

## HETEROGENEOUS TRANSESTERIFICATION OF CASTOR OIL FOR BIODIESEL PRODUCTION BY $\text{Al}_2\text{O}_3$ , $\text{Al}_2\text{O}_3\text{-NiO}$ AND $\text{Al}_2\text{O}_3\text{-CoO}$ MODIFIED BENTONITE AS CATALYST

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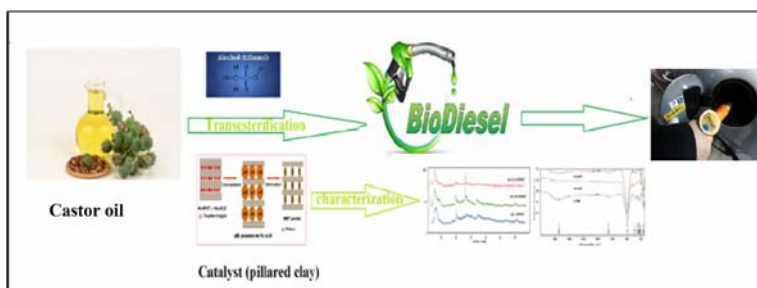
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Received June 3, 2020

Bentonite clay from Maghnia (Algeria), very rich in montmorillonite (~ 90 %) purified and intercalated with pillars  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3\text{-NiO}$  and  $\text{Al}_2\text{O}_3\text{-CoO}$ , was applied as catalyst for the conversion of a mixture of castor oil-ethanol to biodiesel. The pillared clay with  $\text{Al}_2\text{O}_3\text{-CoO}$  (10%) led to 98% ester conversion. The highest yield of biodiesel production was obtained at 1/15 molar ratio of oil/ethanol, a temperature of 250 °C and 7.5 wt% of catalyst. This behaviour was ascribed to a synergetic effect of the largest surface area developed in the clay and the highest catalytic activity of cobalt in basic medium. The catalysts re-usability experiments revealed that the pillared clays were safely re-used three times without losing their original catalytic effectiveness. The kinetics calculations demonstrated that the transesterification of castor oil in an excess of alcohol using the pillared clay as catalyst followed a pseudo first order kinetics. The biodiesel produced exhibited comparable fuel properties as those of classical fossil diesel.



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### INTRODUCTION

Substitution of conventional energy sources by sustainable ones is not only a research topic for many laboratories, but a critical political and environmental issue. The majority of the greenhouse gases originates from the combustion of fossil hydrocarbons. A second reason behind the active search of new energy sources is the increasing demand on oil due to the increasing needs of emerging countries. This is a crucial economical issue, as the cost of the crude oil will proportionally increase to thresholds that will certainly motivate a search for cheaper substitutes.

Nowadays, tremendous efforts are made in the field of biomass for the development of non-fossil biocarburants including biodiesel, bioalcohols, hydrogen, methane, and vegetable oils. Biofuel output at global scale has drastically increased from 38 billion liter in 2005 to 131 billion liters in 2015.<sup>1</sup> The production of hydrogen by chemical and electrochemical reflects its expensiveness relatively. Vegetable oils suffer from carbon deposit, high viscosity and jellification during the lubrication of engines.<sup>2</sup> The transformation of vegetable oils into biodiesel, which has similar properties to diesel, seems very promising. It can be produced from biological resources as vegetable

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oils, especially the edible oil,<sup>3</sup> recycled vegetable waste and animal fats via transesterification.<sup>4</sup> For two decades, the biodiesel industry has been growing progressively.<sup>5</sup> Biodiesel (Alkyl ester) is obtained by catalytic transesterification of triglycerides with alcohols (Figure 1).

Most vegetable oils used for biodiesel production contain more than 90% triglycerides.<sup>6</sup> For reasons of time and cost-effectiveness of the transesterification reaction homogeneous alkaline catalysis is used in the majority of existing processes; although basic and acidic homogeneous catalysis are known. However, this homogeneous process suffers from competitive side reactions as saponification and hydrolysis reactions of the free fatty acids, which substantially reduce the conversion extent of the produced biodiesel.<sup>7</sup> The acid catalysis method is less popular because it is corrosive to the equipment. To overcome these undesirable effects, much research has been conducted on solid catalysts.<sup>8-11</sup>

Many porous and microporous catalysts have been applied to produce biodiesel in laboratories. Among these solids modified clays, which seem very promising. Pillared clays or support of different metals, and oxides have been used in transesterification reactions of oils and fats.<sup>12-16</sup> The activity of these modified clays is generally attributed to their basics, acidity and large surfaces.<sup>17-19</sup>

In this study a bentonite from Maghnia (Algeria) which is considered to be very rich in

montmorillonite (~ 90%) was purified, interpose with pillars  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3\text{-NiO}$  and  $\text{Al}_2\text{O}_3\text{-CoO}$ , characterized by FTIR DRX, BET, EDS, and SEM. Then, these materials are used as catalysts for the conversion of castor oil to biodiesel.

## 2. Materials and Methods

The physicochemical properties and composition of castor oil used in this work are listed in Tables 1 and 2. These tables show that the oil is very rich in ricinoleic acid and contains very small amounts of water and free acid. The water hydrolysis the oil and release the fatty acid. This one favors saponification, and produces an undesirable reaction.<sup>20</sup>

The natural bentonite from Maghnia (Algeria), a clay is rich in montmorillonite, that was provided by Bental. The 99.9% pure anhydride analytical ethanol was used.

### 2.1. Pillared clay catalyst preparation

The bentonite is purified by physico-chemical treatments according to a method described previously.<sup>21</sup> A fraction of fine particles ( $<2\mu\text{m}$ ) that is rich in montmorillonite is obtained. Then, this clay is sodded with 1M NaOH solution. After filtration, successive washing with distilled and demineralized water and drying at  $110^\circ\text{C}$ , the clay obtained is designated Na-MMT and stored in a desiccator.

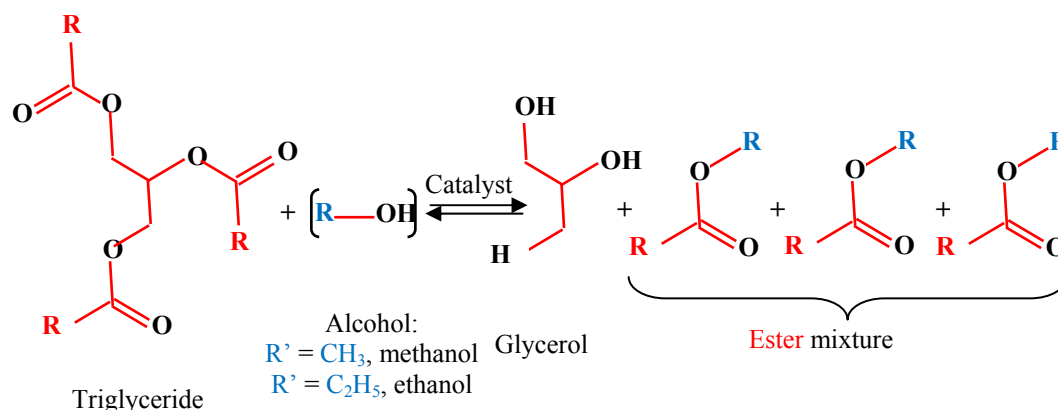


Fig. 1 – Scheme general of the transesterification reaction.

