

Triple Mixed Oxides Modified Jourdiqua Clay in Heterogeneous Methanolysis of Castor Oil

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ABSTRACT: Biodiesel is the fatty acid methyl esters, an alternative to fossil fuels, the strongest factor concern about global pollutant. Clays have very promising future in catalysis, such as esterification and transesterification reactions. In this study clay called Jourdiqua was brought from Sudan, and was modified by triple mixed oxides of MgO, BaO, and SrO, using their nitrates, by impregnation methods and calcined at 500°C for 5 hours. The modified clay was used as catalyst in transesterification reaction of castor oil with methanol. Magnesium nitrate, calcium nitrate, barium nitrate and strontium nitrate from Aldrich company, methanol analytical grade, purity > 99%, potassium hydroxide and hydrochloric acid 37% (w/w) with purity > 99% from Sigma company were brought. Jourdiqua clay was dried in oven at 90°C overnight and then ground, and sieved with mesh scale of 200, and kept in bottle sample. Jourdiqua clay was impregnated with triple mixed oxides of MgO, BaO and SrO, in ratio of 50% of oxides to clay, and atomic ratio of (1:1:1) for Mg: Ba: Sr, in order to improve the catalytic activity of the clay. The raw and modified clay were characterized by Thermogravimetric (TGA-DTG), Brunauer-Emmett-Teller (BET) for the textural properties of the catalysts, Inductively Coupled Plasma Emission Spectroscopy, (ICP-ES), Atomic Absorbance Spectroscopy (AAS), for the elemental analysis, X-Ray diffraction (XRD), Fourier Transform Infrared (FTIR), Field Emission Scanning Electron Spectroscopy (FESEM), basicity test (back titration), and Temperature Programmed Desorption of CO₂ (TPD-CO₂). Transesterification reaction was conducted using castor oil with ratio of methanol to oil of 27:1, for 3 hours, temperature of 65°C, and catalyst loading of 9%. The product was separated and analyzed with GC-FID, and ¹HNMR techniques. The result from BET showed that, there was a little increase in specific surface area after modification from 9.67 to 10.00 m²/g. Elemental analysis by ICP-ES, showed increase content in the elements that, their oxides were impregnated with clay, Mg Ba and Sr, increase in Na, Al was observed, Si, Ca and K were decreased, decreased in Si may be due to the replacing by Ba and Sr, Ca, decrease in other cations may be due to replacing, by Mg, Ba, and Sr cations. TPD-CO₂ showed three catalytic basic sites with total concentrations of 0.7222 mmole/g, GC-FID analysis showed that, the main esters present in biodiesel from castor oil, are methyl ricinoleate with content of 89.12, methyl linoleate 4.11, methyl oleate 3.44, methyl stearate 1.1 and methyl palmitate with content of 0.86%, ¹HNMR technique revealed that the conversion of castor oil to biodiesel using triple mixed oxides of MgO, BaO, SrO modified Jourdiqua clay was 96.59%. Clay, Zeolites, and other aluminosilicate, were intensively, developed in production of biodiesel, as the catalysts. In this study, clay with concentrations of basic sites of 0.6645 mmole had used in transesterification process, and it was achieved conversion of oil to biodiesel of 64.99% as a raw. After modification, with triple mixed oxides of Mg, Ba, and Sr, the basic sites concentrations was increased to 0.7222 mmole/g, achieved conversion of 96.59%. It was observed that basic modification by these triple mixed oxides, have improved tremendously the catalytic capability of the raw clay, while no significance leaching was found after four consecutive cycles of reactions.

Keywords: Biodiesel; Transesterification; Modification; Catalyst; Jourdiqua Clay.

