Sudanese Clays for Heterogeneous Methanolysis of Castor Oil

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Abstract

Objective: To modify two Sudanese clays, called Jourdiqua and Jabbalmarra, with different loading of HCl, 0.1, 0.2, 0.3. 0.4, 0.5 and 1.00 M in order to increase their catalytic activities and then used in methanolysis of castor oil .**Methods/statistical Analysis:** Both raw and modified clay samples were used as catalysts under reaction conditions; 5wt% of catalyst to oil, molar ratio of methanol to oil of 27:1, 4 hours reaction time and temperature of 67 C°. The unmodified and modified clay samples were characterized by, Thermo gravimetric analysis-differential Thermo gravimetric (TGA-DTG), Brunauer-Emmett-Teller (BET), inductively coupled plasma-emission spectroscopy (ICP-ES), atomic absorption spectroscopy (AAS), X-ray powder diffraction (XRD), Fourier transform infra-red (FTIR) and field electron scanning emission microscopy (FESEM). **Finding: Application/Improvement:** BET analysis showed increase in specific surface area for both Jourdiqua and Jabbalmarra clays. Elemental analysis by ICP-ES showed decrease content in elements of Al, Mg, Na and K for both clays, due to the acid leaching. The biodiesel conversion was monitored using nuclear magnetic resonance (NMR) spectroscopy. An increase in conversion was observed for Jourdiqua clay from 51% to 90% when treated with 0.5 M HCl, the optimized concentration for the modification, while for Jabbalmarra 22.5% conversion was obtained with raw clay and after modification gave conversion of 82% in reaction conditions of temperature 65oC, reaction time of 4 hours, molar ratio of methanol to oil of 18:1 and catalyst loading of 9%. It was observed that acid modification with 0.5 M HCl have improved tremendously the catalytic capability of the raw clays.

Keywords: Modification; Characterization: Catalyst; Transesterification; Sudanese Clays.

1.0 Introduction

Biodiesel is the methyl esters of fatty acids develop as an alternative to fossil fuels. The strongest motivation factor is the concern about global pollutant. Biodiesel has many environmental benefits which include less greenhouse effect, less air and soil pollution, leading to less health risk. Today, over 85 biodiesel production plants are working world wide, the biodiesel is produced by transesterification of vegetable oils and fats with short chain alcohol (methanol or ethanol, (Kaura et. al., 2015) In recent years, the development of alternative fuel like bioethanol and biodiesel from renewable sources has received considerable attention. Homogeneous catalysts are used but they have problems such as leaching, saponification which require washing and this cause release of waste water. Heterogeneous solid catalysts such as zeolites and clay minerals have been developed as substitutes for homogeneous catalysts and have benefit of being easy to recover and the process required no washing, (Klooporge et. al., 2005)

It is very important to find cheap raw materials without competition with arable land and food for the development of biofuel, such as non-edible oil, waste oil and fats. Castor oil is a very promising source of biodiesel, a colorless or pale yellowish oil extracted from seeds of castor oil plant, castor (Ricinus communis L) is cultivated around the world because of the commercial importance of its oil which is used in the manufacture of a number of industrial chemicals like surfactants, grease and lubricants, specialty soap, surface coating and cosmetic. Castor seed has an oil content of 42-48%, castor plant grows well under hot and humid tropical conditions and has a growing period of 4-5 months. Castor oil has density of 950 kg/m³ at 15 °C, and molecular weight of 927 g/mol. The main fatty acid present in castor oil is ricinoleic acid with percentage of about 90%, (Vama et. al., 2007).

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Clay minerals can be more acidic if it is modified with dilute hydrochloric acid. The acid modification of the clay improves its catalytic activity. The aim of this study is to produce biodiesel from vegetable oil (castor oil) using clays as acid catalyst.

