

Acid Modified Jourdiqqa Clay for Methanolysis of Castor Oil

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Abstract

Clay and clay minerals have very promising future in catalysis of chemical reactions. In this work Jourdiqqa clay from north of Sudan was acid modified and used as heterogeneous catalyst in transesterification reaction of castor oil with methanol. The clay was modified with hydrochloric acid, HCl, at 30%, 40%, 50%, 60% and 70% weight concentration with respect to the clay, respectively. The raw and acid modified clay were characterized by Fourier transform infrared analysis (FTIR), field emission electron microscope (FESEM), back titration, TPD-NH₃ technique and nitrogen adsorption desorption (BET) analysis, to determine the physico-chemical properties and the acidity of the raw and modified clay. The surface area and active sites of the modified clays were found to increase with the acid treatment. Transesterification of castor oil with methanol were done under the reaction condition of 9% w/w catalyst loading, methanol to oil molar ratio of 18:1, 3 h reaction time and the reaction temperature of 67°C. The biodiesel yield was monitored using nuclear magnetic resonance ¹H NMR spectroscopy. The highest conversion observed is 83.86% achieved by 50% HCl/Clay.

Keywords: Jourdiqqa Clay; Biodiesel; Transesterification; Heterogeneous; Catalyst

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 worldwide. Biodiesel is produced by transesterification of triglycerides or from the esterification of fatty acids, both with a short chain alcohol such as ethanol or methanol in the presence of acid or base catalyst [1].

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, require washing and this cause saponification and release of wastewater. Heterogeneous solid catalysts such as zeolites and clay minerals have been developed as substitutes to homogeneous catalysts and have benefit of being easy to recover and the process does not require washing.

Clays are promising catalyst especially after modification with acids or bases. Clays normally are hydrated aluminum silicate with very fine particle size usually less than 2 μm with layered structure formed by tetrahedral sheets linked to an octahedral sheet through sharing of apical oxygen. The best known clay minerals are the smectite group that are widely used in various branches of industries due to their high cation exchange capacity, swelling ability and high surface area [2].

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 for biodiesel. It is colourless 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, lubricants, soap, surface coating and cosmetics. Castor seed has an oil content of 42% to 48%. Castor plant grows well under hot and humid tropical conditions and has a growing period of 4 months to 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% [3].

The aim of this study is to produce biodiesel from vegetable oil (castor oil) using clays as acid catalyst after modification with hydrochloric acid. Therefore in this work, Jourdiqqa clay was brought from north of Sudan at the shore of River Nile to be used as acid modified heterogeneous catalyst in the transesterification reaction between castor oil and methanol.

Experimental

Reagents and materials

The starting clay samples are natural Sudanese clays, Jourdiqqa (black clay) from north of Sudan. Castor oil was purchased from local shop. Methanol of purity 99%, hydrochloric acid 37% (w/w) and potassium hydroxide were obtained from Aldrich. Deionized water was 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. After that, it was grinded and sieved through 200 mesh (75μ) sieve to obtain Ca 0.075 mm particle size, and kept in sample bottles.

Preparation of the catalysts

About 100 g of Jourdiqqa clay were calcined at 450°C for 4 h then cooled in a desiccator, 10 g of the raw Jourdiqqa clay was weighed and transferred into each of six different 250 mL double neck round bottom flask in order to prepare solutions of different HCl concentrations, followed by addition of 100 mL of 0%, 30%, 40%, 50%,

60% and 70% weight concentration of HCl solutions. The mixture was refluxed at 90°C under stirring at 300 rpm for 3 h. The mixtures were cool to room temperature, then filtered and washed with distilled water. The samples were finally dried in an oven at 80°C overnight. The clay samples are denoted; 0% HCl/Clay, 30% HCl/Clay, 40% HCl/Clay, 50% HCl/Clay, 60% HCl/Clay and 70% HCl/Clay for Jourdiqqa and acid modified samples using, 0%, 30%, 40%, 50%, 60% and 70% weight concentration of HCl respectively.

Characterization of acid modified clay

All of the prepared catalyst were labelled and characterized by using, Fourier transform infrared spectroscopy (FTIR), X-ray Diffraction (XRD), Brunauer-Emmet-Teller (BET) and temperature programmed desorption for base (NH₃-TPD).

Transesterification of castor oil with methanol

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 9%, reaction time of 3 h 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 min. 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 and then characterized by ¹HNMR technique [4].