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I. 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) [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, 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 [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 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% [3] Clay minerals can be more catalytic active if it is modified with suitable modifier. The modification of the clay improves its catalytic activity. The aim of this study is to produce biodiesel from vegetable oil (castor oil) using triple mixed oxides that had incorporated into clay layers. The incorporation of triple mixed oxides into the clay layers, will increase the catalytic activity of the clay more than the incorporation of single or double mixed oxides into the clay layers [4]. In this work triple mixed oxides of MgO, BaO, and SrO were inserted into the clay layers, the inclusion of oxides was conducted by wet impregnation method using nitrates of these oxides.

II. MATERIALS AND METHODS

2.1 Materials

The starting clay samples are natural Sudanese clays; Jourdiqia, from north of Sudan (Suba). Castor oil was purchased from Johor Bahru. Magnesium nitrate, barium nitrate, strontium nitrate from sigma company, analytical grade, 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.

2.2 Preparation of the Clay

The clay sample was 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 bottle [5].

2.3 Modification of Clay

50 grams of the raw clay was transferred to 500mL beaker, desired weights of magnesium, barium and strontium nitrates, were added in atomic ratio of (1:1:1) for Mg:Ba: Sr. 200mL of deionized water was added to the beaker, the mixture was transferred to 500mL round bottom flask equipped with reflux condenser, with magnetic stirring ratio of 300rpm at 90°C for 3 hours, then cooled to room temperature, then filtered and washed with distilled water. Then dried in an oven at 90 °C overnight and calcined at 500°C for 5 hours cooled in desiccator and kept in sample bottle.

2.4 Characterization of Clays

The ICP-ES and AAS analyses were 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-K α radiation (40 kV, 40 mA, $\lambda = 1.5406\text{\AA}$) (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) (SupraTM 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 Micrometrics Pulse ChemiSorb 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 10⁻²Torr 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. For TPD-CO₂ technique, the analysis was performed in micrometrics Autochem 2920 Chemisorption analyser. Probe

molecule of CO₂ was used in temperature programmed desorption technique (TPD-CO₂) to determine the base sites density and sites strength of solid catalyst.

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 GC-FID and ¹HNMR technique.[6]

III. RESULTS AND DISCUSSION

3.1 Thermal Gravimetric Analysis-Differential Thermal Gravimetry (TGA-DTG)

Figure 1 depicts the TGA-DTG curve. For the raw clay, the first weight loss was around 60 °C, due to the evaporation of adsorbed water molecules on the clay surface. The loss at this temperature was about 8%. The second weight loss was around 275 °C of around 6.32%, which may be due the evaporation of carbonate, bicarbonate and other volatile species. The third loss was around 750 °C of about 4.7%, this may be due the loss of volatile species and hydroxide structures, present between clay layers the total loss for the raw clay was 18.52%[7].

The triple mixed oxides catalyst of 50%(1:1:1) MgO-BaO-SrO/Clay, shows the first loss at about 60°C for evaporation of adsorbed water molecules on clay surface, the loss was represented 2.0% of the sample weight, the second loss was about 100°C due to evaporation of adsorbed interlayer water molecules from the clay and it represented 2.7% of the sample weight, the third loss was at about 900°C, due to dehydroxylation of hydroxyls groups of clay structure and liberation of remaining carbonates and bicarbonates, the loss was 2.4% of the sample weight the total loss in weight for the modified clay was 7.10%. It was observed that from the profile temperature of the both catalysts, the weight loss at temperatures higher than 500°C, not exceed than 5% of the samples weight, indicating that these catalysts were stable and suitable for transesterification reaction.[8].