2.0 Experimental

2.1 Materials

The starting clay samples are natural Sudanese clays; Jourdiqua (black clay) from north of Sudan (Suba), and Jabbalmarra (white clay) from the west of Sudan at Darfur state, Nyala city Jabbalmarra region. Castor oil was purchased from Indian shop in Skudai, Johor Bahru. Methanol of purity >99%, hydrochloric acid 37% (w/w) and potassium hydroxide were obtained from Aldrich. Deionized water is used for the preparation of solution. All chemicals are of analytical grade and used without further purification. The clay samples were dried in an oven at 80 °C overnight, grinded and sieved through 200 mesh (75μ) sieve to obtain 0.075 mm particle size, and kept in sample bottles.

2.3 Modification of Clays

Both clay samples were calcined at 450 °C for 4 hours then cooled in a desiccator, 10 g of each sample was weighed and transferred into six different 250 mL double neck round bottom flask, followed by addition of 100 ml of 0.1, 0.2, 0.3, 0.4, 0.5 and 1.00 M HCl solutions. The mixture was refluxed at 90 °C under stirring at 300 rpm for 3 hours, cooled to room temperature, then filtered and washed with distilled water. The sample is then dried in an oven at 80 °C overnight and kept in sample bottles. The clay samples are denoted; JB, JB0.1, JB0.2, JB0.3, JB0.4, JB0.5 and JB1, and JQ, JQ0.1, JQ0.2, JQ0.3, JQ0.4, JQ0.5 and JQ1 for raw Jabbalmarra and Jourdiqua and acid modified samples using 0.1, 0.2, 0.3, 0.4, 0.5 and 1.0 M HCl, respectively.

2.4 Characterization of Clays

The ICP-ES analysis was performed by digesting about 1 g of the clay sample using HF acid and aqua regia, and diluting to 250 ml with distilled water, the solution is then analyzed. The XRD analysis was carried out on a Bruker D8 having Siemens Diffractometer D5000 with Cu-Kα radiation (40 kV, 40 mA, λ = 1.5406Å) (USA), the sample was scanned at the rate of 0.05 s/step and 2θ range of 10-70°. The morphology was determined using field emission electron microscope (FESEM) (Supra TM 35 VP operating at 10kV) (Germany). The TG-DTG analysis was carried out using Perkin Elmer Simultaneous Thermal Analyzer (STA 8000) (USA) in the temperature range of 50 °C to 1200 °C and heating rate of 10 °C/min. Nitrogen adsorption-desorption was used to determine the surface area at -196 °C using Micro meritics Pulse Chemi Sorb 2705 (USA), prior to analysis all samples were dehydrated and degassed for 1 hr. at 473 K under nitrogen gas flow condition. The samples were then evacuated to 10^{-2} Torr and immersed in the liquid nitrogen. Perkin Elmer 1650 Infra-Red Spectrometer (USA) was used for FTIR analyses of samples in the range of 4000 cm^{-1} to 400 cm^{-1}. The pH was measured using EUTECH INSTRUMENT pH Tutor (Singapore), the clay was mixed with deionized water in the ratio of 1:1, the measurement was performed by placing the glass electrode in the clay mixture at room temperature. The density of the clay was determined by taking a known amount using metal ring pressed into the clay, and the weight is determined after drying. From the weight and volume the density is obtained. Moisture content of the clay sample was determined by weighing known amount of clay and placing it in an oven, the sample was dried until a constant weight is obtained. From the weight loss, the moisture content of the clay sample was calculated.

2.4.1 Acidic Test (Back Titration)

About 0.2 g of the clay sample was taken in small tube and 10 ml of distilled water was added and left overnight and then centrifuged at 3000 rpm for 15 minutes, the mixture was filtered and transferred to a conical flask, 10 ml of 0.05 M KOH was added to the filtrate, followed by 3 drops of phenolphthalein indicator and titrated against 0.02 M HCl solution to the end point.

