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# Biodiesel synthesis from oleic acid by Nano-catalyst ($ZrO_2/Al_2O_3$) under high voltage conditions

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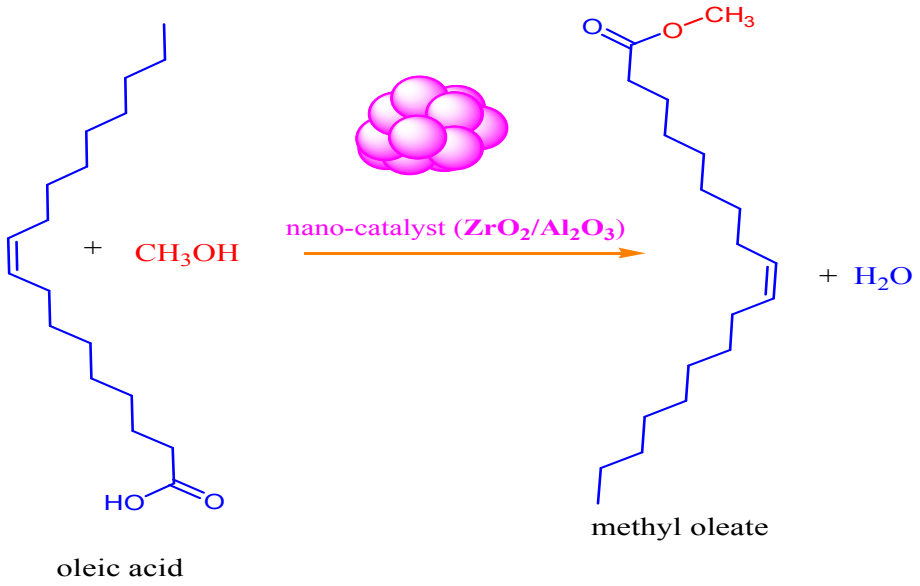
This paper describes synthesis and catalytic activity of $ZrO_2/Al_2O_3$ nano-catalyst as a highly effective heterogeneous and active catalyst that converts oleic acid and methanol into fatty acid esters under high voltage conditions in a low temperature and atmospheric pressure process. Using an inexpensive and reusable catalyst, excellent yields in short time and environmental benignity are some of the important features of this protocol. In the final, results were confirmed by GC, FTIR, FESEM and XRD.

## 1. Introduction

Due to the potential shortage of non-renewable resources with their high cost and their impact on global pollution, the investigates for finding the alternative resources of energy have been created much attentions. Therefore, seeking efficient and simple methods for synthesis of high quality biodiesel is an attractive scientific challenge. Biodiesel has emerged as a non-toxic and biodegradable fuel to replace traditional diesel fuel[1-5]. Biodiesel is a clean burning fuel when derived from plant or alga oils or animal fats[6-8]. Each biodiesel product has a different composition and purity, and may require different engine setting for optimum performance. Biodiesel is currently synthesized *via* esterificative reaction of long-chain fatty acids with alcohols. Synthesis of biodiesel has been reported in the presence of various catalysts and conditions[9-15]. Synthesis of biodiesel should be flexible, facile, rapid and useful from cost-effectiveness and industrial point of view. Since the lower catalytic activity of liquid or solid acids compared with base catalysts, most of the acid-catalyzed esterificative reactions generally accomplish under high temperature and high pressure conditions. In the other hand, the use of base catalysts are limited, to use of refined vegetable oils, leading to impracticable and uneconomical methods, due to high cost feed stocks. The free fatty acids (FFA) existing in the feed stock react with the base catalyst and form soap and decrease the ester yields. Solid acid catalysts have attracted considerable attention in recent years owing to less sensitive to FFA contamination[16-18]. Heterogeneous solid acids and especially those based on $Al_2O_3$ and $ZrO_2$ has been explored as powerful catalysts for various organic transformations. In comparison to conventional catalysts, nano-catalysts matrixes have higher activities because of their very extensive surface areas[19-22]. We wish to report here in a highly efficient procedure for the esterification of oleic acid using solid acid nano-catalyst ($ZrO_2/Al_2O_3$) as an efficient and robust catalyst under high voltage conditions (Scheme 1).