Table 1

Physicochemical characteristics of castor oil

Properties	Color	Acid value (mg KOH/g)	Saponification number	Water content (w/w %)	Iodine value
Values	clear yellow	0.014	84	0.6	190

Table 2

Fatty acid composition of the castor oil

Fatty acid	%
Palmitic acid C <sub>16:0</sub>	2.0
Stearic acid C <sub>18:0</sub>	2.5
Oleic acid C <sub>18:1</sub>	2.5-6.0
Linoleic acid C <sub>18:2</sub>	2.5-7.0
Linolenic acid C <sub>18:3</sub>	<1.0
9,10-dihydroxystearic acid	0.3-0.7
Ricinoleic acid C <sub>18:1</sub>	86-92
Eicosenoique acid C <sub>20:1</sub>	<1.0
Other fatty acids	<1.0

Table 3

Preparation conditions of the bridging solution

Bridging solutions	polycation of aluminum [22]	Polycation of Al-Ni	Polycation of Al-Co
Polycation formula	[Al <sub>13</sub> O <sub>4</sub> (OH) <sub>24</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>7+</sup>	N.D	N.D
Symbol	Al <sub>x</sub> (OH) <sub>y</sub>	(Al-Ni) <sub>x</sub> (OH) <sub>y</sub>	(Al-Co) <sub>x</sub> (OH) <sub>y</sub>
Molar Ratio	1.8	2	2
Aging time	48h	24h	24h

The pillaring solutions of hydroxyl-metal (Al,<sup>22</sup> Ni and Co) were prepared by slow alkaline hydrolysis (0.2 M NaOH) of 0.2 M aqueous solutions of Metal nitrates with an OH / Me ratio = 2. These solutions were left to mature at room temperature for 48 hours to obtain polycations of metal (Table 8).

The pillaring of Na-MMT by the metal (Al, Ni and Co) oxides is carried out according to a standard procedure which is cation exchange followed by calcination under air. A solution of hydroxyl-Al or a mixed solution (Al-Me (%)) of hydroxyl-Al and hydroxyl-Me (Me = Ni or Co) is added drop wise to a suspension (10 g.L<sup>-1</sup>) of Na-MMT with vigorous stirring.

The suspension was separated by centrifugation and washed three times with distilled and demineralized water then, dried at 40°C during 24 h. The obtained solid particles were calcined at 400°C during 2 h. The resulting pillar clays were designated Al-PILC<sub>x</sub> and Al/M-PILC<sub>x</sub> (x = 5, 10 or 20 and Me = Ni or Co).

## 2.2. Catalysts characterization

The catalysts were characterized by : FTIR, DRX, BET, EDS and SEM. The FTIR spectroscopy on BRUKER Alpha spectrophotometer which is equipped with ATR Alpha platinum, a unique reflection, and an ATR diamond module. X-ray diffraction patterns were collected on a BrukerD8-Advance model using copper monochromatic radiation K $\alpha_1$  (1.54 Å). The specific surface and the pores volume were

obtained by BET measurements on an ASAP 2000 Micrometrics apparatus. Prior to testing, the powders were degassed at 200°C during 5 hours. All the measurements were carried out at 77 K. The chemical composition of the catalysts was carried out by energy dispersive spectroscopy (EDS) on a HIROX SH4000 scanning electron microscope.

## 2.3. Application of catalysts in the transesterification of castor oil

The main transesterification products of a triglyceride Fig.1 are a mixture of esters and glycerol. The catalysts dispersed in ethanol, which is mixed with castor oil in a three-neck round bottom flask.

The reaction mixture was refluxed at a fixed temperature with continuous mechanical stirring at 500 rpm for 5 hours. Then, the catalyst was separated by centrifugation. The obtained reaction product was mixed with a saturated solution of NaCl and that allowed its settlement during the night. The glycerol was recovered from biodiesel by decantation and the unreacted ethanol was eliminated by evaporation at 100°C. The conversion of the biofuel produced was calculated according to equation 1. The characteristics of the biodiesel obtained were compared with those of diesel and standard biodiesel (Table 9):

$$\text{Yield of biodiesel} = \frac{\text{volume of ester mixture}}{\text{initial volume of oil}} \times 100$$

The optimal transesterification conditions were determined by optimizing of the temperature, the oil/ethanol molar ratio and the amount of catalyst used as well as its *re-usability*. The reaction kinetics were monitored by using a UV spectrophotometer at wave lengths corresponding to glycerin and oil, respectively.

## RESULTS AND DISCUSSION

### 1. Characterization of the catalyst

#### 1.1. Characterization by FTIR

The infrared absorption spectrum of the bentonite Fig. 2 shows a wide band around  $3400\text{ cm}^{-1}$ , a peak around  $3600\text{ cm}^{-1}$  corresponding respectively to the OH valence vibrations of the adsorbed water and those of the lattice. The peak at  $1636\text{ cm}^{-1}$  corresponds to the deformation of the O-H bond. The intense band located between  $800\text{--}1100\text{ cm}^{-1}$  and centered at  $950\text{ cm}^{-1}$  corresponds to the valence vibrations of the Si-O bond. These results show that bentonite is very rich in montmorillonite. The intensities of the OH bands are very small after purification, modification and calcination as shown by the Na-MMT and pillared clay spectra Fig. 3.

The Si-O absorption band at  $1034\text{ cm}^{-1}$ , characterizes of the Na-MMT is shifted to lower frequencies as the Na is substituted in the tetrahedral and octahedral sites with different metals or their combination. For example this band appears at  $970\text{ cm}^{-1}$  for the Al-PILC, at  $989\text{ cm}^{-1}$  for Al/Co PILC and at  $991\text{ cm}^{-1}$  for the Al/Ni-PILC. Furthermore, the absorption band of the silanol group Si-O-Al which appears at  $520\text{ cm}^{-1}$  in the spectrum of Na-MMT, Al- PILC, Al/Co- PILC and Al/Ni- PILC was shifted to  $516\text{ cm}^{-1}$  with less intense peaks when the Al atoms were substituted with Ni.