From the result in table 1 below, it can be seen that raw Jourdiqua, 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 raw 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 oxides modified clay has low value of ignition loss of about 4.50%, which make it suitable to be regarded as refractory clay. The high pH value of the raw clay of 11.13 can be attributed to its high basicity. This may be due to the high percentage of metal carbonate and bicarbonates in the sample that hydrolyzed to form basic solution[9]. The combustible volatile matter content of the raw clay was high as evidence from the high ash content, while it was low for the oxides modified clay. The five physical parameters determined for the two clays are listed in Table 1

3.2 Elemental Analysis

The chemical compositions of the two catalysts were determined using (ICP-ES) and atomic absorption spectroscopy (AAS), 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 (SiO₂:Al₂O₃) in the raw clay is greater than unity, making it suitable for zeolite synthesis, while the other that oxides modified does not. The high sodium content for the both catalysts may be due to the high percentage of carbonate and bicarbonates, as well as from the high weight loss due to the liberation of carbonate in the TGA result. This makes the raw Jourdiqua clay suitable as traditional medicine for stomach ache especially in Sudan. Also the high sodium content make it suitable as an ion exchanger, for purification of water. Other oxides present in both clays make them suitable for ion exchange process. After triple mixed oxides treatment, it was observed increase of Al, while there was decrease in Si, due to the replacing by elements, of Mg, Ba and Sr, which were observed high increasing in the modified clay, while other cations were observed decreasing, due to the ion exchange process.

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

Figure 2 (a) and (b) shows the spectra for the raw and triple mixed oxides modified clay, respectively. Table 3 shows the observed for the raw and modified clay cations. [10].

After modification of the raw clay by insertion of the triple oxides of MgO, BaO and SrO, it was observed from the FTIR spectra of modified clay, the peak around 1002 cm⁻¹ was increased in its intensity,

confirming the insertion of the oxides into the clay layers, the rest of the peaks were shifted to the higher frequencies (blue shift)

3.4 X-rays Diffraction analysis (XRD)

Figure 3 (a), shows the diffractogram of raw Jourdiqua clay, 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 montmorillonite pdf 00-154-5943[8]. The peaks at 2θ values, of 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, pdf 00-101-4986, while peaks at 2θ of 26.66 (3.34 Å), 50.00, (1.816 Å), and 60.00 (1.514 Å), corresponding to, 0 0 6, 1 1 2 and 2 1 1 planes respectively pdf 00-210-4387, designating the presence of quartz. The main clay minerals in raw Jourdiqua clay are therefore Quartz, muscovite and montmorillonite[11]. When the raw clay was impregnated with the solution of three nitrates of magnesium, barium and strontium and calcined at 600°C for 5 hours, to insert the triple mixed oxides of Mg, BaO and SrO into the clay layers, it was observed that the clay had lost its crystallinity and became amorphous due to the effect of heat. As it was shown in Figure 3.(b)[12]

3.5 Basicity Test (Back Titration)

Basicity test was carried out before and after modification to measure the catalytic activity of the two catalysts. The basicity of the two catalysts were determined using back titration for the raw clay and modified clay and it was found that the catalysts have basicity of 0.6645 and 0.7685 mmole/g respectively. [13]

3.6 Temperature Programmed Desorption (TPD-CO₂)

Triple mixed oxides modified clay, was analyzed by Temperature Programmed Desorption for CO₂, (TPD-CO₂) in order to determine the basicity and distribution of basic sites of the catalyst, and it was observed that, this catalyst had three characteristics peaks, the first peak is at 89.9°C (weak site), the second at 578.4°C (strong site), the third at 627.3°C (strong site), with total basicity of 0.7222 mmole/g, as it was shown in the figure 4, and table 5.

3.7 Textural Properties of the Catalysts

The raw Jourdiqua clay catalyst has surface area of 9.6744 m²/g, and pore volume of 0.0337 cm³/g, with average pore diameter of 199.37 Å, while the oxides modified one has surface area, of 11.8681 m²/g, the increase in surface area was due to insertion of oxides into the clay layers, and it has pore volume of 0.0297 cm³/g, the decrease in pore volume was, due to the deposition of oxides into the pore wall of the clay[14], and it has average pore diameter of 170.85 Å, which was less than that of the raw clay due to the deposition of oxides into the wall pore of the clay[15], the two catalysts follow type IV in classification of IUPAC for the mesoporous materials, the two catalysts have hysteresis loop type H3, which is characterized by unlimited desorption at high relative pressure p/po [16], as it was shown in figure 5 (a) and (b) respectively