Scheme 1. Esterification of oleic acid using $ZrO_2/Al_2O_3$ nano-catalyst

## 2. Results and discussion

The catalyst was prepared by sol-gel procedure using aluminium nitrate and zirconium oxychloride. The morphology and particle size of $ZrO_2/Al_2O_3$ nano-powder was investigated by FESEM as shown in Fig. 1. The particle size and surface area of the white powder were estimated by FESEM and BET measurements to be 20.59-29.86 nm and 253-283 $m^2g^{-1}$, respectively. The XRD pattern for $ZrO_2/Al_2O_3$ nano-powder is shown in Fig. 2. The XRD pattern for the catalyst exhibited two sharp diffraction peaks at 2θ angles of 29-32° and 49-52°, which were attributed to tetragonal phase $ZrO_2$. Two broad and weak diffraction peaks at 44-49° and 66-68°, were attributed to α-$Al_2O_3$ phase. Fig. 3 shows a FTIR spectrum of $ZrO_2/Al_2O_3$ nano-catalyst. The bands at 872 and 618$cm^{-1}$ were assigned to Al–O and Zr-O stretching and bending modes. Based on XRF analysis the weight ratio of $ZrO_2$ to $Al_2O_3$ was 20:80.

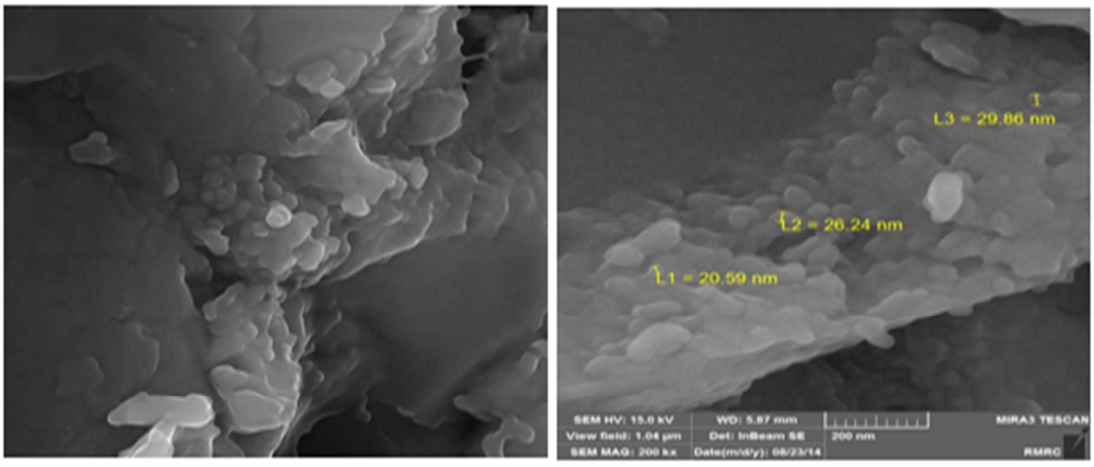



Figure 1. FESEM image of $ZrO_2/Al_2O_3$ nano-catalyst

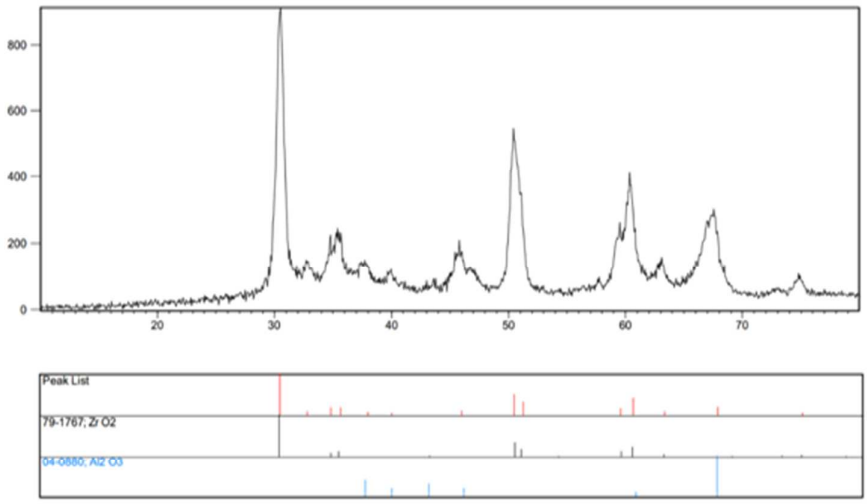



Figure 2. XRD pattern of $ZrO_2/Al_2O_3$ nano-catalyst

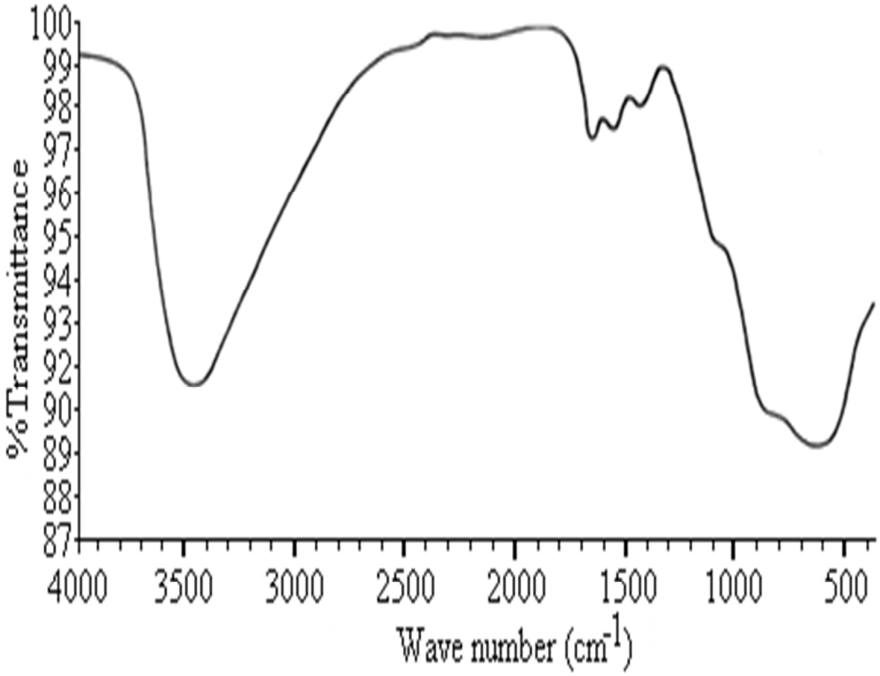



Figure 3. FTIR spectrum of $ZrO_2/Al_2O_3$ nano-catalyst

Table 1 shows the results for the esterification of oleic acid and methanol at 340 K by $ZrO_2/Al_2O_3$ nano-catalyst in various conditions. The oleic acid raw material has a 79/56% purity. During the esterification process under high voltage condition, 71/95% of raw material was converted to biodiesel, thus, the process yield was 90/47%. When the reactions were carried out in the absence of high voltage power, the product could be obtained in low to moderate yields from 19 to 73% in various reaction times (2-12 h).

Table1. Esterification of oleic acid by $ZrO_2/Al_2O_3$ nano-catalyst[a]

| No. | Catalyst | Catalyst wt% | time (h) | Yield of methyl oleate (%) |
