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Bentonite functioned by potassium compounds as a solid catalyst for biodiesel production

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Abstract

Heterogeneous catalysts, especially those produced with functionalized clays, can be used for methyl transesterification at moderate temperatures. The use of bentonite clay functionalized by potassium compounds (KF, KOH, K_2CO_3, KCl and K_2SO_4) in the methyl transesterification of cottonseed oil is the object of the present study. The catalysts were produced by contacting aqueous solutions with the clay and subsequent drying. The catalysts were characterized by Hammett indicators to determine alkalinity. The methyl transesterification reactions were made in a flask with stirring and reflux at 70°C for 2 h. The performance evaluation of the reaction was carried out using regression between the absorption band area and the concentration of a biodiesel-oil mixture by infrared spectroscopy. The catalytic activity is directly associated with the alkaline character of the catalysts. The catalysts produced with KCl and K_2SO_4 did not show conversion in the methyl transesterification reaction, while the catalysts produced with KF, KOH and K_2CO_3 showed a conversion greater than 90%.

Keywords: clay, bentonite, catalysts, biodiesel.

1. Introduction

Natural or functionalized clays can be used as heterogeneous catalysts in the transesterification reaction of oils and fats for biodiesel production. This has some advantages over conventional homogeneous synthesis, such as the possibility of clay recycling and a reduction in the number of steps in the biodiesel purification process.

Several types of clay minerals can be used as heterogeneous catalysts in the ethyl or methyl transesterification of vegetable oils, residuals and fats, such as kaolinite, halosite, clinoptiloite, smectite, vermiculite and even zeolites given their rich and complex surface chemistry (Ballotin *et al.*, 2020).

Methyl transesterification, catalyzed in a heterogeneous way, exhibits some advantages over homogeneous catalysis. These include for example a reduction in effluent generation, catalyst regeneration capacity, the possibility of applying continuous processes and greater simplicity in product separation (Macario *et al.*, 2010). Heterogeneously catalyzed transesterification still presents some challenges to be solved, such as improving the conversion rate, optimizing the quality of the mixture between the catalyst, the oil and the alcohol, as well as reducing the proportion of alcohol in the mixture (Kim *et al.*, 2010; Endalew *et al.*, 2011).

Potassium-containing compounds have been applied in heterogeneous catalysts with high alkalinity and chemical stability, supported on various solids. Notably, diluted solutions of KF, KI, K_2CO_3, KNO_3, KOH, KH_2PO_4 and $KBrO_3$ have been used primarily as a source of potassium, although other sources, such as KCl and K_2SO_4 have also been used (Boz & Kara, 2009; Ye *et al.*, 2014). However, potassium salts used alone as a heterogeneous catalyst, do not show satisfactory catalytic activity (Ranucci *et al.* 2015; Sun *et al.* 2014).

Heterogeneous transesterification using supported potassium salts can be carried out with some success under different reaction conditions. The temperature of the methyl transesterification can vary from 65 to 90°C, with a reaction time of up to 150 min and conversion that can reach 90%. Catalyst concentration is also an important parameter that can vary widely, with concentrations as high as 15% solids in relation to oil mass. (Abukhadra *et al.*, 2020; Abukhadra & Sayed, 2018; Liu *et al.*, 2011). Additional investigations are needed to verify the efficiency of clays activated by other potassium compounds, such as KCl and K_2SO_4, to catalyze the methyl transesterification of vegetable oils.

To determine the efficiency of a transesterification reaction, ASTM D5196-06 and EN 14214 are normally used to quantify the formed esters. Biodiesel varies in quality due to changes in the molecules of the esters due to the presence of contaminants, changes in the size of the carbon chain and displacement in the position of unsaturation, making the use of gas chromatography sensitive to such changes. The analysis by gas chromatography is expensive, mainly given the high cost of standards, column and reagents.

Some attention has been given to infrared spectroscopic techniques, such as Fourier transform (FT-IR) because they are fast and low-cost analytical techniques that require little or no sample preparation (Rabelo *et al.*, 2015; Rosset & Perez-Lopez, 2019). Infrared spectroscopy has been applied to estimate qualitative and quantitative parameters in biodiesel samples, often associated with complex statistical methods (Tirla *et al.*, 2013). Some studies relate the intensity of the absorbance band to the concentration of biodiesel present in a mixture of vegetable oil. Using the KBr pressed disc technique (Reyman *et al.*, 2014), it was found that the attenuated total reflectance (ATR) band intensity is sensitive to sample volume (Rabelo *et al.*, 2015; Dubé *et al.*, 2004).