The absorption band of Al-O links, has occurred due to the modification of the clay, with Al polycations appears at  $694\text{ cm}^{-1}$ . The Al-O bond is in tetrahedral coordinates in the center of a Keggin type structure. This result proves the existence of this structure of the  $\text{Al}_{13}$  polycation ( $\text{Al}[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ ) in pillaring solution [23]. The visible absorption peak at  $718\text{ cm}^{-1}$  is due to the hydroxide or oxide forms ( $\text{CoO}$  and  $\text{Co}_2\text{O}_3$ ) of cobalt. The band centered at  $650\text{ cm}^{-1}$  is associated to the vibration of the hydroxyls of nickel ( $\text{Ni-OH}$ ) inserted in the interlayer space. The bands visible at  $461\text{ cm}^{-1}$  and at  $481\text{ cm}^{-1}$  correspond to Si-O-Co and Si-O-Ni, respectively. This FTIR information constitutes an additional proof that the metal substitution has effectively occurred in the interfoliar space.<sup>24</sup>

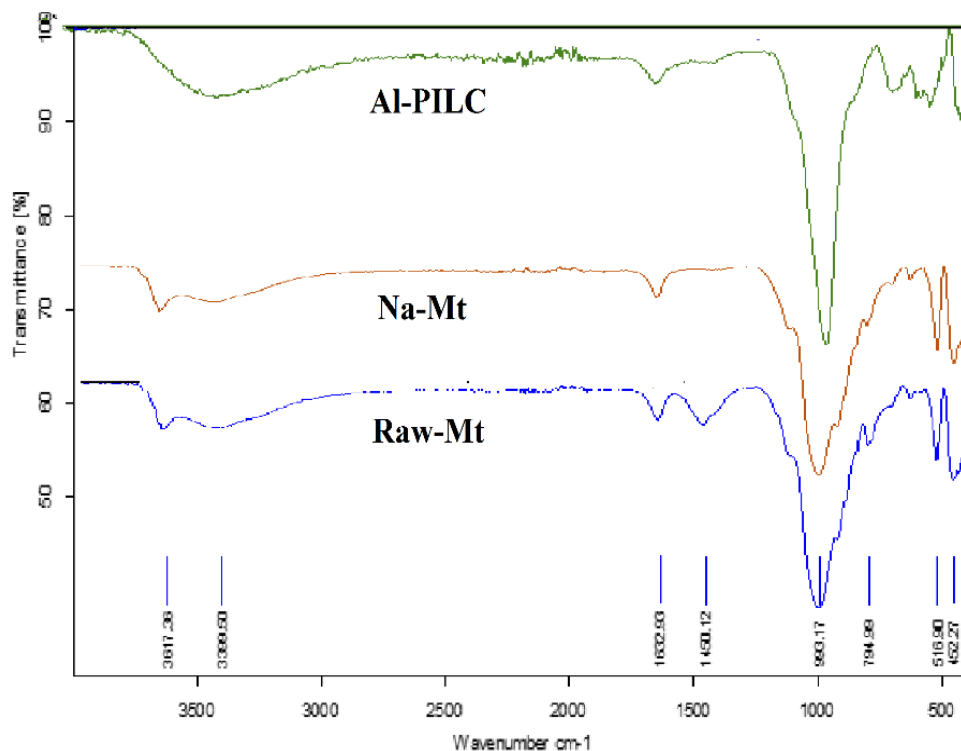


Fig. 2 – FTIR spectrum of raw Mt, Na-Mt and Al-PILC.

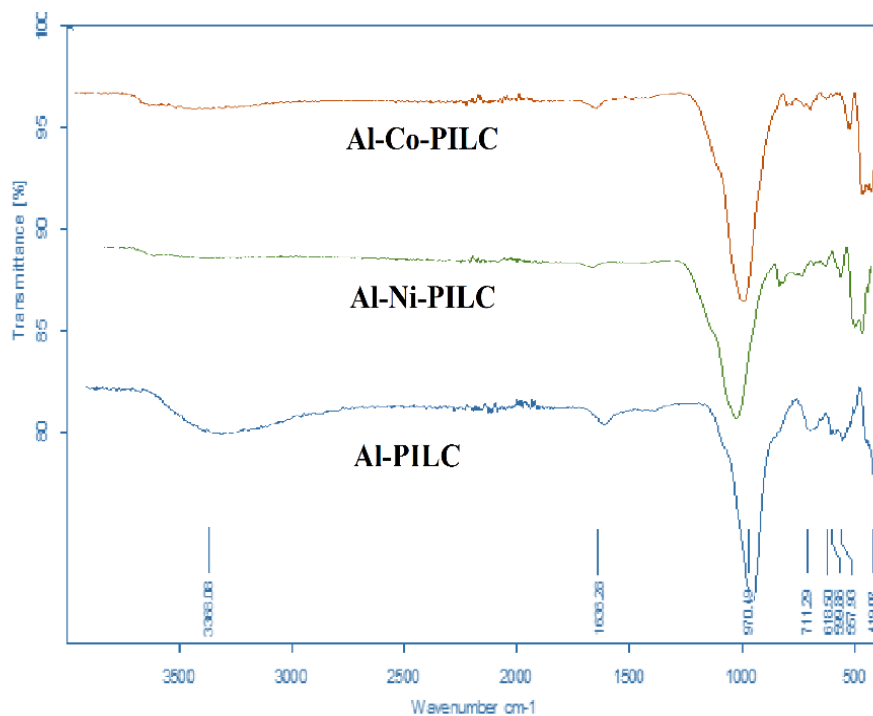


Fig. 3 – FTIR spectra of Al-PILC, Al, Co-PILC and Al, Ni-PILC.

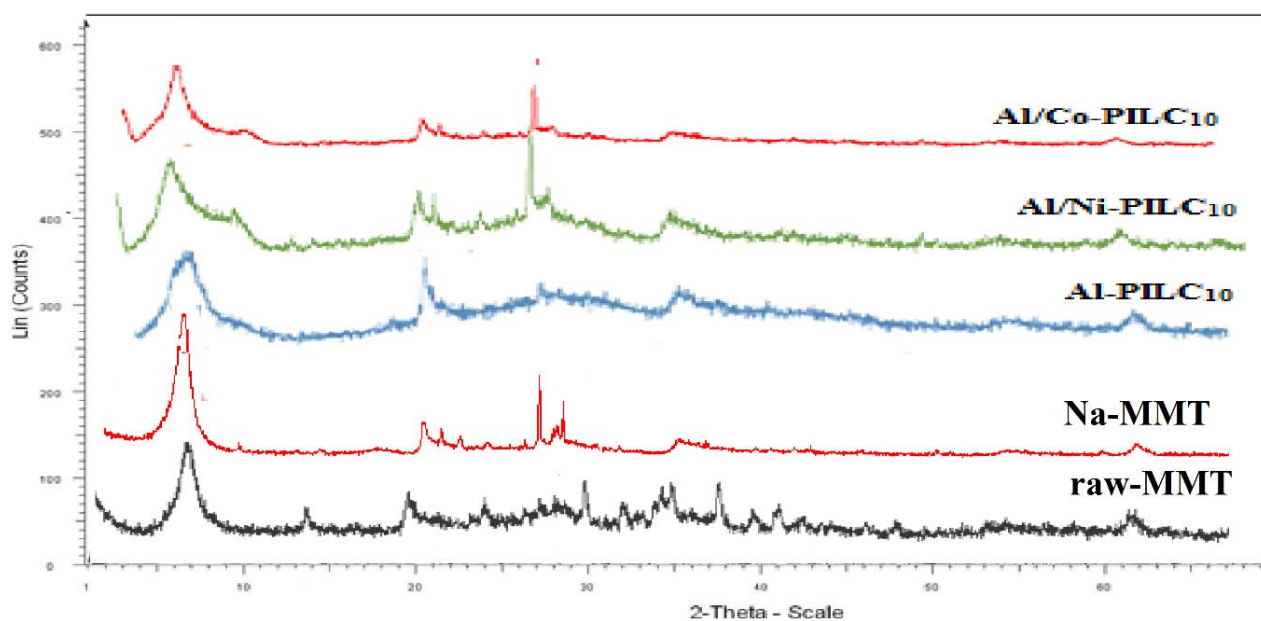


Fig. 4 – X-ray diffractograms of Raw-MMT, Na-MMT Al-PILC, Al, Ni-PILC and Al, Co-PILC.