2.5 Transesterification Process

The Transesterification reaction of the castor oil was conducted, using the raw and modified clays in 250 ml double neck round bottom flask with methanol to oil molar ratio of 18:1, catalyst loading 5%, reaction time of 3 hours at 67 °C, under stirring at 300 rpm. After completion of the reaction the products are allowed to settle overnight and centrifuged at 3000 rpm for 15 minutes.

Three layers were observed; upper layer of methanol was distilled, while the middle layer of biodiesel and the lower layer of glycerol and settled catalyst were separated using separation funnel. Biodiesel was dried over sodium sulfate and then characterized by NMR technique, ((Jin et. al., 2007)

3.0 Results and Discussion

3.1 Physical Characterization and TGA-DTG

Figure 1 depicts the TGA-DTG curves of JB and JQ clays. For the JB clay, the first weight loss was around 60 ℃, due to the evaporation of absorbed water molecules between layers of clay. The loss at this temperature was about 8%. The second weight loss was around 275 ℃ of around 6.32%, which may be due the evaporation of carbonate, bicarbonate and other volatile species. The third loss was around 750 ℃ of about 4.7%, this may be due the loss of volatile species and hydroxide structures, present between clay layers. For the JQ clay, the first loss was at 60 ℃, also due to the evaporation of water molecules between layers, which is about 16%. The second loss was around 270 ℃, may be due to the liberation of carbonates, bicarbonates and some volatile species from the sample, the loss at this temperature is about 6.32%. The third loss is around 4.2% at 690 ℃, and may be due to the loss of volatile species from the simple, (Lotero et. al., 2005).
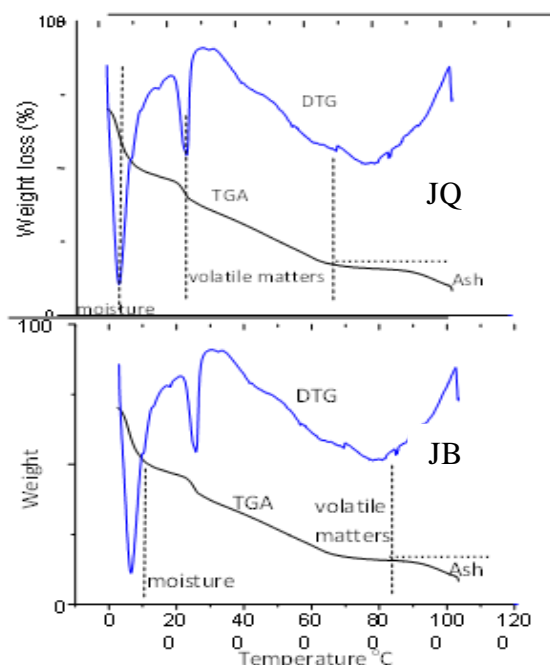

Figure 1 Thermo gram of clay samples

From the result it can be seen that JQ clay has high percentage of moisture of about 16% indicating the availability of swelling water molecules, pointing to its plasticity and strength. High densities were observed for both clays making them suitable for many applications such as the brick production. Loss on ignition is high for the JQ clay reaching about 19%, this may be due to the high amounts of volatile species present in the clay, such as carbonate and bicarbonate, which make this clay not suitable as refractory clay. On the other hand, the JB clay has low value of ignition loss of about 10.33%, which make it suitable to be regarded as refractory clay. The high pH value of JQ clay of 11.13 can be attributed to its high basicity. This may be due to the high percentage of metal carbonate in the sample that hydrolyzed to form basic solution. The combustible volatile matter content of the JQ clay was high as evidence from the high ash content, while it was low for the JB clay. The five physical parameters determined for the two clays are listed in Table 1.