The main infrared absorbance bands used to differentiate biodiesel from mineral diesel are located in some regions of the spectra, around 1750 cm⁻¹ referring to the ester carbonyl stretch, and peak in the region of 1300 to 800 cm⁻¹, which indicates overlapping of bands present in both the oil and the ester corresponding to the spectral positions at 1000 to 900 cm⁻¹ referring to the CH bond of olefins, bands at 1200 cm⁻¹ referring to the CC(=O)-O bond of the ester (Donnell *et al.*, 2013). The study by Dubé *et al.* (2004) analyzes the change in absorbance at 1378 cm⁻¹. These are attributed to the terminal CH_3 groups of mono, di and triglycerides, free fatty acids and methyl esters and to the OCH_2 groups in the glycerol portion, during the transformation of triglycerides into methyl esters, whick involves the loss of the glycerol portion, resulting in a decrease in peak height at 1378 cm⁻¹.

In view of the scarcity of studies in this field, this research aims to evaluate the efficiency of clay catalysts functionalized with potassium compounds in the methyl transesterification of cottonseed oil.

2. Materials and methods

For this research, a bentonite from Brazilian Bentonite Company Ltda (CBB) was used. Bentonite is mainly composed of clay minerals of montmorillonite and kaolinite, containing 62.5% of SiO_2, 20.5 % of Al_2O_3, 10.2 % of Fe_2O_3, 4.8 % of e MgO and 2.0 % are other elements (da Costa & de Andrade Lima, 2021).

This clay was pulverized (<147 μm) and dried at 60°C for 24 h to be used as catalyst support. For the synthesis of the catalyst KF, K_2CO_3, KOH, KCl and K_2SO_4 were used for the transesterification tests, commercial cotton oil from ICOFORT Agroindustrial LTDA and methyl alcohol (Scientific Exodus: 98%) were used.

2.1 Clay activation

The catalyst synthesis used KF, KCl, K_2CO_3 and KOH solutions at 2 mol L⁻¹ and a 0.6 mol L⁻¹ solution of K_2SO_4. In each of the solutions, an aqueous dispersion of 10% by mass of clay was used, which was kept in a round-bottom flask with reflux and temperature control in a glycerine bath at 90°C. Then, the mixture was dehydrated at 100°C for 12 hours in a rotary evaporator. The paste removed from the rotary evaporator was dried at 60°C for up until 12 h and then pulverized (<147 μm) and subsequently heated at 400 or 700°C for 3 hours with natural cooling inside the oven. Some catalysts were only heated to 400°C to avoid forcing acidic sites.

2.2 Clay characterization and functionalization

The use of Hammett indicators can determine the alkalinity (H_0) of a solid catalyst. However, despite the limitations of these methods, it is possible to obtain comparative results of great practical use (Yazici & Bilgiç, 2010). To determine the mean basic force, 0.01 g of the sample was stirred in 3 mL of ethanol with the addition of 1 mL of the Hammett indicator solution (0.1 mg L^{-1} in ethanol) and after shaking and resting for 4 h the color of solution was noted. The indicators used are shown in Table 1.

Table 1 - Hammett indicators: Colors and H_0 index values.

Indicators	Alkaline Color	Acid color	H_0
4- Chloroaniline	Pink	Colorless	26.5
4- Nitroaniline	Orange	Colorless	18.4
2,4 Dinitroaniline	Violeta	Yellow	15.0
Tropaeolin O	Orange	Yellow	11.0
Phenolphthalein	Pink	Colorless	9.9
Bromothymol Blue	Blue	Yellow	7.2
Neutral Red	Yellow	Red	6.8
Dimethyl Yellow	Yellow	Red	3.3