3.8 Field Emission Scanning Electron Microscopy (FESEM)

Figure 6, shows FESEM image of raw Jourdiqua clay, magnified 10KX times, it was observed that its micrograph shows flaky particles shape, which is characteristic of montmorillonite clay mineral[17], with size range of 0.5-5.00 μm, the clay contains many cations, such as, Na, K, Ca, Fe and Mg, which make it capable for ion exchange processes, as it was shown in figure 6. Figure 7, shows the FESEM image of the clay, that magnified 10KX times, for the catalyst of 50% (1:1:1) MgO-BaO-SrO/Clay, it was observed that from the figure, the particles of the triple oxides were dispersed on and beside the clay particles in fibers shape like, at nano size. 200-700 nm

3.9 Gas Chromatography- Flame Ionization Detector (GC-FID) Analysis

The GC-FID GC analysis was carried out with GC-FID model 5890N equipped with column SP 2560 from Sigma Aldrich. Analysis in this study was mainly carried out to confirm the conversion of oil to biodiesel and the presence of the different methyl ester present in biodiesel from castor oil qualitatively. The most predominant methyl esters observed are 1- Methyl Ricinoleate, 89.12% 2- Methyl linoleate, 4.11% 3-Methyl oleate, 3.44% 4-Methyl stearate, 1.1% 5- Methyl palmitate, 0.86% 6-Methyl Eruciate, 0.73% 7-Methyl Eicosadinoate 0.62%. Figure 8, show GC-FID spectrum of 96.59% biodiesel as calculated from ¹H NMR, as, Table 6 reveals the percentages of esters present in biodiesel from castor oil.

3.10 Hydrogen Nuclear Magnetic Resonance (¹H NMR) Analysis

The product of biodiesel from transesterification of castor oil with methanol was analyzed by ^1H NMR technique, from Bruker analysis 400, the raw Jourduqua clay was achieved conversion of oil to biodiesel of 64.99%, while that produced from triple mixed oxides modified clay was 96.59%, as it was shown in figure

3.10 Catalyst Reusability

The catalyst of 50%(1:1:1) MgO-BaO-SrO/Clay was evaluated, for reusability, the catalyst was used in transesterification, for four consecutive cycles of reaction, and the result of the conversion was found as follows: 96.59%, 94.62%, 92.11%, and 90.50%, respectively, so no significance drop in conversion after four consecutive cycles of reaction, which concluded from that, the catalyst was very stable. Figure 11, shows the reusability of 50%(1:1:1) MgO-BaO-SrO/Clay [18]

3.11 Conclusion

From the results of characterization of the two catalysts, it was found that, the main minerals in the raw clay were identified, montmorillonite, muscovite and quartz, while for the triple mixed oxides modified clay, in addition of these minerals, barium oxide, magnesium oxide, and strontium oxide were present. And this was confirmed by ICP-ES and FTIR analyses. The result further revealed that the raw clay is rich in sodium and iron, while oxides modified one is rich in barium, magnesium and strontium due to the incorporation of oxides of these metals into the clay, and so increased its catalytic activity, which resulted in high biodiesel yield after modification of 96.59%, while the raw one gave 64.99%.