### 1.2. Characterization by XRD

The diffractograms of the samples are shown in Fig. 4.

After that the results shows that aluminum alone or associated with nickel or cobalt allows the formation of pillars inside the clay. This is evidenced by the peaks at  $2\theta = 21^\circ$  and  $26.5^\circ$  which are characteristics of the intercalation of the structure of Keggin derived from  $Al_{13}$  polycation.

The values of the lattice distance  $d_{001}$  (Table 1) show that the interfoliar space of the modified clay increases with respect to that of montmorillonite (MMT and Na-MMT). The value of  $d_{001}$  increases with the percentage of aluminum and nickel; for cobalt samples a maximum is noted for Al/Co-PILC<sub>10</sub>. This sample displayed two peaks at  $2\theta$  equal to  $31.2^\circ$  and  $37.2^\circ$  corresponding to  $CoO$  and  $Co_2O_3$  cobalt oxides, respectively [25]. When Ni is

used instead of Co three peaks appear at  $2\theta$  equal to  $19.5^\circ$ ,  $24^\circ$  and  $28^\circ$  corresponding to the presence of Ni polycations. This is in agreement with the FTIR results.

### 1.3. Surface and porosity

The volumetric analyzes by nitrogen adsorption (Table 4) shows that the specific surface (BETN<sub>2</sub>) and the porosity of the clay increase when it is modified by 10 and 20% of metals. When the Na-MMT is modified by 10% Al/Ni and Al/Co, its area is multiplied by 1.5 and 2, respectively. The increase of the surface and the porosity of these samples can be explained by the insertion of the hydroxides of the metals into the clay and their transformation into oxides after calcination; an operation giving a microporous structure to pillared clay.<sup>24,26,27</sup>

### 1.4. Chemical composition of catalysts

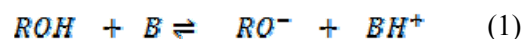
The analysis of the chemical composition obtained by EDS (Table 5) confirms the presence of Ni and Co and the increase of the aluminum content in the clay. Nickel and aluminum are more important in the form of oxides. The rates of these metals are very close to the theoretical rates, notably for the Al/M-PILC<sub>10</sub> samples.

## 2. Parameters influencing the transesterification reaction

Prior to a systematic investigation, the reaction conditions were optimized using the pillared clay based on Al substitution. In Fig. 5 we have represented the variation in the conversion of the ester as a function of the oil / alcohol molar ratio. Similar results are obtained with all the catalysts studied, an excess of alcohol causes the displacement of the reaction towards the direction of formation of the ester. The uses of high oil / ethanol molar ratios are usually used to increase the solubility of glycerides in alcohol, which improves contact between the reagents. When a ratio of 1/15 was used, a conversion which is as

high as 98% was obtained. Transesterification in supercritical alcohol gives almost complete conversion (95%) of frying oil using zinc alumina (ZnAl<sub>2</sub>O<sub>4</sub>) as a catalyst with a molar ratio = 1/40.<sup>28</sup> The same ratio that was obtained is better for a yield of only 67% obtained in the conversion of soybean oil with a hydrocalcite catalyst. This was expected as the excess of alcohol shifts the esterification reaction equilibrium towards the production of glycerol and ester. We note that, the other ratios tested led to comparable conversions. A decrease in conversion has been obtained with an oil / alcohol ratio greater than 1/20, due to the practical difficulties encountered in separating the glycerol from the ester,<sup>29</sup> which can lead to a shift in the transesterification reaction towards the left of balance. Consequently, the content of ethyl ester is lowered to the detriment of the formation of MG essentially, or even of DG and TG. The density of the ester decreases as the molar ratio increases.<sup>30</sup>

In Fig.6 the effect of the weight of the pillared clay catalyst with respect to the oil weight on the ester conversion is presented. As expected, the conversion has substantially increased as the amount of the catalyst in the reaction medium was increased. The activity of these catalysts is due to the basicity of their specific surface area (pH = 10.3), the availability of active sites and the pores volume.



The adsorption of the alcohol on our catalysts, which are of a basic nature, leads to the formation of the catalytic species of the reaction (R-O<sup>-</sup>) by the proton withdrawal of alcohol from the base. A nucleophilic attack of the carbonyl (triglyceride) is done by the alcoholate anion to form an intermediate carbanion (addition phase). Then, when folding the doublet of oxygen (elimination phase) a departure nucleofuge occurred. The alcoholate is regenerated at the onset of a glycerol alcoholate function. Above 7.5wt % of catalyst no significant change in the conversion was depicted.

Table 4

Basal spacing (d and BET measured Surface area of Al,Ni-PILC and Al,Co-PILC)

Sample	d <sub>001</sub> basal spacing (Å)	Total BET surface area (m <sup>2</sup> /g)
Al,Ni- PILC (5%)	18	72
Al,Ni- PILC (10%)	18.2	153
Al,Ni- PILC (20%)	19.53	55.2
Al,Co- PILC (5%)	18.9	65.4
Al,Co- PILC (10%)	19.2	205.5
Al,Co- PILC (20%)	18.5	165



Table 5

The chemical composition of the investigated samples

Samples	Na	Na <sub>2</sub> O	Si	SiO <sub>2</sub>	Al	Al <sub>2</sub> O <sub>3</sub>	Fe	Fe <sub>2</sub> O <sub>3</sub>	Ni	NiO	Co	O <sub>2</sub>
Raw-B	Nd	0.5	37	69.4	7	14.7	2	1.2	nd	nd	Nd	50
Na-Mt	7.7	2	30	69	6	14.6	1.7	0.71	nd	nd	Nd	53
Al-PILC	11	14	15	40	22	42.9	1.3	1.7	00	00	00	45
Al,Ni-PILC	1	1.5	33	69	13.	26.5	0.27	0.5	1.6	2	00	50
Al,Co- PILC	23	31	17	37	15	29	0.07	0.09	00	00	1.4	42

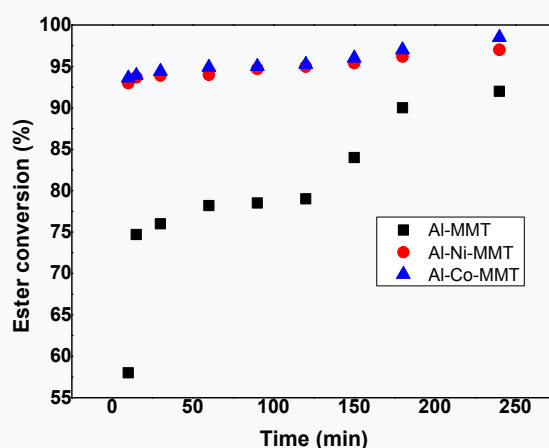


Fig. 5 – Effect of molar ratio on ester conversion at  $T^{\circ} = 473$  K, speed of agitation of 5000 rpm,  $t = 5$  hours and weight of catalyst = 7.5 % of the oil weight.