Results and Discussion

Fourier transform infrared analysis (FTIR)

The infrared spectra of raw Jourdiqqa clay and acid modified clay are as shown in Figure 1.

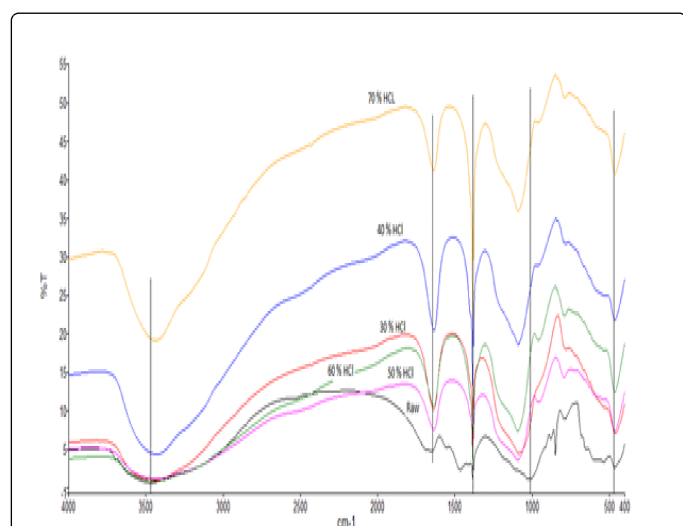


Figure 1: FTIR spectra of raw and acid modified Jourdiqqa clay with 30%, 40%, 50%, 60% and 70% HCl.

The FTIR spectra for raw Jourdiqqa clay and acid modified Jourdiqqa clay displayed similar characteristic peaks, which are at 3483 cm⁻¹ indicating the stretching vibration of OH group of clay structure.

The absorption band at 1607cm⁻¹ which is due to the OH deformation of water. The presence of silica is confirmed from the absorption peaks at 1174 cm⁻¹ and 1024 cm⁻¹ that is correspond to Si-O stretching vibration and band at 498 for Si-O-Si deformation, it was observed that the most of the bands were shifted to the lower wavenumber after acid modification.

Acid sites concentration by back titration

The acid sites concentration of raw and modified clay was determined by back titration method. Figure 2 shows the amount of acid sites for raw Jourdiqqa clay and Jourdiqqa clay modified with 30% HCl, 40% HCl, 50% HCl, 60% HCl and 70% HCl. Raw Jourdiqqa clay shows the acid sites concentration of 0 mmol/g. This is due to the presence of plenty amount of sodium carbonates and sodium bicarbonates (Na₂CO₃ and NaHCO₃) in the natural clay. After the Jourdiqqa clay was modified with 30% HCl, 40% HCl, 50% HCl, 60% HCl and 70% HCl, it shown that, the acid sites concentration increase to 1.2670, 3.2550, 5.3782, 4.2158 and 2.7152 mmol/g respectively. This is because during acid treatment, ion exchange process took place and the protons replaced the cations between clay layers. Thus, the acidity of modified clay increased with increasing acid concentration used, to the certain limit, from 30% (1.2670 mmol/g) up to 50% (5.3782 mmole/g). After that, the acidity start to decrease with increasing acid concentration, acid sites for 60% and 70% are 4.2158 mmol/g, 2.7152 mmol/g respectively. This reduction in acidity occurred when high concentration of acid was used, due to the fact that octahedral Al³⁺ cations were removed which results in the formation of silanol groups and thus decreasing the acidity of the catalyst [5]. Based on the back titration analysis, 50% HCl/clay gives the highest acid site. Thus, only 50% HCl/clay will be used for further analysis.