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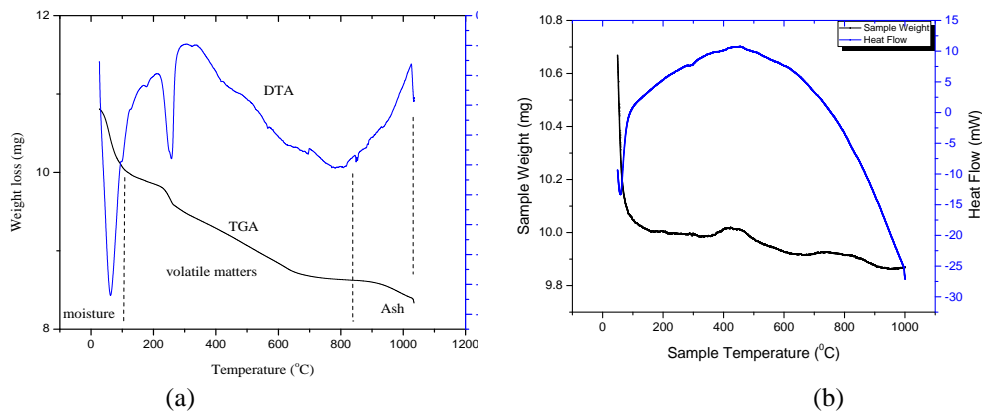


Figure 1: Thermogram (TGA-DTG), (a) raw, (b) triple mixed oxides modified clay samples

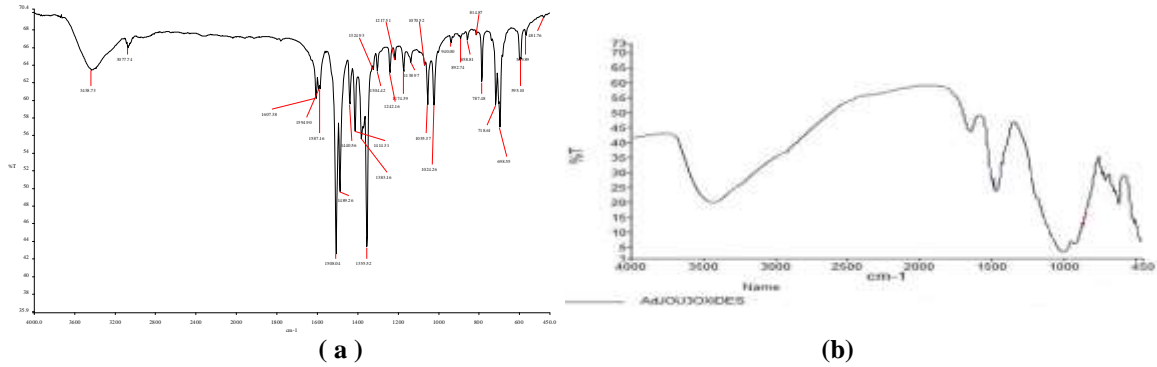


Figure 2 (a): FTIR spectrum of the raw Jourdiqqa Clay Figure 2 (b): FTIR spectrum of triple mixed oxides Modified Jourdiqqa Clay.

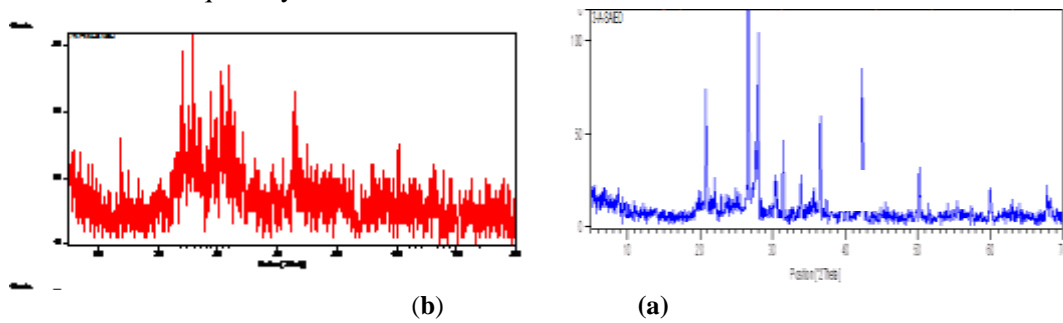


Figure 3: XRD diffractograms of(a) unmodified and (b) triple mixed oxides modified Jourdiqqa Clay,