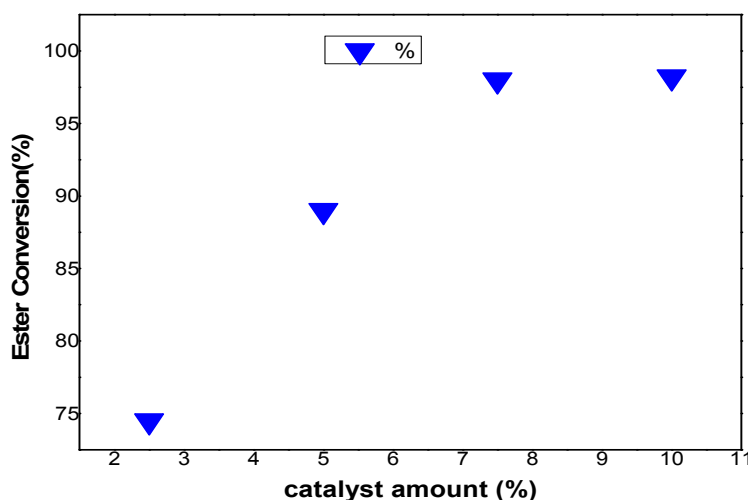


Fig. 6 – Effect of catalysts amount on ester conversion at  $T^{\circ} = 473$  K, speed of agitation of 5000 rpm,  $t = 5$  hours and molar ratio = 1/15 of (H/A).

This is the fastest step of the transesterification reaction. It corresponds to the conversion of triglyceride to monoglyceride with the diglyceride as the intermediate product. A slow conversion step is observed during the following 3h 30 minutes (fig7). It reached a conversion of 98% of monoglyceride to glycerin. In this type of reactions the temperature plays a crucial role on the

conversion. The ester conversion is increasing as a function of temperature until 250°C. It varies only slightly between 200 and 300°C as shown in the kinetics section. This can be explained by the presence of polycyclic aromatic hydrocarbons resulting from the thermal degradation of the oil at around 300°C. It presence affects the miscibility of the reactants.

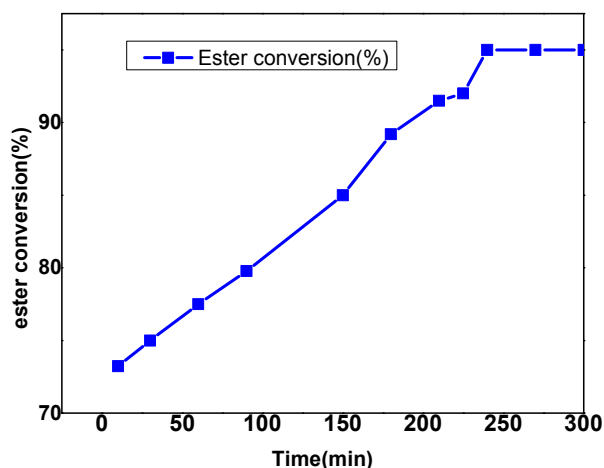
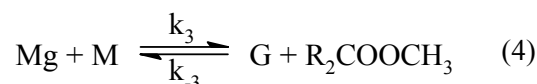
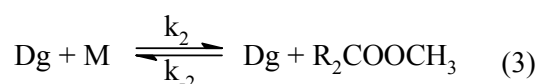
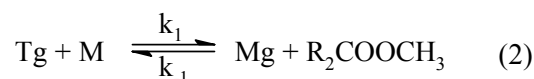


Fig. 7 – Reaction time of transesterification of castor oil at  $T^\circ = 473$  K, speed of agitation of 5000 rpm,  $t = 5$  hours and molar ratio = 1/15 of (H/A) and weight of catalyst = 7.5 % of the oil weight.

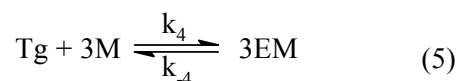
### 3. Transesterification Kinetics

The kinetics of the transesterification of castor oil by ethanol using Al-pillared clay catalyst was studied between 200°C and 300°C with 7.5% of catalyst and 1/15 molar ratio of oil/ethanol. The concentration of alcohol is considered as constant. That means that the reaction is pseudo order 1. This was the case in literature reports on the methanolysis reaction of the palm oil and of the sunflower.<sup>31</sup> Other studies claimed a pseudo order 2 for these types of reactions.<sup>29,32</sup> This discrepancy means that the transesterification kinetics is very sensitive to the reaction conditions.

If Tg, M, G, Dg and Mg refer to triglyceride, methanol, glycerol, diglycerides and monoglycerides respectively, and Dg and Mg being the intermediates of the transesterification reaction then the following chemical equations are obtained:<sup>33</sup>



If EM denotes the methyl esters ( $\text{R}_1\text{COOCH}_3$ ,  $\text{R}_2\text{COOCH}_3$  and  $\text{R}_3\text{COOCH}_3$ ), the overall reaction is therefore:



$$\frac{1}{[\text{M}]} \frac{d[\text{Tg}]}{dt} = -k_1[\text{Tg}] - k_4[\text{Tg}][\text{M}]^2 + k_{-1} \frac{[\text{Dg}][\text{EM}]}{[\text{M}]} + k_{-4} \frac{[\text{G}][\text{EM}]^3}{[\text{M}]} \quad (6)$$

If the alcohol is in excess the last two terms of the second member are negligible compared to the first:

$$\frac{1}{[\text{M}]} \frac{d[\text{Tg}]}{dt} \approx -k_1[\text{Tg}] - k_4[\text{Tg}][\text{M}]^2 \quad (7)$$

The step (1) is the limiting step; the kinetic is a pseudo order 1 with respect to the triglyceride

$$\frac{1}{[\text{M}]} \int_{t_0}^t \frac{d[\text{Tg}]}{[\text{Tg}]} \approx -k_1 \int_{t_0}^t dt \Rightarrow \frac{1}{[\text{M}]} \text{Ln}[\text{Tg}]_t = \frac{1}{[\text{M}]} \text{Ln}[\text{Tg}]_{t_0} - k_1 t \quad (8)$$

The equation of the appearance rate of G is:

$$\frac{d[\text{G}]}{dt} = k_3[\text{Mg}][\text{M}] - k_{-3}[\text{G}][\text{EM}] + k_4[\text{Tg}][\text{M}]^3 - k_{-4}[\text{G}][\text{EM}]^3 \quad (9)$$

The rate can be expressed as:



$$\frac{d[G]}{dt} = k_3 [Mg][M] - k_{-3} [G][EM] + k_4 [Tg][M]^3 - k_{-4} [G]^2 \quad (10)$$

The methanol is in excess, and  $[G]^2 \gg [G]$ ; therefore :

$$\frac{d[G]}{dt} \approx -k_{-4} [G]^2 \Rightarrow \int_{t_0}^t \frac{d[G]}{[G]^2} \approx -k_{-4} \int_{t_0}^t dt \Rightarrow \frac{1}{[G]_t} = k_{-4} t \quad (11)$$

To determine and confirm the kinetic order of the reaction in the present investigation, the integral method of analysis of the rate data was studied.