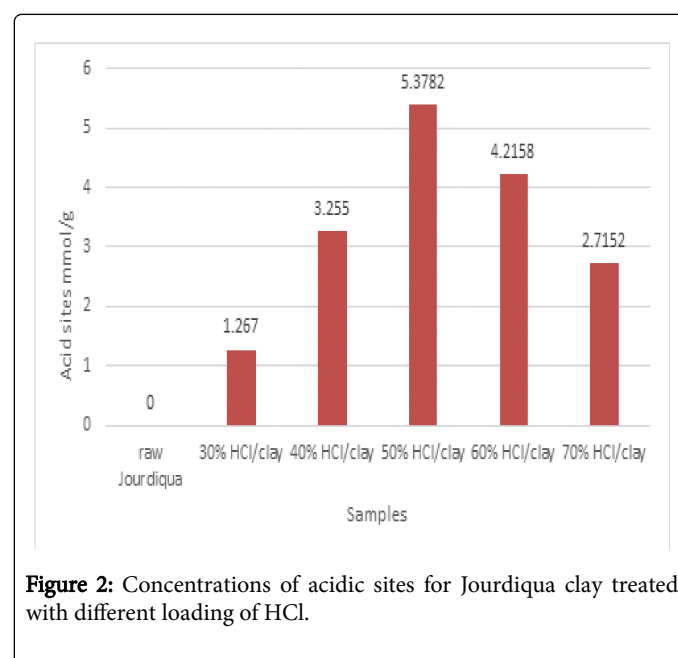


Figure 2: Concentrations of acidic sites for Jourdiqqa clay treated with different loading of HCl.

Temperature programmed desorption (NH₃-tpd)

Acid sites measurements were carried out via thermal programmed desorption (TPD) of NH₃. In the temperature ranged from 50°C to 800°C, using nitrogen as the carrier gas. The strength distribution of the acid was estimated by TPD pattern deconvolution. Two catalysts,

30% HCl/clay and 50% HCl/clay were used for TPD technique to reveal the amount and strength of acidic sites in the catalysts. The profile for the two catalysts is shown in Figure 3. It was observed that 30% HCl/clay in (red) has three peaks for acidic distribution; the first peak is at 93.7°C, which is considered to be weak site with a value of 0.4576 mmol/g. The second peak is at 660.3°C, which is classified as strong site with value of 0.6677 mmol/g. Third peak appeared at 793.4°C and it is considered to be strong site with a value of 0.1416 mmol/g. The total acidity of the catalyst is the sum of the three sites concentration which is 1.2670 mmol/g.

50% HCl/clay in (black), illustrate four characteristic peaks. First peak being at 612.4°C, which is strong acidic site with value of 2.8433 mmol/g. Second peak appeared at 700.7°C, which is also considered as strong site with value of 2.3653 mmol/g. The third peak appeared at 784.6°C, which is a strong site with a value of 0.11567 mmol/g. while the last peak appeared at 794.8°C with a value of 0.05382 mmol/g that is a strong site. The 50% HCl/clay catalyst has a total acidity of 5.3782 mmol/g. This result reconfirms the back titration analysis.

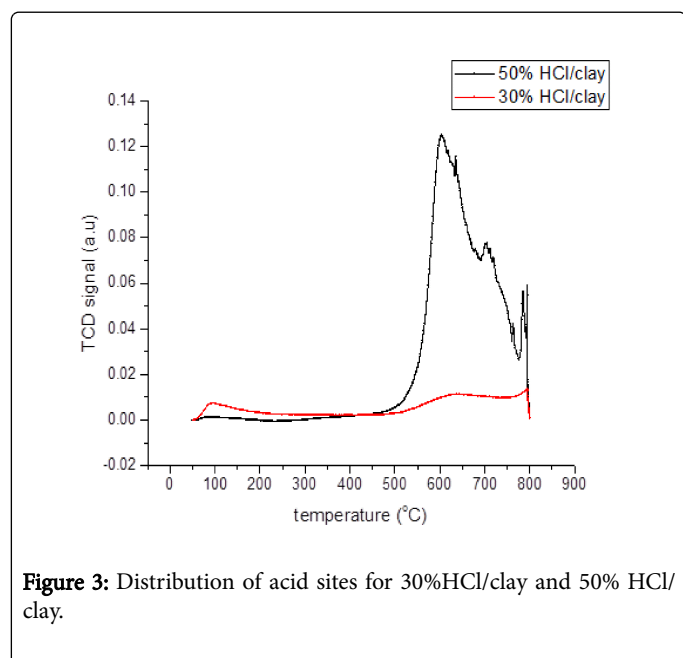


Figure 3: Distribution of acid sites for 30%HCl/clay and 50% HCl/clay.