Table 1 Physical characterization for the clay samples

Clay	pH	Moisture (%)	Loss on Ignition (%)	Ash content (%)	Density (g/mL)
JB	6.61	8	10.33	6.32	1.42
JQ	11.13	16	18.72	11.62	1.12

3.2 Elemental Analysis

The chemical compositions of the two clays were determined using (ICP-ES) and atomic absorption spectroscopy and the result is shown in Table 2. The low content of alumina for the two clays makes them unsuitable for use as high melting clay.

The ratio of silicate to alumina ($SiO_/:Al_2O_3$) in both clays is greater than one, making them suitable for zeolite synthesis. The high silicate content of JB clay makes it appropriate for the production of floor tiles. The high content of silica and alumina compared with other oxides in JB clay suggests that it is Kaolinite. For the JQ clay, its high sodium content may be due to the high percentage of carbonate and bicarbonates as can be seen from the presence of peak around 1720 cm^{-1} in FTIR spectra due to carbonates, as well as from the high weight loss due to the liberation of carbonate in the TGA result. This makes it suitable as traditional medicine for stomach ache especially in Sudan.

Also the high sodium content makes it suitable as an ion exchanger, for purification of water. Other oxides present in both clays make them suitable for ion exchange process and can increase their acidity and basicity. After acid treatment many elements were leached out as a result their percentage decreased in the samples, while the percentage of silica and alumina increased.

Table 2 Elemental analysis for the two raw clays

Elements	Raw JB (%)	Raw JQ (%)
Si	75.239	14.120
Al	10.240	4.170
Ba	0.391	1.610
Mg	0.315	1.150
Li	0.201	1.020
Fe	3.250	20.500
Rb	0.063	00.30
Ga	0.037	0.140
As	0.019	0.220
Pb	0.018	0.002
Sr	0.015	0.120
Cs	0.007	0.000
Zn	0.007	0.040
Se	0.004	0.001
Ni	0.003	0.013
Cu	0.001	0.009
Ca	2.550	10.400
Na	6.641	41.500

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 2 shows the spectra for the raw and modified JB and JQ clays, respectively. The layer structure reveals four well resolved [OH] bands in the IR spectra. Three of these bands are assigned to the stretching vibrations of surface hydroxyl groups at 3620, 3654 and 3696 cm^{-1} while the fourth at 3456 cm^{-1} is attributed to the vibrations of the inner hydroxyl groups. Bands at 694, 795, 913 and 936 cm^{-1} are additional bands associated with surface hydroxyls. The band near 467 cm^{-1} is due to the Si-O-Si deformation, and that at 541 cm^{-1} is due to Si-O-Al deformation. While bands at 694 and 795 cm^{-1} are due to the Si-O stretching, band at 1031 cm^{-1} is attributed to the V[Si- O] planar stretching [6]. The peaks assignment is presented in Table 3. When the clay is samples are modified with different concentrations of HCl, two new bands at 2924 and 2855 cm^{-1} appeared, which may be related to the stretching vibrations of H_2O and OH groups due to the clay hydrolysis by aqueous solution of HCl. The rest of the hydroxyl groups bands shifted to the lower frequency after acid modification, (Santo et al., 2007). For JQ, after acid modification three new bands appeared. This may be due to the stretching vibrations of inner hydroxyls formed after acid modification; these bands are at 2958, 2925 and 2825 cm^{-1} that can be attributed to the stretching vibrations of H_2O and OH groups. Also new band at 1450 cm^{-1} related to Lewis acid was appeared. The rest of the hydroxyl groups bands were shifted to the lower frequency, (Zhao et. al., 2007)
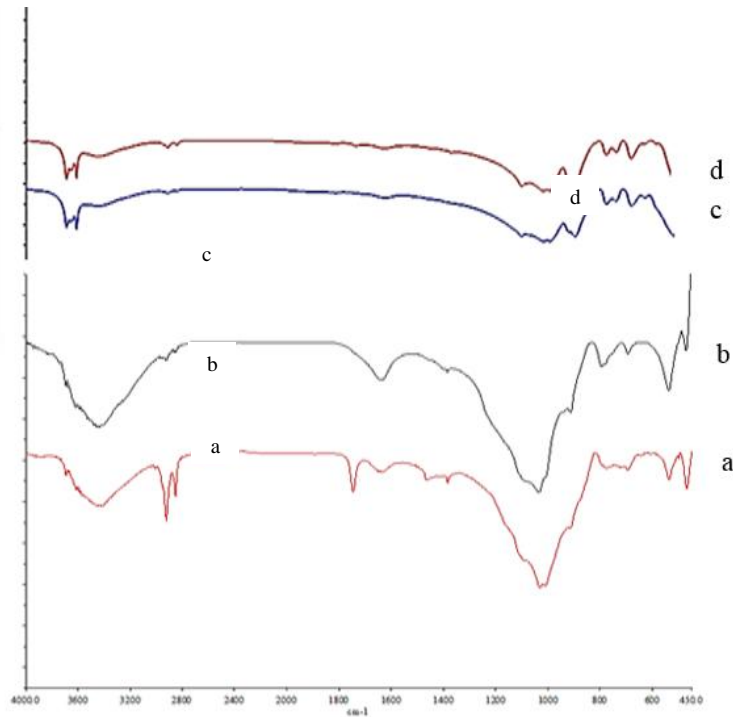
Figure 2 FTIR spectra of (a) JQ1, (b) JQ, (c) JB and (d) JB1