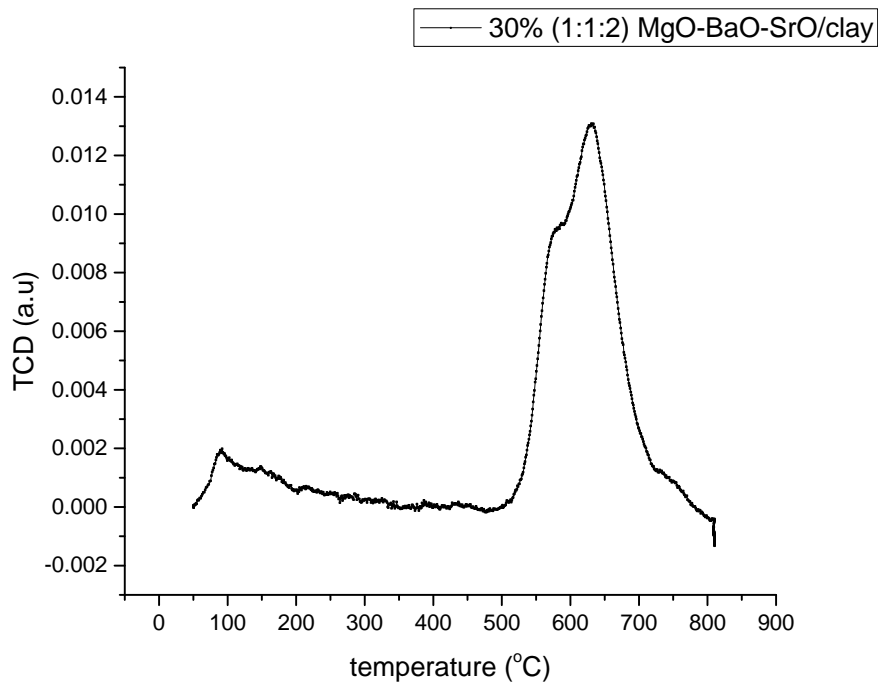


Figure 4: TPD-CO₂ spectrum for triple mixed oxides modified Jourdiqqa clay

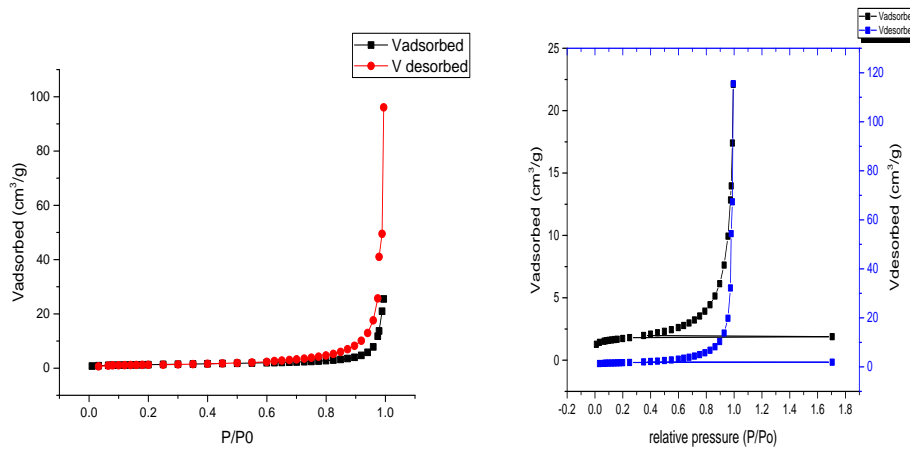


Figure 5(a) : N₂ Adsorption-Desorption isotherm for Jourdiqqa Clay
 Figure 5(b): N₂ Adsorption-Desorption for triple mixed oxides Modified Jourdiqqa Clay