2.3 Transesterification

Transesterification was carried out with a powdered catalyst (<147 μm) in a round-bottomed flask with stirring and refluxing at 70°C for 2 hours (reaction temperature stabilized). The molar ratio (alcohol/oil) was 5:1 to 20:1 and the catalyst concentration between 5 and 20% in relation to the oil mass. After transesterification, the catalyst was separated by using vacuum filtration. The liquid phase was washed with deionized water and the oil phase was centrifuged and dehydrated at 100°C for 6 hours. Table 2 presents the reaction conditions. To evaluate the cottonseed oil transesterification reaction and build a calibration curve, the attenuated total reflection technique (FT-IR/ATR) was used, obtained using a Shimadzu spectrophotometer, with ZnSe crystal. Each spectrum was recorded as an average spectrum resulting from 100 scans, employing a resolution of 2 cm^{-1}. At each measurement performed, the ATR equipment was cleaned with organic solvent before performing a new measurement.

Table 2 - Reaction conditions.

Test #	Catalyst types	Catalyst Concentration (%)	oil/alcohol molar ratio
1	Natural clay	15	10
3	Clay heated to 400°C	20	20
2	Clay heated to 700°C	20	20
4	Clay+KF heated to 400°C	20	20
5	Clay+KF heated to 400°C	10	5
6	Clay+K$_2$CO$_3$ heated to 400°C	10	10
7	Clay+K$_2$CO$_3$ heated to 700°C	10	10
8	Clay+KOH heated to 400°C	10	10
9	Clay+KCl heated to 400°C	10	10
10	Clay+K$_2$SO$_4$ heated to 400°C	10	10

A biodiesel sample supplied by Petrobras was used for the construction of standards of different concentrations of biodiesel by mixing it with cottonseed oil. Solutions with concentrations of 0, 25, 50, 80, and 100% biodiesel were used (Table 3). Infrared spectra for the standard solutions were carried out and the integral of each of the absorbance bands between 2,000 - 800 cm^{-1} was performed. For the construction of the regression models, the areas of the absorption bands that showed some evident correlation with the biodiesel concentration were used (Rosset & Perez-Lopez, 2019).

Table 3 - Characteristics of standard biodiesel and cottonseed oil.

Parameters	Cottonseed oil (%)	Biodiesel (%)
Free glycerol	0.08	0.09
Total glycerol	1.21	0.28
Monoglyceride	0.005	0.22
Diglyceride	2.09	0.46
Triglyceride	7.79	0.64

3. Results and discussions

3.1 Clay characterization and functionalization

The color hue change of the Hammett indicators was used to determine the basic resistance range (H_0) of the montmorillonite and catalysts. The alkalinity obtained by Hammett indicators can be seen in Table 4.

Table 4 - Alkalinity of clay and catalysts.

Solids	Index H_0
Clay+K_2SO_4 heated to 400°C	3.3 > H_0
Clay heated to 400°C	6.8 < H_0 < 3.3
Clay heated to 700°C	6.8 < H_0 < 3.3
Clay+KCl heated to 400°C	6.8 < H_0 < 3.3
Natural clay	9.8 < H_0 < 6.8
Clay+K_2SO_3 heated to 700°C	11.0 < H_0 < 9.8
Clay+KOH heated to 400°C	11.0 < H_0 < 9.8
Clay+KF heated to 400°C	15.0 < H_0 < 11.0
Clay+K_2CO_3 heated to 400°C	26.5 < H_0 < 18.4

Natural clay can be acidic sites. However, heating the clay favors the creation of stable acidity sites, as also suggested by the results presented in Table 2 (Liu *et al.*, 2011). Clay naturally has a slightly alkaline character, 9.8 < H_0 < 6.8. After heating to 400°C and 700°C, a change in alkalinity of natural clay is observed (6.8 < H_0 < 3.3). This change can be attributed to the polarized water in the space between the layers and the presence of rehydrated unsaturated Al_3^+ ions formed by the heating process (Liu *et al.*, 2011).

Previous studies suggest that the catalytic capacity of K_2CO_3 supported on aluminum silicates may be attributable to high alkalinity. This is attributed to the formation of K_2O species and Al–O–K groups, due to the thermal decomposition of the K_2CO_3.