The plotting of the linear equations gives a graph of  $\ln[G]t$  against time  $t$  for the first order and  $1/[G]t$  against time  $t$  for the second order (Figs. 8 to 11).

The rate constants and the correlation coefficients of the linear regression of these plots are grouped in Tables 6 and 7. The correlation coefficient of the pseudo-first order is better than that of the pseudo-second order. Therefore, the transesterification of castor oil in an excess of alcohol follows a pseudo-first order kinetics.

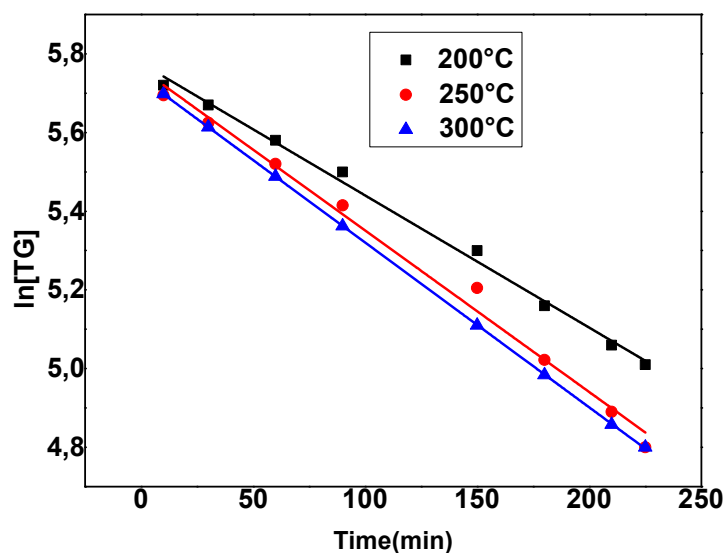


Fig. 8 – Plot of  $\ln [TG]$  against time (molar ratio 1/15, 7.5 wt % of catalyst, 240 minutes reaction time,  $T=250^\circ\text{C}$ ).

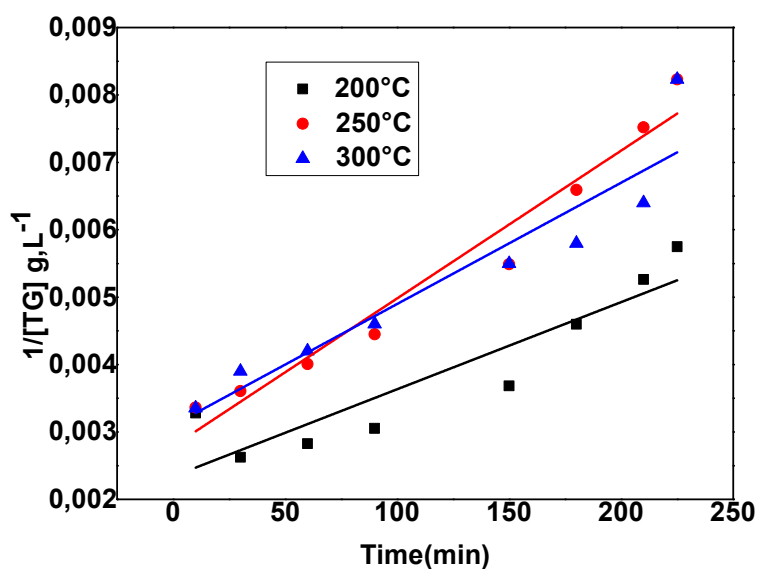


Fig. 9 – Plot of  $1/[TG]$  against time (oil/alcohol molar ratio 1/15, 7.5 wt % of catalyst, 240 minutes reaction time,  $T=250^\circ\text{C}$ ).

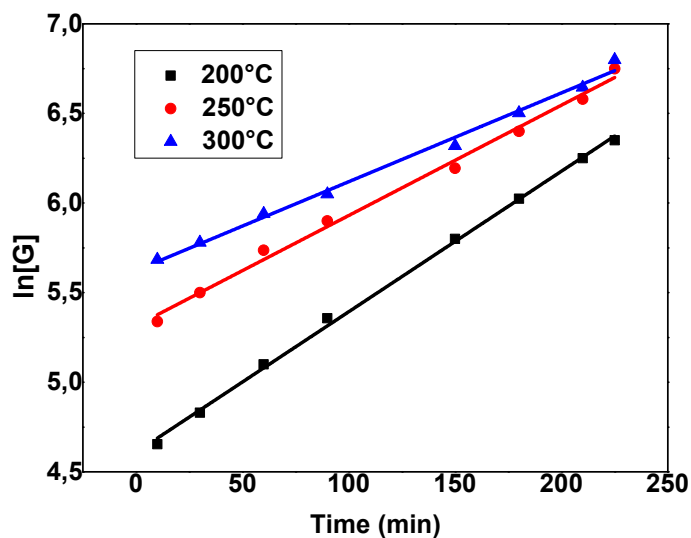


Fig. 10 – Plot of  $\ln [G]$  against time (molar ratio 1/15, 7.5 wt % of catalyst, 240 minutes reaction time,  $T= 250^{\circ}\text{C}$ ).

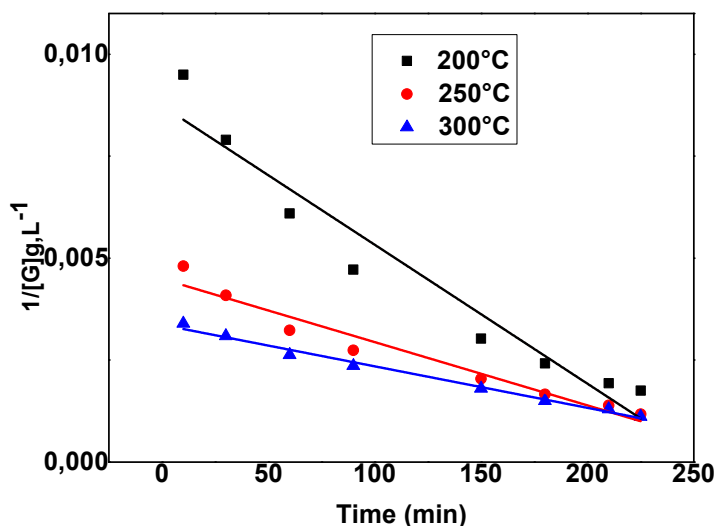


Fig. 11 – Plot of  $1/[G]$  against time (oil/alcohol molar ratio 1/15, 7.5 wt % of catalyst, 240 minutes reaction time,  $T = 250^{\circ}\text{C}$ ).