Field emission scanning electron microscopy (FESEM)

The morphology and approximate particle size of the samples were examined using FESEM analysis. Figure 4 shows FESEM images at magnification of 10000 times of raw Jourdiqia clay and 50% HCl/Clay respectively. It can be observed from the micrograph that raw Jourdiqia clays shows a flaky particles shape which is the characteristic of montmorillonite clay with particle size ranging from 0.5 μm to 5.00 μm [6]. After the modification of Jourdiqia clay with 50% HCl, the morphology of the clay changed from larger layers to fragments pieces. Acid modified clays are arranged in needle like shape with particles sizes of 50 nm to 100 nm in width and of 0.25 μm to 1.00 μm in length. EDX analysis indicates the reduction percentage of some cations in the clay due to their elimination by the acid. EDX elemental analysis of raw Jourdiqia clay and 50% HCl/Clay are shown in Table 1. It shows that raw Jourdiqia clay contains many cations such as Na, K, Ca, Fe and Mg. While 50% HCl/Clay shows that base treatment, reduce some of the cations.

Element	Mass %	
	Raw Jourdiqia	50% HCl/Clay
Silicon	6.03	69.5
Aluminium	1.95	13.8
Magnesium	0.988	1.52
Barium	0.599	0.046
Strontium	0.143	0.043
Potassium	4.98	2.09
Sodium	40.5	2.09
Calcium	17.4	2.88
Titanium	4.63	2.22
Chromium	0.154	0.026
Manganese	0.394	0.072
Ferum	20.5	5.25
Cobalt	0.136	0.037
Zinc	0.038	0.007
Lead	0.036	0.003
Copper	0.003	0.003

Table 1: XRF analysis of raw Jourdiqia and 50% HCl/Clay.

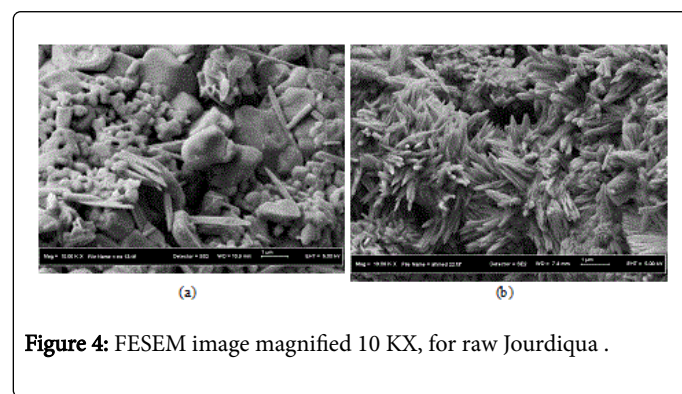


Figure 4: FESEM image magnified 10 KX, for raw Jourdiqia .

X-ray fluorescence (XRF) analysis

This technique was used to determine the elemental analysis of raw and modified 50% HCl/clay. The results are shown in Table 1. Raw Jourdiqia clay has a higher amount of silica (6.030%) compared to alumina (1.950%) and the ratio of silica to alumina SiO₂/Al₂O₃ is greater than unity which make it suitable for zeolites synthesis [7]. Other cations present in the raw Jourdiqia clay can be replaced by ion exchange process with desired cations leading to higher catalytic activity. Modified 50% HCl/clay resulted in increase in Si and Al percentage with respect to other cations from 6.03% to 69.5% and 1.9% to 13.8%, respectively. Other cations decreased, because of the removal from the exchangeable sites of the clay [8].

X-ray diffraction (XRD) analysis

X-ray diffractogram of raw Jourdiqia clay and that modified 50% HCl/clay are illustrated in Figures 5, 6 respectively. It is found that raw Jourdiqia clay shows peaks at 2θ of 21.00 (4.12Å), 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. This indicates the presence of montmorillonite, (JCPDS, pdf card No, 00-154-5943). The peaks at 2θ values of 20.00 (4.20 Å), 26.66 (3.33 Å) and 36.50 (2.475 Å) corresponds to the planes of [1 1 1], [1 2 0] and [1 1 2] respectively. This indicates the presence of muscovite, (JCPDS, pdf card No, 00-010-4986). While peaks at 2θ of 26.66 (3.34 Å), 50.00 (1.816 Å), and 60.00 (1.514 Å), corresponding to the planes of 0 0 6, 1 1 2 and 2 1 1, indicating the presence of quartz, (JCPDS, pdf, card No, 00-210-3487). The main clay minerals in Jourdiqia clay are montmorillonite, muscovite and quartz [9].