Table 3: Observed bands for the raw JB and JQ clay

Wave number (cm^{-1})	Assignment
3438.73	Stretching vibration of OH of water.
1607.74	OH deformation of wáter .
1440.56	Traces of carbonate
1174.39	Si-O stretching.
1024.26	Si-O stretching.
940.00	Al-Al-OH deformation
892.74	Traces of carbonate.
858.81	Al-O deformation
787.48	Al-O-Si deformation
698.55	Si-O stretching
481.76	Si-O-Si deformation.

3.4 X-rays Diffraction analysis (XRD)

Figure 3 shows the diffractogram of raw JQ, peaks at 2θ of 21.00 (4.12 Å), 26.66 (3.33 Å) and 28.00 (3.19 Å) corresponding to [1 1 0], [6 0 0] and [1 1 1] planes, respectively, were observed indicating the presence of montomorillonite, (Ezeet al., 2012). The peaks at 2Ө values, 20.00 (4.20 Å), 26.66 (3.33 Å) and 36.50 (2.475 Å) equivalent to the of [1 1 1], [1 2 0] and [1 1 2] planes respectively, indicates the presence of muscovite, while peaks at 2θ of 26.66 (3.34 Å), 50.00 (1.816 Å), and 60.00 (1.514 Å), corresponding relatively to, 0 0 6, 1 1 2 and 2 1 1 planes, designating the presence of quartz. The main clay minerals in JQ clay are therefore montomorillonite, muscovite and quartz, (Department of Commerce USA, 1989). After acid modification the diffractogram showed some loss of crystallinity, due to the removal of octahedral cations, resulting in destruction of some octahedral layers.
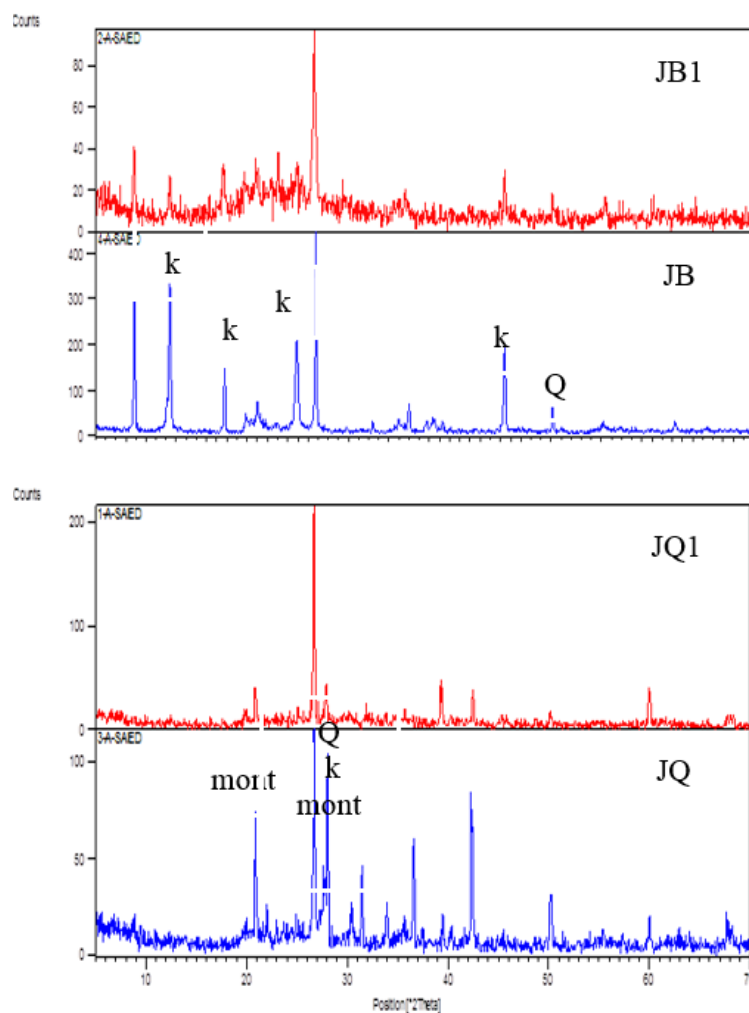
Figure 3 XRD diffractograms of unmodified and modified clays