Table 6

The kinetics data for the transesterification of castor oil at different temperatures (oil/alcohol mole ratio of 1/15, 7.5 wt% of catalyst, 240 minutes reaction time)

Triglyceride Temperature	First order		Second order	
	Rate constant (K) ( $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ )	Correlation coefficient	Rate constant (K) ( $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ )	Correlation coefficient
200	$3.36 \cdot 10^{-3} \pm 0.04$	0.99	$1.29 \cdot 10^{-5} \pm 0.02$	0.80
250	$4 \cdot 10^{-3} \pm 0.03$	0.99	$2.19 \cdot 10^{-5} \pm 0.03$	0.95
300	$4.2 \cdot 10^{-3} \pm 0.01$	0.99	$1.79 \cdot 10^{-5} \pm 0.04$	0.87

Table 7

The kinetics data for the formation of glycerol at different temperatures (oil/alcohol mole ratio of 1/15, 7.5 wt% of catalyst, 240 minutes reaction Time)

Glycerol Temperature	First order		Second order	
	Rate constant (K) ( $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ )	Correlation coefficient	Rate constant (K) ( $\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ )	Correlation coefficient
200	$7 \cdot 10^{-3} \pm 0.03$	0.998	$3.4 \cdot 10^{-5} \pm 0.03$	0.93
250	$6.6 \cdot 10^{-3} \pm 0.05$	0.993	$1.55 \cdot 10^{-5} \pm 0.038$	0.94
300	$5 \cdot 10^{-3} \pm 0.04$	0.992	$1.01 \cdot 10^{-5} \pm 0.03$	0.98

#### 4. The reuse of the catalyst

The reuse of the catalyst is a vital economical issue for the industrial application. The reuse of the Al/Co-PILC<sub>10</sub> catalyst was investigated on three cycles of transesterification reaction with ethanol at an oil/alcohol ratio of 1/15 and a reaction temperature of 250°C. Figure 12 shows the conversion of ester as a function of time. We note that : after the third use of the same catalyst the reduction is from 98% to 91% was dropped from the conversion. A loss of 7% of efficacy is considered as an excellent output of the reused catalyst. The relative loss of catalyst activity was expected as a part of the surface area and the active sites were no more available for the reaction after cycling reuse.

#### 5. Comparison of the performances of the various catalysts

In Figure 13, we compare the catalytic yield of Al-PILC<sub>10</sub>, Al / Ni-PILC<sub>10</sub> and Al / Co-PILC<sub>10</sub> on the transesterification reaction of ricin oil for the production of biodiesel. We note a rapid first phase of the activity of the three catalysts, giving a best yield varying from one catalyst to another. For the case of Al-MMT and after 30 min, a conversion rate 76% is reached. The introduction of a second metal into Al- MMT resulted in a significant improvement in catalytic activity.

Significant yields are obtained with Al-Ni-MMT and Al-Co-MMT (93%) after only 10 min. A second stable phase characterizes the transesterification. This stability tends to improve in the presence of Ni and Co bimetallic catalysts, as being basic and very reactive, leading to the use of basic active sites.

#### 6. Characterization of the biodiesel obtained

The biodiesel obtained after purification was characterized according to the ASTM methods. As compared in the Table 8, the biodiesel produced in this work from castor oil transesterification using appropriated pillared clays as catalyst exhibits comparable properties to those of classical fossil diesel. These properties fit very well the recent ASTM standards of fuels. Note that the viscosity of our castor oil biodiesel is greater than that of the standardized biodiesel by a factor of five. This could be considered as a weak point, but if one compares it to the viscosities of pure vegetable oils usually employed it is a good achievement. The esters produced in the present research have a viscosity 16 times lower than that of the vegetable oil frequently used in some engines. This is a strong advantage for the engine industry. The flash point of the castor oil biodiesel is larger by a factor of 2 than that of fossil diesel. This imparts our biodiesel an advantage characteristic of a less dangerous fuel to handle.

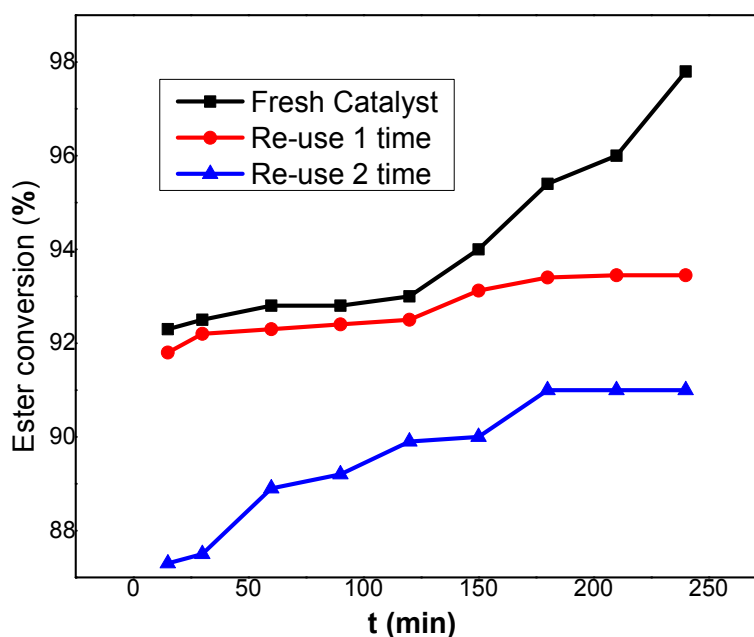


Fig. 12 – The yield of ester conversion catalyst fresh and after the 1st and 2nd reaction cycles.

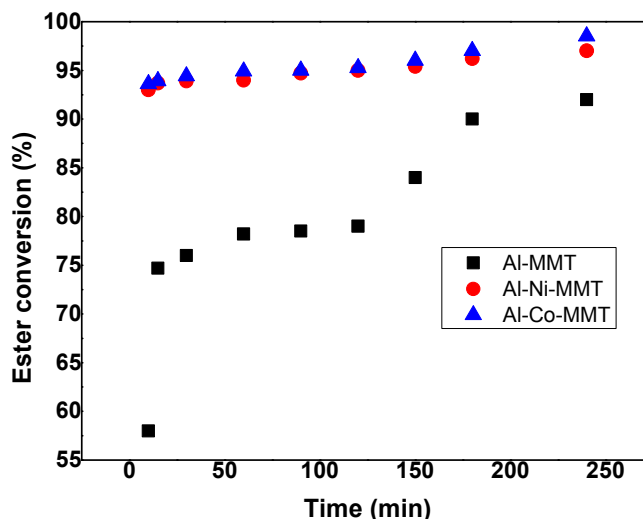


Fig. 13 – The reactivity of Al-PILC, Al,Ni-PILC and Al,Co-PILC.

Table 8

Characteristics of castor oil, biodiesel and fossil fuel

Property	Castor oil	Castor biodiesel	Fossil Diesel	Biodiesel standards	
				ASTM, DIN	
Density (15°C, Kg.L <sup>-1</sup> )	0.96	0.87	0.85	-	86-90
Viscosity (Cst)	20°C: 96 40°C: 24.5	15	2.6	1.9-6,	3.5-5
Flash point (°C)	314	155	68	>130,	>120
Pour point (°C)	-18(±3)	-15	-20	-15	
Cetane number	-	49	Min 45		
Water content (%)	0.6	0.03	0.02	<0.03,	<0.05
Acid value (mg KOH g <sup>-1</sup> )	0.014	-	-	<0.8,	<0.5

## CONCLUSIONS

The objective of this study was the development of pillared clay by metal substitution techniques and their use as heterogeneous catalysts for the transesterification of castor oil. The ultimate objective was the production of biodiesel fuel using a green chemical pathway. Simple aluminum and combined aluminum/nickel and aluminum/cobalt based clays were successfully prepared with different percentage. Pillarization was achieved through the formation of metal oxides and hydroxides pillars. The Al, Ni (10%)- PILC and Al, Co (10%)- PILC were selected because their larger basal spacing and higher surface area.