When the catalyst synthesis temperature rises, there is a partial decomposition of K_2O species and Al–O–K groups, resulting in a reduction in alkalinity, which is also favored by the intensification of Al_3^+ ions formed by the heating process (Shan *et al.*, 2016; Sun *et al.*, 2014). The results presented in Table 4, support this assumption, since the alkalinity of the catalyst 'Clay+K_2CO_3 heated to 400°C' outside 26.5 < H_0 < 18.4 when heated to 400°C and when heated to 700°C was modified for 11.0 < H_0 < 9.8, indicating that not all alkaline sites were degenerated.

After functionalization with potassium fluoride (Clay+KF heated to 400°C), the clay acquires a strong alkaline character (15.0 < H_0 < 11.0). Previous studies have associated the high catalytic activity of impreg-nated KF with the basicity of the surfaces. The basicity is related by the formation of groups Al–O–K and F^-, partially replacing oxygen, due to the thermal decomposition of charged K compounds, and by interactions supporting salt. The presence of K_2O and free Al–O–K and -OH groups at the edges of the clay are associated with the high alkalinity of these solids (Boz *et al.*, 2013; Sun *et al.*, 2014).

It can be seen that the treatment process with K^+ ions produced changes in the basic strength of bentonite, K_2SO_4 with the catalyst being the one with the lowest alkalinity. The alkalinity of the K_2SO_4 catalyst suggests a very acidic surface, possibly attributed to the presence of sulfide ions in the clay, resulting from the dissociation of this salt in an aqueous medium.

3.2 Estimation of biodiesel concentration with infrared spectroscopy

The region of the infrared spectrum of greatest relevance for the analysis of the conversion of triglyceride to methyl ester is between 1700 to 800 cm^{-1} (Mahamuni & Adewuyi 2009). Figure 1 shows the infrared spectra of the blend of cottonseed oil and biodiesel. The bands in 1744, 1462, 1435, 1359, 1245, 1195, 1160, 1118, 1096 and 1017 cm^{-1} seem to change. Therefore the variation in their areas (obtained by integration) were compared with the change in the concentration of biodiesel.
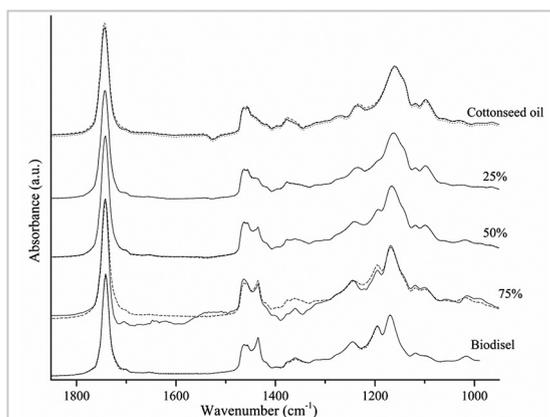

Figure 1 - Infrared spectrum of cottonseed oil and methyl biodisel blends.

Figure 2 shows the relationship between the areas of the absorbance bands that showed some correlation with the concentration of biodiesel in the sample.