From the diffractogram of raw JB, peaks at 2θ of 12.41 (7.14 Å), 17.91 (4.97 Å), 21.25 (4.18 Å) and 24.85θ (3.576 Å), related to the planes of [0 0 1], [1 0 0], [1 1 1] and [0 0 2], respectively indicate the presence of kaolin. The peaks at 31.10 (3.3A), 26.66 (3.34Å), and 50.00 (1.816Å), related respectively, to the planes of [1 0 1], [0 0 6] and [1 1 2], were observed indicating the presence of quartz in JB. Hence, the main minerals in JB clay are kaolin and quartz. After acid modification the clay had lost more of its crystallinity due to removal of some of its octahedral cations, (Gerpen et. al., 2006).

3.5 Acidic Back Titration

Acidity test was carried out before and after acid modification to measure the catalytic activity of the clay samples. The acidity of clay samples were determined and listed in Table 3. Increase in the number of active sites was observed for the two clay samples after acid treatment due to ion exchange, and this was confirmed by the FTIR spectra of the clay, which shows appearance of the band at 1450 cm^{-1} related to Lewis acid. JQ gained more acid sites than JB due to its higher cation exchange capacity (C.E.C) compared to that of JB clay, (Renzende et al., 2013).

Table 3 Acid sites of the catalysts before and after modification

Catalyst	Number of acid sites (mmol/g)
JQ	0.125
JQ1	0.523
JB	0.115
JB1	0.245

3.6 Nitrogen Gas Adsorption Analysis (BET)

The two clays were characterized by nitrogen gas adsorption analysis (BET) before and after acid modification. The heat and acid treatment affect the surface area of clays causing increase in surface area due to the removal of octahedral cations and extending the spaces between clays layers. The surface area as presented in Table 4 was found to increase from 3.75 to 7.78 m²/g for JB, while for JQ the increment is from 12.12 to 54.64 m²/g.