The pillared process is obtained through the formation of metal oxide and hydroxide pillars between the clay sheets, it is a result of the intercalation of Al, Al-Ni and Al-Co to the Na-MMT. The introducing of the second metal enhanced the catalytic properties of Al-MMT, a higher yield was obtained with Al-Co-MMT (98%)

because it has a larger surface area, in addition to more activity of Cobalt than the order metals in basic middle.

FTIR, XRD and EDS are confirmed the pillaring process, the enlarger of the basal spacing obtained by the increase of the radius atomic and the inorganic matrix. Textural characterization exhibits the increase of the specific surface area by the creation of the microspores structure and more actives sites in the catalyst.

The optimization of the ethyl ester production result a suitable molar ratio of O/A = 1/15, an increase of ester conversion is directly proportional with the catalyst amount until 7.5% of weight of oil. A high temperature is necessary in the heterogeneous process, a maximum yield was obtained around 250°C. The satisfactory results are obtained in the reuse in three cycles of catalyst; this is an interesting object in the heterogeneous catalysis.

The studies physicochemical properties of biodiesel are very close to the fossil diesel for use

in diesel engines. A good cetane index was obtained with a secured pour point. The viscosity does not really meet the standards, but it was able to reduce it compared to the starting viscosity of castor oil that is very important.

We can conclude from the present study that it is possible to produce a biodiesel starting from castor oil and using pillared clays; an ecologically heterogeneous catalytic system. From economical view, the proposed investigation is cost effective as it allows re-using the catalysts at least three times.

Biodiesel becomes a renewable resource because it has an environment benefits especially when it is obtained with a heterogeneous way using a green sustainable catalyst like clay.

*Acknowledgements.* I would like to thank the responsables of the Société de l'Union des Technologies de la Production Algérienne (UTPA) and those of the Laboratoire des Polymères (Senia-Oran-Algérie) for being a part of the present work.

## REFERENCES

- R. L. Naylor and M. M. Higgins, *J. Food. Secur.*, **2018**, *16*, 75-84.
- F. Maa and M. A. Hannab, *Bioresour. Technol.*, **1999**, *70*, 1-15.
- S. Adipah, *J. Environ. Sci. Public Health.*, **2019**, *3*, 113-121.
- W. Parawiran, *Sci. Res. Essays.*, **2010**, *5*, 1796-1808.
- A. Muhammad and A. Ahmad Zuhairi, *J. Renewable and Sustainable Energy Reviews.*, **2012**, *16*, 2671-2686.
- A. Srivastava and R. Prasad, *Renew Sust Energy Rev.*, **2000**, *4*, 111-133.
- R. C. Ehiri, I. I. Ikelle and O. F. Ozoaku, *Am. J. Engineer. Research (AJER)*, **2014**, *3*, 174-177.
- V. Egidio, B. Alessandro, V. Vito, G. Ivan, Z. Francesco, B. Giacobbe and G. Girolamo, *Catal. Today.*, **2012**, *179*, 185-190.
- R. M. Manriquez, G. Ricardo, J. G. Hernandez-Cortez, Z. M. Abel, M. Carmen, G. Reza-San, O. Sergio and V. Flores, *Catal. Today.*, **2013**, *212*, 23-30.
- S. D. Manali and D. Y. Ganapati, *Catal. Today.*, **2018**, *309*, 161-171.
- S. Swati, S. Varun, B. Anupriya, C. Pranjali and P. Lalit Mohan, *Mater. Sci. Eng., A.*, **2018**, *1*, 11-21.
- Z. Hong-Yan, F. Zeng, D. Xin and L. Yu-Qin, *Fuel.*, **2008**, *87*, 3071-3076.
- Z. Hong-Yan, F. Zeng, D. Xin and L. Yu-Qin, *J. Appl. Clay Sci.*, **2014**, *91-92*, 16-24.
- N. Degirmenbasi, *Appl. Catal., B.*, **2014**, *150-151*, 147-156.
- A. F. F. Farias, *Fuel.*, **2015**, *160*, 357-365.
- A. N. Nabel, H. S. Galal, I. H. Onsy, Z. Yehia and A. M., *J. Mol. Liq.*, **2017**, *237*, 38-44.
- S. Yahaya Muhammad, A. W. Wan Mohd and A. Appl. Catal., **2014**, *470*, 140-161.
- M. Kurian and S. A. Kavitha, *J. Appl. Chem.*, **2016**, 47-54.
- Z. Shfeng, Z. R. Enxian and Q. Chenze, *J. Rare Earths.*, **2011**, *29*, 52-57.
- H. J. Berchmans and S. Hirata, *J. Bioresour. Technol.*, **2008**, *99*, 16-21.
- Z. Meçabih, S. Kacimi and B. Bouchikhi, *J. of water Sci.*, **2006**, *19*, 23 - 31.
- O. Bouras, J. C. Bollinger and M. Baudu, *J. Appl. Clay Sci.*, **2010**, *50*, 58-63.
- D. Guerra, V. P. Lemos, R. S. Angélica and C. Airoidi, *Ceramica.*, **2006**, *52*, 200-206.
- H. Guo, B. X. Zhao, J. C. Luo, W. Wu, W. Ye, Q. Wang and X. L. Zhang, *J. Micropor. Mesopor. Mat.*, **2014**, *196*, 208-215.
- Z. Mojović, P. Banković, A. Milutinović-Nikolić, B. Nedić and D. Jovanović, *Appl. Clay Sci.*, **2010**, *48*, 179-184.
- J. Carriazo, E. Guelou, J. Barrault, J. M. Tatiboue, R. Molina and S. Moreno, *Water Res.*, **2005**, *39*, 3891-3899.
- J. G. Carriazo, L. M. Martínez, J. A. Odriozola, S. Moreno, R. Molina and M. A. Centeno, *Appl. Catal., B.*, **2007**, *72*, 157-165.
- C. T. Alves, A. S. de Oliverira, S. A. V. Carneiro, R. C. D. Santos, S. A. B. Vieira de Melo, H. M. C. Andrade, F. C. Marques and E. A. Torres, *Procedia Engineering*, **2012**, *42*, 1928-1945.
- O. S. Stamenkovic, Z. B. Todorovic, M. L. Lazic, V. B. Veljkovic and D. U. Skala, *Bioresour. Technol.*, **2008**, *99*, 1131-1140.
- M. Canakci and J. V. Gerpen, *J. Am. Soc. Agric. Engineers (ASAE).*, **1999**, *42*, 1203-1210.
- E. S. Song, J. W. Lim, H. S. Lee and Y. W. Lee, *J. Supercrit. Fluids.*, **2008**, *44*, 356-363.
- P. C. Narvaez, S. M. Rincon and F. J. Sanchez, *J. Am. Oil Chem. Soc.*, **2007**, *84*, 971-977.
- S. Fernando, P. Karra P. Hernandez and S. K. Johan, *Energy.*, **2007**, *32*, 844-851.