The results show that the absorbance bands exhibit a nonlinear behavior that can be fit by a second order regression model.
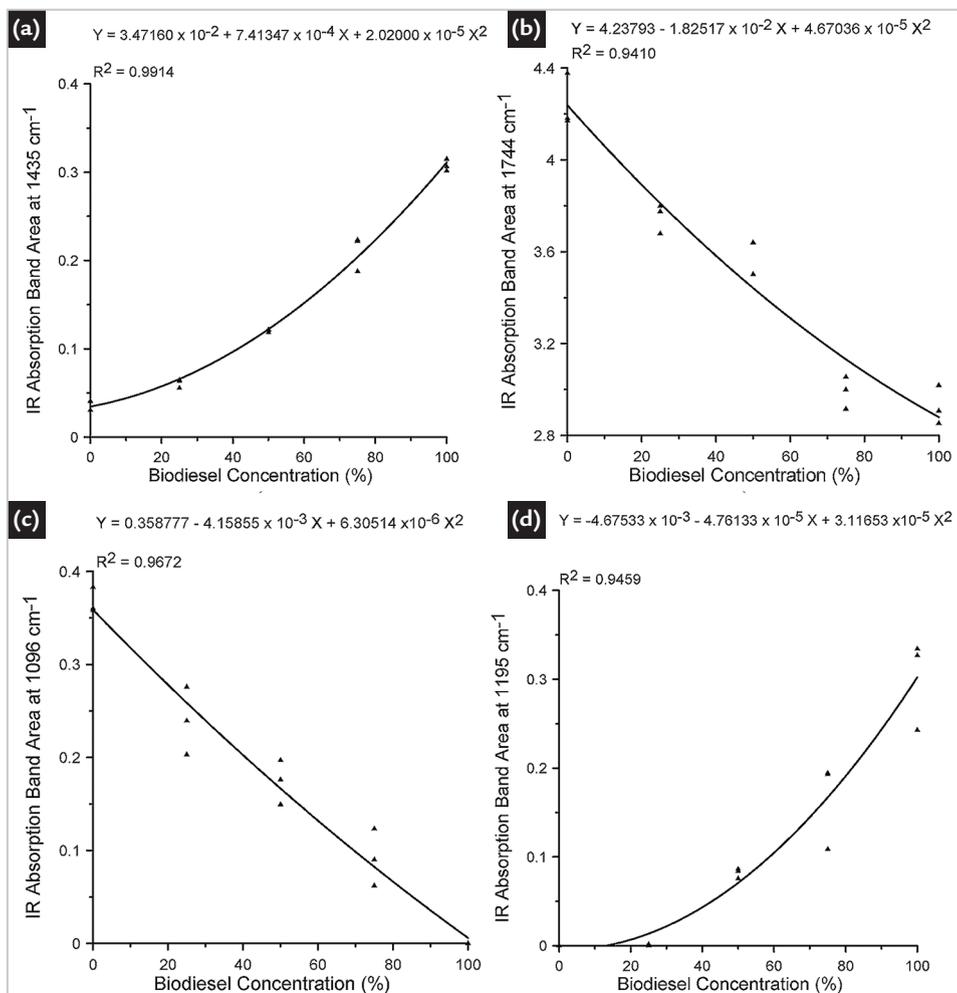

(a) $Y = 3.47160 \times 10^{-2} + 7.41347 \times 10^{-4} X + 2.02000 \times 10^{-5} X^2$
$R^2 = 0.9914$

(b) $Y = 4.23793 - 1.82517 \times 10^{-2} X + 4.67036 \times 10^{-5} X^2$
$R^2 = 0.9410$

(c) $Y = 0.358777 - 4.15855 \times 10^{-3} X + 6.30514 \times 10^{-6} X^2$
$R^2 = 0.9672$

(d) $Y = -4.67533 \times 10^{-3} - 4.76133 \times 10^{-5} X + 3.11653 \times 10^{-5} X^2$
$R^2 = 0.9459$

Figure 2 - Regression of areas of relevant absorbance bands versus biodiesel concentration. a) 1435, b) 1744, c) 1096, d) 1195 cm^{-1}.

3.3 Transesterification reaction

The results of the infrared spectra of the product of the cotton oil methyl transesterification, performed under the conditions shown in Table 2, at a temperature of 70°C for two hours, can be seen in Figure 3.

The vibrational bands present only in biodiesel at 1435 and 1195 cm^{-1}, attributed to the CH$_3$ and O-CH$_3$ bonds, can be seen in tests 4 to 8. The vibrational band at 1096 cm^{-1} is related to the -CH$_2$ bond and can be identified in tests 1, 2, 3, 4, 7 and 10. The bands at 912, 1032-1017 and 1270 cm^{-1} are identified in cotton oil, but not differentiated in the reaction product, and may be related to =CH$_2$, O-CH$_2$-C and C-C bonds, respectively (Donnell *et al.*, 2013; Máquina *et al.*, 2019).

The reactions that used catalysts with high acidity showed a low conversion, and some studies also report that the methyl
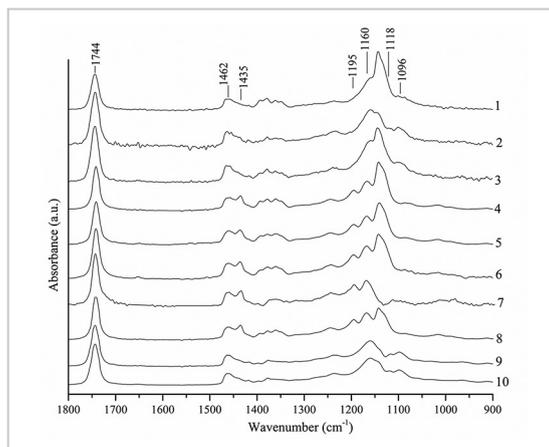

Figure 3 - Infrared spectra of the methyl transesterification product of cottonseed oil for test #1 to 10.

transesterification catalyzed by solids with an acid character require high temperatures (greater than 100°C) to obtain some conversion (Jothiramalingam & Wang, 2009).