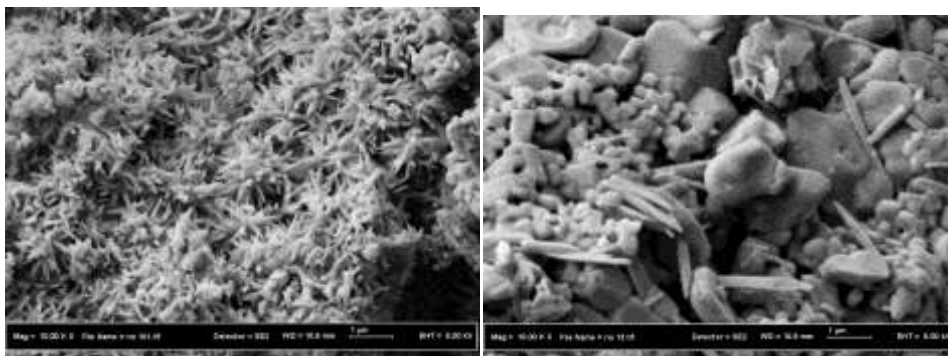


Fig 6: FESEM image magnified 10KX for Raw Jourdiqqa Clay
 Figure 7: FESEM image, magnified 10KX

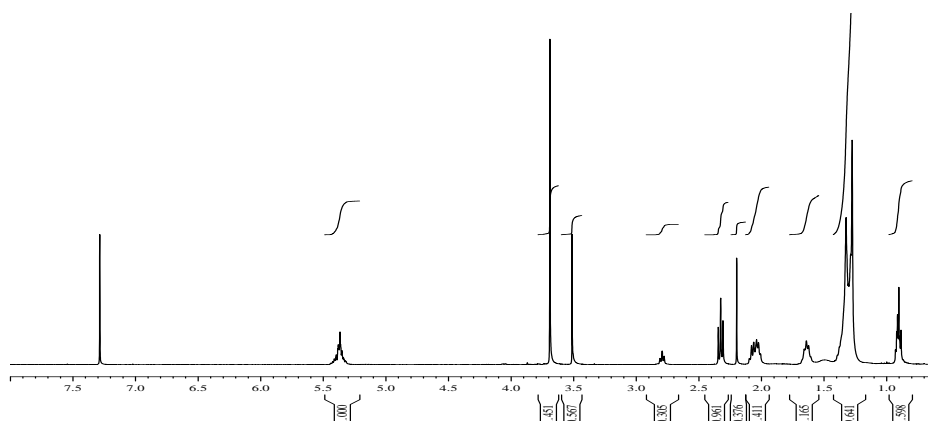


Figure 10: ¹H NMR spectrum of biodiesel from castor oil in CDCl₃, catalyzed by triple mixed oxides modified Jourdiqqa clay, conversion 96.59%