Table 4: Specific surface area of the two clays before and after modification

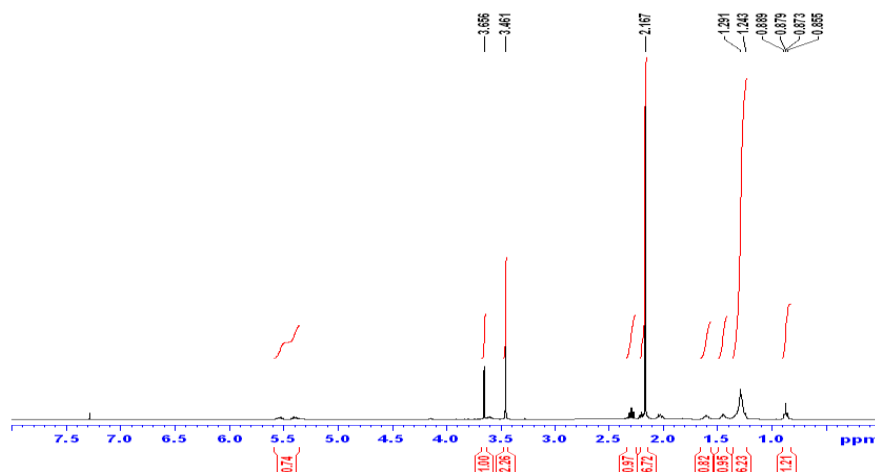| Catalyst	S.A. before (m²/g)	S.A. after (m²/g)	% change in S.A.
JQ	12.12	54.65	350.91
JB	3.75	7.78	107.47

Figure 4: ¹HNMR spectrum of biodiesel from castor oil in CDCl₃catalyzed by Raw Jourdiqua clay, conversion 51%
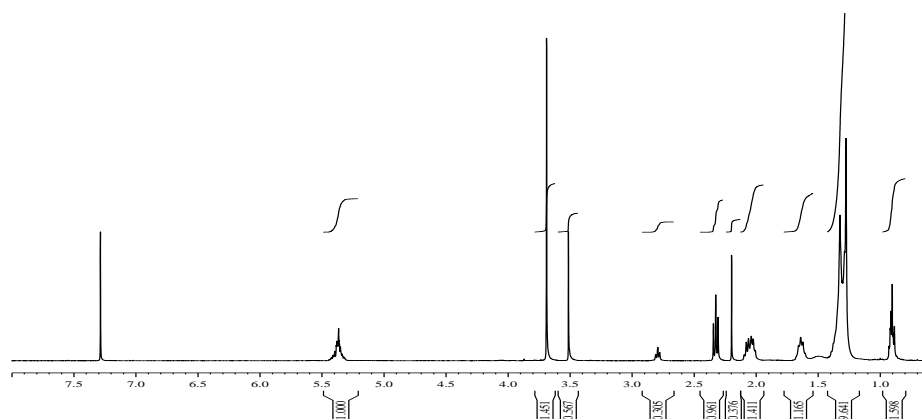