|---|---|---|---|---|
| 1 | Nano $ZrO_2/Al_2O_3$[b] | 1 | 2 | 19 |
| 2 | Nano $ZrO_2/Al_2O_3$[b] | 1 | 4 | 35 |
| 3 | Nano $ZrO_2/Al_2O_3$[b] | 1 | 6 | 46 |
| 4 | Nano $ZrO_2/Al_2O_3$[b] | 1 | 8 | 62 |
| 5 | Nano $ZrO_2/Al_2O_3$[b] | 1 | 10 | 67 |
| 6 | Nano $ZrO_2/Al_2O_3$[b] | 1 | 12 | 73 |
| 7 | Nano $ZrO_2/Al_2O_3$[c] | 1 | 2 | 90.47 |

[a] Molar ratio of methanol to oleic acid: 8:1 at 340 K

[b] Reflux without high voltage power

[c] High voltage power: 1.3 kV, electric current: 15-23 mA

The reusability and recycling of nano-catalyst was also investigated in four runs. The results showed the nano-catalyst can be reused several times without noticeable loss of catalytic activity (table 2). After each reaction, the nano-catalyst was separated, washed, and dried at 80 $^{\circ}$C for subsequent reaction.

Table 2. Reusability of $ZrO_2/Al_2O_3$ nano-catalyst in methyl oleate synthesis [a]

| Run | Yield of methyl oleate(%) (Time: 2h) |
|---|---|
| fresh | 90.47 |
| 1 | 90.27 |
| 2 | 90.22 |
| 3 | 90.11 |

[a]Molar ratio of methanol to oleic acid: 8:1, catalyst: 0.2 g, temperature: 340 K, reaction time: 2h, voltage: 1.3 kV, electric current: 15-23 mA, pressure: 1atm

Different reaction parameters such as reagents molar ratios, reaction times, voltage and catalyst wt%, were explored and optimized for esterification of oleic acid by methanol at 340 K and high voltage condition (Table 3). The result product of high voltage process can be purified more than 96.5% by reaction mixture with a weak alkali material such as $Na_2CO_3$, to eliminate unreacted free fatty acids. In 8:1 molar ratio of methanol to oleic acid and 1.3 kV power, the yield was 90 %. In the lower voltages than 1.3 kV, the reaction yields decreased substantially, and in higher voltages the reaction progress was prevented by short circuit. In the absence of catalyst, the reaction yields decreased substantially, and the catalyst had a promotional effect on the esterification of rapeseed oil in 1.3 Kv.