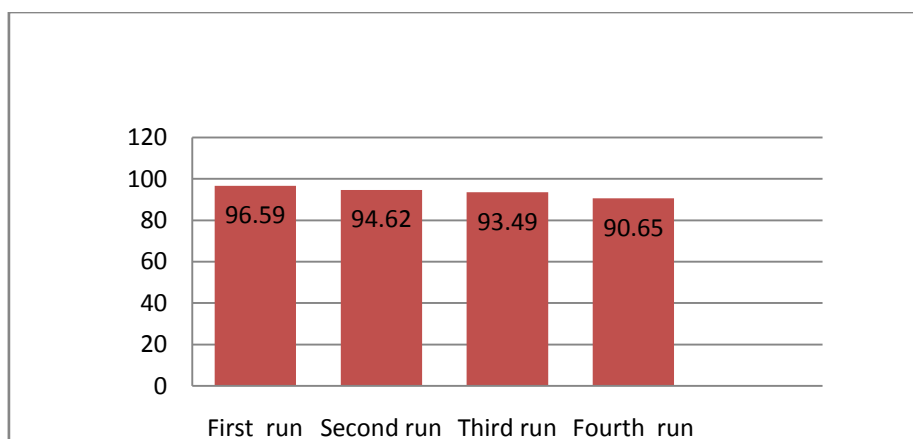


Figure 11: Reusability of 50%(1:1:1)MgO-BaO-SrO/Clay in biodiesel conversion

Table 1 Physical characterization for the clay samples

Clay content (%)	pH	Moisture (%)	Loss on Ignition (%)	Ash
Oxides modified	10.50	8.00	4.50	4.32
Raw Jourdiqqa clay	11.30	16.00	18.72	11.62

Table II. Elemental analysis for the raw and 50%(1:1:1) MgO-BaO-SrO/Clay catalysts, by(ICP-OES) and (AAS)

Elements	Raw clay (%)	50%(1:1:1) gO-BaO-SrO/Clay (%)
Si	6.03	0.25
Al	1.94	2.88
Ba	0.59	14.80
Mg	0.98	9.29
Li	0.20	1.02
Fe	20.50	3.19
Rb	0.06	00.30
Ga	0.04	0.14
As	0.02	0.22
Pb	0.04	0.01
Sr	0.14	21.00
Cs	0.01	0.00
Zn	0.01	0.04
Se	0.01	0.01
Ni	0.01	0.01
Cu	0.01	0.01

Ca	17.40	1.22
Na	40.50	46.80
K	10.20	2.01

Table III: Observed bands for the raw and mixed oxides modified clay catalysts

Raw Clay, Wave number (cm ⁻¹)	Mixed oxides modified	Assignment
3438.73	3437.73	Stretching vibration of OH of water, not effected after modification
1607.74	1637.5	OH deformation of water , shifted to the higher wave number, after modification.
1440.56	1460.65	Stretching of M-O, M= Fe, Al, Mg, Ba, Sr,Traces , shifted to the higher wavenumber after modification
1174.39	1174.54	Si-O stretching. not effected by modification
1024.26	1024.26	Si-O stretching., not effected by modification
984.00	1002.50	Stretching of M-O, M= Mg, Ba, and Sr, increase intensity shifted to higher wavenumber
940.00	998.76	Al-Al-OH, deformation, shifted to the higher wave number
892.74	906.67	Traces of carbonate, shifted to the higher wave number
858.81	858.81	Al-O deformation, not effected
787.48	787.48	Al-O-Si deformation , not affected by modification
698.55	698.50	Si-O stretching, not effected
481.76	481.76	Si-O-Si deformation, not affected by modification

Table IV Summary of XRD data for raw and triple mixed oxides modified Jourdiqua Clay

Catalyst Name	Minerals present	2θ	d-spacing in Å	Particle size in nm
Raw Jourdiqua Clay	Montmorillonite			
Muscovite				
Quartz		21.00		
		20.01		
		26.66	4.12	
		4.20		
		3.33	837.50	
		177.54		
		158.40		
50%(1:1:1) MgO-BaO-SrO/Clay	It had been lost its crystallinity and became amorphous			

Table V.: Basic Sites Distribution for 50% (1:1:1) MgO-BaO-SrO/clay

Catalyst	Peak(1)	Peak(2)	Peak(3)	Total basicity
50%(1:1:1)MgO-BaO-SrO/Clay		89.9 °C	0.1666mmole.g	
(Weak site)	578 ^C			
(strong site)				
0.1755 mmole/g	627.3			
0.3799, mmole /g				
(strong site)	0.7221			

Table VI. :Esters Contained in biodiesel From Castor Oil

Name of the ester	Percentage%
Methyl Ricinolate	89.12
Methyl Linoleate	04.11
Methyl Oleate	3.44
Methyl Stearate	1.10
Methyl Palmitate	0.86
Methyl Eruciate	0.73

Methyl Eicosadinoate

0.62

Table VII.: ¹HNMR 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 methylene back bone
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

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