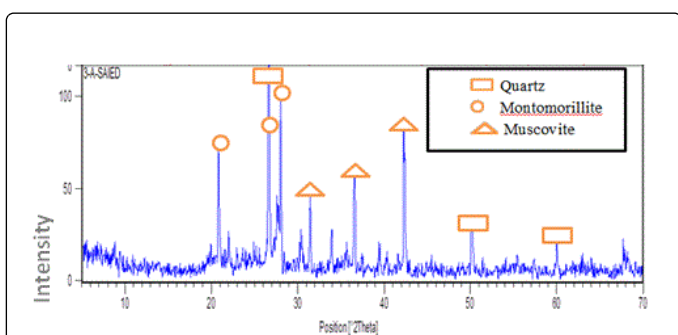


Figure 5: XRD spectrum of raw Jourdiqia clay.

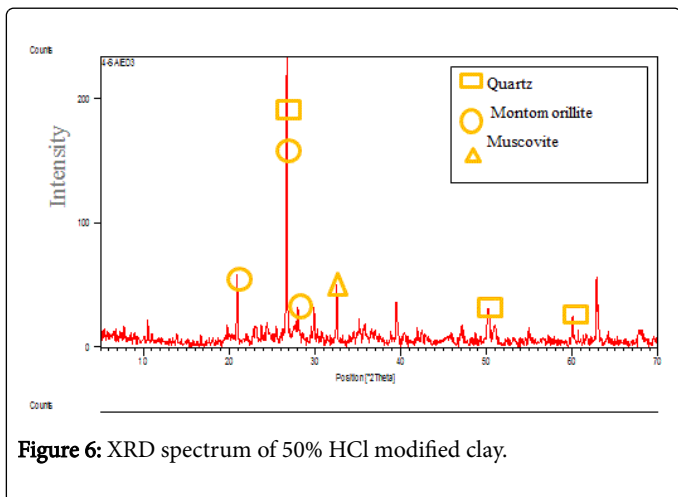


Figure 6: XRD spectrum of 50% HCl modified clay.

After acid modification under the optimum conditions, XRD spectrum of 50% HCl modified clay shows decreasing in intensity for the peaks at 2θ of 21.00 (4.12Å), plane of 1 1 0, and at 2θ of 28.22 (d) spacing of (3.19Å) plane of 1 1 1, which were related to montmorillonite mineral. This is due to the removal of octahedral sheet cation, and further leaching of acid and heat leading to the decrease in mineral crystallinity. The peaks of muscovite at 2θ of 20.00°, and 36.50° relate the planes, of 1 1 1 and 2 1 1 show greater decrease in intensities. While the peak at 2θ 26.66° related to plane of 6 0 0 which belong to the quartz mineral shows considerable increase intensity. Other peaks show decrease in their intensities due to the removal of cations from octahedral sheets, resulted from the effect of acid.

Nitrogen adsorption analysis

The porosities of raw Jourdiqia clay and acid modified clay were determined by nitrogen adsorption/desorption analysis of BET adsorption measurements. From the nitrogen adsorption/desorption isotherm of raw Jourdiqia and 50% HCl/clay that are, shown in Figure 7. Both catalysts exhibit type IV isotherm, which was related to mesoporous pore and this is confirmed by determination of pore diameter from BET analysis as is shown in Table 2. The two catalysts follow H3 hysteresis loop which is characterized by, unlimited adsorption at high relative pressure of P/Po. [10].

Parameters	Raw Jourdiqia clay	50% HCl/acid
BET surface area (m2/g)	4.5835	59.87
BET surface area of pores (m2/g)	5.833	2.893
t-plot external surface area (m2/g)	3.8414	56.967
Pore volume cm3/g	0.0337	0.13842
BET average diameter Å	335.5	92.481
BJH average diameter desorption Å	199.37	88.618

Table 2: Textural properties of raw Jourdiqia clay and 50% HCl/clay.

After acid modification, increase in both surface area and pores volume was observed, due to the removal of silica and alumina caused by the acid. The two catalysts have complex pore structure, formed from interconnected networks of pores with different sizes and shapes, which are common to many inorganic oxides gels, zeolites and clays, normally indicates the presence of mesoporous with ink-bottle pores [11].