Table 5 shows the biodiesel concentration obtained through the regression equation using the absorbance band at 1435 cm^{-1}, using the

equation shown in Figure 2(a), since this spectral region presented the best correlation between the band area and the biodiesel concentration.

Table 5 - Reaction conditions of methyl transesterification.

Test #	Catalysts	Catalyst Concentration (%)	Ratio oil/alcohol molar	Biodiesel concentration (%)
1	Natural clay	15	10	0.0
3	Clay heated to 400°C	20	20	0.0
2	Clay heated to 700°C	20	20	0.0
4	Clay+KF heated to 400 °C	20	20	98.5
5	Clay+KF heated to 400 °C	10	5	≈ 100
6	Clay+K$_2$CO$_3$ heated to 400°C	10	10	99.5
7	Clay+K$_2$CO$_3$ heated to 700°C	10	10	99.7
8	Clay+KOH heated to 400°C	10	10	94.3
9	Clay+KCl heated to 400°C	10	10	0.0
10	Clay+K$_2$SO$_4$ heated to 400°C	10	10	0.0

Clays exhibit a complex and versatile distribution of surface ions, with a high cation exchange capacity, which gives them some catalytic activity for several chemical reactions (Busca, 2007; Lee, 2014). However, the results suggest that there is no catalytic activity in the methyl transesterification reaction applying natural montmorillonite clay or clay heated to 400 or 700°C, as also observed in other studies (Farias *et al.*, 2015; Alves *et al.*, 2014). Direct transesterification of vegetable oils, carried out at a temperature below 100°C and under atmospheric pressure, is favored in the presence of solid alkaline catalysts. The natural montmorillonite applied in this investigation, exhibits a moderate acidity (9.8 <H$_0$< 6.8), due to the heating process.

An increase in acidic sites due to crystallite deformation and partial rupture of Si-OH and Al-OH bonds is favored, hindering the catalytic activity of montmorillonite in the transesterification reaction.

Potassium-containing compounds are applied to functionalize various solids due to their ability to promote active sites of high alkalinity (Boz & Kara, 2009; Alves *et al.*, 2014). However, the application of potassium chloride and potassium sulfate to functionalize montmorillonite intensified the acidic characteristic of the natural clay. The results suggest that the application of solid KCl heated to 400°C (6.8 <H$_0$< 3.3) and K$_2$SO$_4$ heated to 400°C (H$_0$ < 3.3) in the methyl transesterification did not present catalytic activity.

Methyl transesterification catalyzed by alkaline solids requires a milder reaction temperature than catalysis with acidic solids. Montmorillonite functionalized by potassium fluoride, potassium carbonate and potassium hydroxide exhibits high alkalinity and some catalytic activity. Catalysts KF heated to 400°C (15.0 <H$_0$< 11.0), K$_2$CO$_3$ heated to 700°C (11.0 <H$_0$< 9.8), K$_2$CO$_3$ heated to 400°C (26.5 <H$_0$ < 18.4) and KOH heated to 400°C (11.0 <H0< 9.8) showed conversions higher than 90%. Other investigations have obtained similar results, applying other solids functionalized by potassium compounds to catalyze methyl transesterification, analyzed by gas chromatography (Ali *et al.*, 2015; Silveira *et al.*, 2019).

4. Conclusions

The efficiency of bentonite clay alkalinity catalysts in the transesterification reaction is related to the alkalinity of the catalyst. The application of catalysts produced with bentonite functionalized by KCl and K$_2$SO$_4$ provides an acidic character, and consequently, they do not exhibit catalytic activity. The methyl transesterification of cottonseed oil catalyzed by bentonite functionalized by KF, K$_2$CO$_3$ and KOH presents a conversion rate which is higher than 90%.

Acknowledgements

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