Figure 5:¹HNMR spectrum of biodiesel from castor oil in CDCl₃catalyzed by 0.5 M HCl modified Jourdiqua clay, conversion 90%
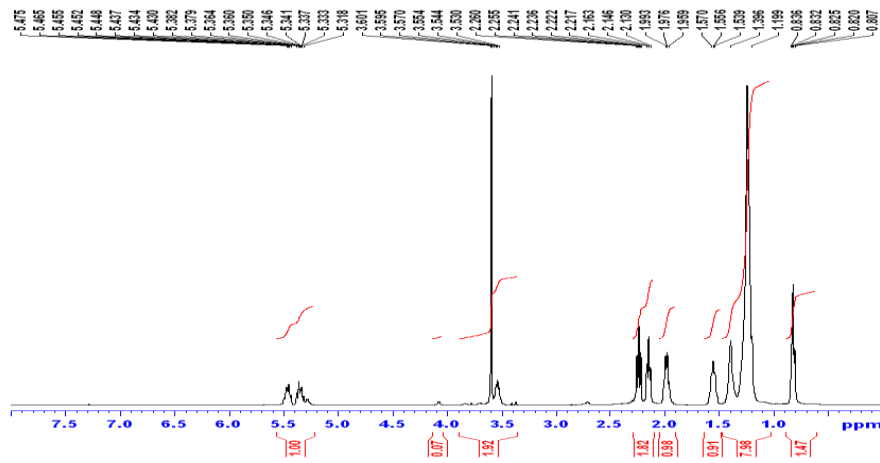
Figure 6: ^{1}HNMR spectrum of biodiesel from castor oil in CDCl$_3$catalyzed by raw Jabbalmarra clayconversion 22.5%
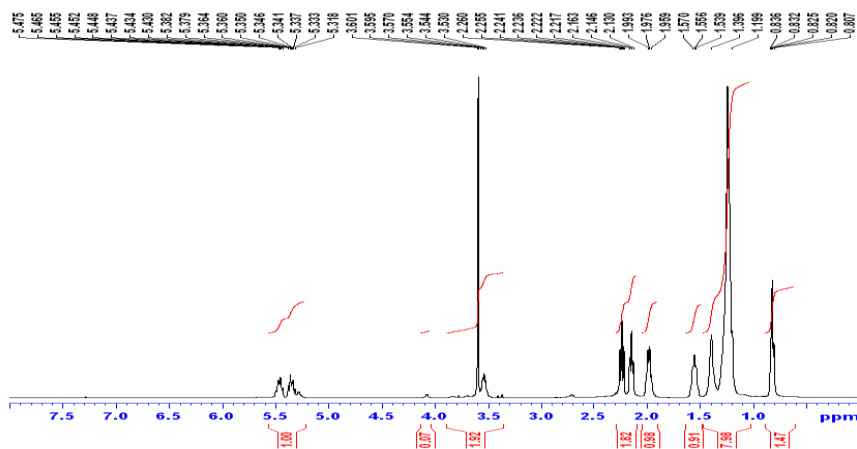

Figure7:^{1}HNMR spectrum of biodiesel from castor oil in CDCl$_3$catalyzed by 0.5 M HCl modified Jabbalmarra clay,conversion 82%

Table 5: NMR Assignment of biodiesel from castor oil

Peaks in ppm	Assignment
0.98-1.00	Terminal methyl protons C-CH$_3$ of triglycerides chain
1.20-1.40	Methyl group protons of remaining methanol CH$_3$OH
1.50-1.75	β methylene protons, CH$_2$-C-CO$_2$Me
2.3-2.4	α methylene protons of esters CH$_2$-CO$_2$-Me
3.49	Methyl group protons of remaining methanol CH$_3$OH
3.66	Methoxy protons of biodiesel-O-CH$_3$
5.31-5.36	Olefinic protons CH$_2$=CH$_2$

Table6. Percentage yield of biodiesel using the raw and acid modified clay catalysts

HCl Modified Clays (M)	Biodiesel Yield from JQ (%)	Biodiesel Yield from JB (%)
0.0	71.00	20.00
0.1	74.31	30.22
0.2	79.53	39.41
0.3	81.88	50.54
0.4	84.71	60.50
0.5	90.85	70.22
1.0	82.82	68.13

4.0 conclusión

From the results of characterization of the two clays, the main minerals in JB were identified to be kaolinite and quartz, while montomorillonite, muscovite and quartz are present in JQ. The result further revealed that JB is rich in silica and alumina, while JQ is very rich in sodium; this gives it high basicity that resulted in high biodiesel yield even before the acid modification. Both clay samples are rich in metal cations. Acid treatment of the clay samples resulted in an increased in acid sites and surface area which leads to the increase in their catalytic activities. The percentage yield of biodiesel was found to increase with increase in acid concentration. Clay modified with 0.5 M HCl give the highest biodiesel yield of 90.85 and 70.22% for both JB and JQ, respectively.

Acknowledgement

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