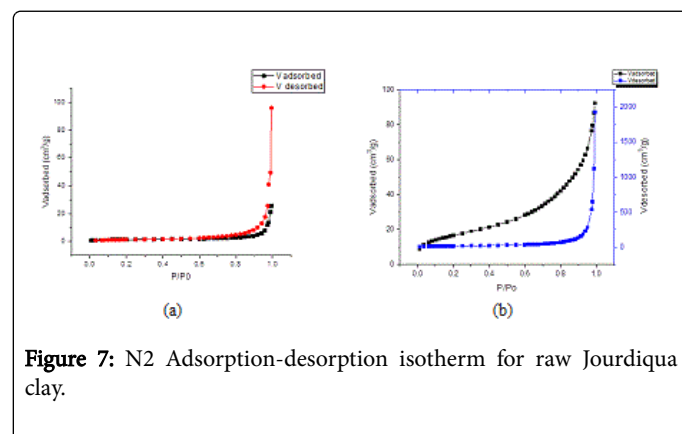


Figure 7: N2 Adsorption-desorption isotherm for raw Jourdiqia clay.

Biodiesel production

Biodiesel was prepared in transesterification reaction of castor oil with methanol using raw Jourdiqia clay and acid modified Jourdiqia clay as heterogeneous catalysts. Figure 8 summarize the percentage conversion of transesterification reaction between castor oil and methanol in the presence of heterogeneous raw and acid modified Jourdiqia clay [12]. Raw Jourdiqia clay has a pH value of 11.30, indicating that the clay is basic. Transesterification reaction using raw Jourdiqia clay gave a conversion of 64.99%. Jourdiqia clay modified by HCl with different percentage of acid to clay at 30%, 40%, 50%, 60% and 70% concentration resulted in ion exchange process between

protons of HCl and cations present in exchangeable region between the clay layers. As the acid concentration increases, the conversion of oil to biodiesel increased, the biodiesel conversion was found to be as follows: 17.94%, 57.86%, 83.86%, 64.93% and 29.34% conversion for 30%, 40%, 50%, 60% and 70%, respectively.

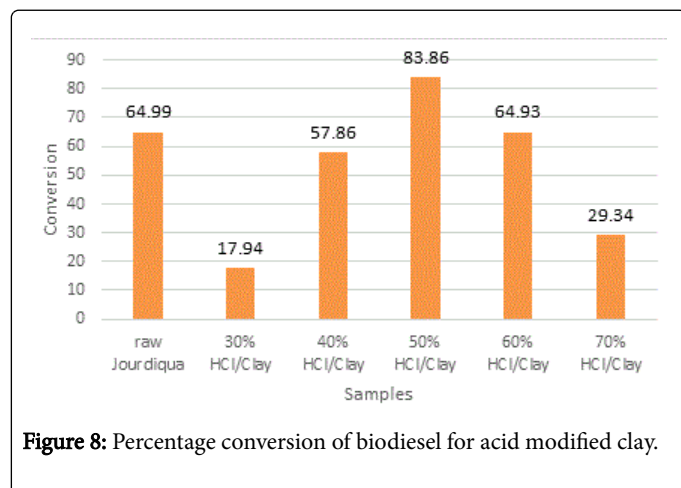


Figure 8: Percentage conversion of biodiesel for acid modified clay.

This is due to the increase of the catalytic activity in the modified clay. However, further increase of acid in the modified clay result in lower conversion yield. Beyond 50% concentration of HCl, the conversion decreased to 64.93% and 29.34% for 60% HCl/Clay and 70% HCl/Clay respectively. This is due to the formation of silanol groups between clay layers, and decreasing of catalytic activity [5].

Conclusion

The prepared acid modified Jourdiqia clay was identified and could be an effective and potential heterogeneous acid catalyst in transesterification of castor oil to biodiesel. The effect of structure and modification of the clay by acid were evaluated on the conversion of oil to biodiesel. Transesterification process showed a promising conversion yield due to the improvement of the clay catalytic activity after the modification with acids. The percentage conversion of biodiesel for 30% HCl/Clay, 40% HCl/Clay, 50% HCl/Clay, 60% HCl/Clay and 70% HCl/Clay were 17.94%, 57.86%, 83.86%, 64.93%, and 29.34% respectively. Highest percentage conversion was obtained from 50% HCl/Clay. This showed that, the conversion of methyl ester in biodiesel depends on the concentration and the strength of the acid catalytic sites of the prepared modified clay. However, higher percentage loading of HCl will eventually decreased the conversion

yield. Thus, the optimum concentration of HCl for the clay modification is 50% HCl/Clay.

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