanol can be solved by increasing the oil/alcohol molar ratio of 1:6¹³.

The transesterification reaction of soybean oil with ethanol catalyzed by mesoporous molecular sieve [CTA⁺]-Si-MCM-41 and KF-clay was monitored with oil/alcohol molar ratio of 1:15 and 1:12, using 4% and 15% of catalyst in relation to the oil mass, respectively. Reaction time for both catalysts was of 4 hours and temperature of 100°C. KF-clay showed the highest catalytic activity with 63% conversion in 4 hours of reaction. [CTA⁺]-Si-MCM-41 showed lower activity in the synthesis of ethyl esters with 6% conversion in 4 hours of reaction.

These results show that even with the high oil/alcohol molar ratio the yield was low when using [CTA⁺]-Si-MCM-41. Pereira *et al.*¹⁷ evaluated the ethyl esters yield with the application of Al-MCM-41 in the transesterification of soybean oil and found conversions of 16% with reaction time of 180 min. Oil/alcohol molar ratio was of 1:9 and temperature of 200°C. Carmo *et al.*¹⁸ found ester conversions of 67% with elevated temperature of 130°C in the esterification process using ethanol and mesoporous molecular sieve MCM-41.

One of the factors that might have influenced this low ethyl ester conversion by [CTA⁺]-Si-MCM-41 can be associated with the presence of surfactant CTA⁺ in the pores of this material, what makes interaction with ethanol difficult due to its amphiphilic arrangement. Another factor that influenced conversion was the oil/alcohol molar ratio. This ratio was 1:15 and according to Kucek

*et al.*¹⁹, oil/alcohol molar ratios above 1:12 cause the increase of glycerin solubility, generating problems in the phase separation of the reaction.

KF-clay proved to be more favorable in the ethyl transesterification reaction, even though conversion results are still low when comparing to results of reactions using methanol. The size of the alcohol molecule might influence catalytic activity. In linear chains, the activity is minimized with the increase in chain length, which is probably related to alcohol polarity that leads to a reduction in ethylic ester yield²⁰.

Ethanol has hygroscopic characteristics and can generate an azeotrope with water, generating undesired compounds, such as soap. There is also a predisposition to the formation of a stable emulsion between the main products of transesterification (biodiesel and glycerol), what makes its separation complicated²¹.

The formation of emulsions is an important factor taken in consideration in biodiesel production because it hinders phase separation and ester purification. The reaction utilizing methanol forms less stable emulsions; therefore, phase separation is facilitated. The emulsion is denominated a disperse system in which the liquid phase of the compounds involved is immiscible or partially miscible²².

Catalytic test with potassium fluoride: Some heterogeneous catalysts are obtained from the impregnation of potassium fluoride in clays and other compounds. This combination proves to be favorable in the transesterification reaction. Besides, it is a practical and cheap medium that provides catalytic specie with good results²³. Therefore, with the intention of assessing the catalytic capacity of potassium fluoride, experiments were conducted using KF without support, KF-clay and *in natura* clay in the transesterification reaction with two different types of alcohol, methanol and ethanol (Table 4).

Table 4. Ester conversion values of transesterification with KF, KF-clay and *in natura* clay.

Catalyst	Alcohol	t (h)	T (°C)	Conversion (%)
KF	Ethanol	4	100	6.50
	Methanol	1	80	63.7
KF-clay	Ethanol	4	100	63.3
	Methanol	1	80	85.2
<i>In natura</i> clay	Ethanol	4	100	No conversion
	Methanol	1	80	No conversion

The transesterification reaction employing 2.45 g of KF with ethanol and methanol provided 6.50% and 63.7% conversion, respectively. The clay, treated with this salt, used in the transesterification reaction contained 1.17 g of KF and the conversion observed was of 63.3% in the presence of ethanol and 85.2% in the presence of methanol. Consequently, a higher concentration of this salt tends to generate higher conversion levels even without catalytic support, though the combination with supports tends to increase results with a lower KF concentration.

Even with elevated concentration in the reaction of pure KF with ethanol, conversion presented inferior results than those found when employing KF impregnation. KF solubility decreases along with the increase of the molecular weight of the alcohol used as solvent, even if KF has a great capacity of forming strong hydrogen bonds²³.

There was excess in the pure KF amount applied to react with methanol, what led to lower yield verified with the increase in KF quantity. Xu *et al.*²⁴ state that KF applied in excess in a catalytic support decentralizes layers and causes deactivation of active centers, hindering the catalyst functioning.

Higher concentration of KF impregnation generates increase in the basic heterogeneous catalytic force. Gao *et al.*²⁵ used an oil/methanol ratio of 1:12, 5% catalyst mass of oil, reaction time of 5 hours and temperature of 65°C in their study. The yield of methyl esters was much higher when catalyzed by KF/Ca Al-HT other than by Ca Al-HT, what means that the KF concentration widely increased catalytic activity. The reaction using just KF obtained yield lower than 1%. Catalysts KF/CaAl-HT and KF/Mg Al-HT presented reaction yields of 95.6% and 88.7%, respectively.

Murugan and Bajaj²⁶ evaluated ethyl biodiesel yield using KF/Al₂O₃ as basic heterogeneous catalyst and obtained conversion of 91.3% with 40% KF mass. In another experiment, assessing only KF concentration, the conversion found was of 59.8%. Catalytic activity is related to KF concentration.

Leaching test: This is a very important test that must be performed for being associated to catalytic activity. Many catalysts, during the process, lose their activity or mass in the reaction medium. Furthermore, it aims at avoiding possible contamination of the esters produced (Table 5). [CTA⁺]Si-MCM-41 showed the highest mass loss with methanol, what can be associated to its higher polarity. This provides more contact with the surfactant retained in the pores, thus promoting its bigger leaching. KF-clay proved to be more stable than [CTA⁺]Si-MCM-41 with the use of either methanol or ethanol. Both catalysts proved to be favorable to the use of ethanol in the process. The best result was obtained using KF-clay with ethanol, in which the mass loss corresponded to 16.7%

Table 5. Mass loss by means of leaching tests of [CTA⁺]Si-MCM-41 and KF-clay with methanol and ethanol.

Catalyst	Alcohol	% mass loss
MCM-41	Methanol	33.4
KF-clay	Methanol	26.9
MCM-41	Ethanol	22.5
KF-clay	Ethanol	16.7

Conclusions

The characterization of [CTA⁺]-Si-MCM-41 and KF-clay catalysts was similar to that found in the literature. Bentonite clay modified with potassium fluoride saline treatment obtained the highest conversion of methyl and ethyl esters at 95.2% and 63.3% for reaction times of 2 and 4 hours, respectively. Catalytic test evaluated the conversion of the reaction using KF and it showed to be favorable to the application of this salt. Ethanol proved to be more stable than methanol in the leaching test. The use of this alcohol was favored in the reaction, what indicates its application can be more satisfactory in future studies.

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