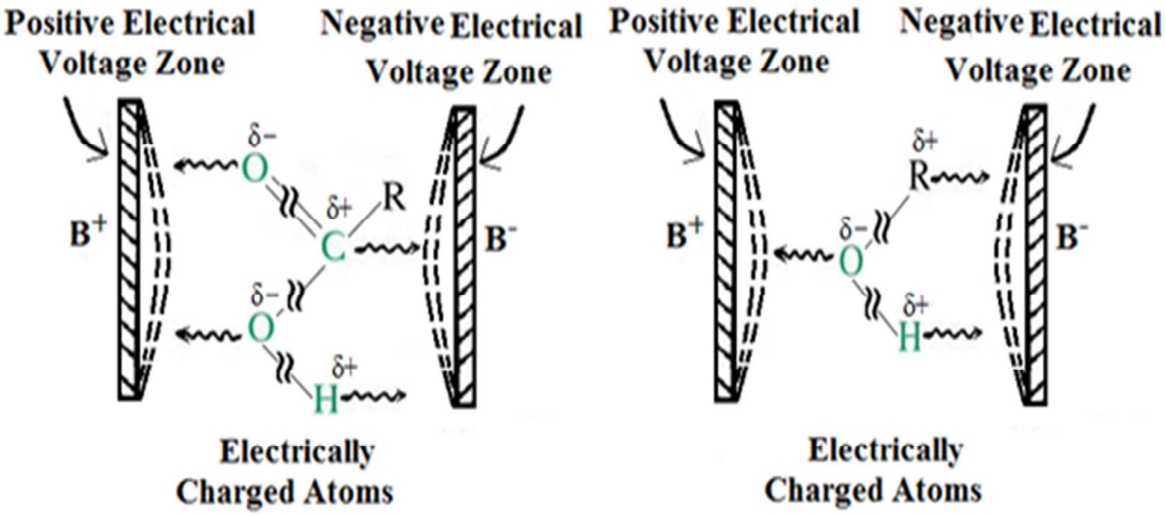
It is noticeable that the esterification reaction under high voltage condition is not an electrochemical reaction, since at the electrochemical reactions for each equivalent of reactants, one Farad electrical charge (96500 coulomb charges) is necessary. The observed electric currents (15-23 mA) in these reactions are caused by the movement of ions between

counter electrodes and are not related to electrochemical reactions. The energy consumption for 2 hr reaction time was about 0.039-0.0598 kWh, (V.I.t=W.h) so the exchanged electric charge was in the range of 0.0195-0.023 coulomb (Q=W/V). So, the exchanged electric charge is a certain reason for a non-electrochemical reaction. Such low energy consumption for reaction is very economic and cost effective for biodiesel mass production.

Table3. Esterification of oleic acid by $ZrO_2/Al_2O_3$ catalyst at 340 K and electric current: 15-23 mA

| Catalyst (wt %) | Molar ratio of methanol to oleic acid | Voltage: (kV) | Time: (h) | Methyl oleate ( wt%) |
|---|---|---|---|---|
| 0 | 30:1 | 1.3 | 1 | 24.5 |
| 0 | 30:1 | 1.3 | 2 | 67.33 |
| 0 | 30:1 | 1.3 | 3 | 68.4 |
| 0 | 30:1 | 1.3 | 4 | 67.8 |
| 0.75 | 5:1 | 1.3 | 1.5 | 62.66 |
| 0.75 | 5:1 | 1.3 | 2 | 67.00 |
| 0.75 | 5:1 | 1.3 | 2.5 | 68.93 |
| 0.75 | 5:1 | 1.3 | 3 | 69.33 |
| 1 | 5:1 | 1.3 | 1.5 | 72.00 |
| 1 | 5:1 | 1.3 | 2 | 73.66 |
| 1 | 5:1 | 1.3 | 2.5 | 66.66 |
| 1.5 | 5:1 | 1.3 | 2 | 56.33 |
| **1** | **8:1** | **1.3** | **2** | **90.47** |
| 1 | 10:1 | 1.3 | 2 | 89.33 |
| 1 | 12:1 | 1.3 | 2 | 81.33 |

In fact this reaction is a catalysed reaction under sharp polarization. The electrically charged atoms of methanol and oleic acid carboxyl group, under the influence of a high voltage field, promote the nucleophilic reaction in the presence of $ZrO_2/Al_2O_3$ nano-catalyst (Scheme 2).




Scheme 2. Electrically charged atoms in methanol and oleic acid for nucleophilic reaction

The water produced during the esterification, did not affect the efficiency of the process. It seems that, under the high voltage condition the water has a promotional effect by hydrolysis to H+ and OH- ions. So there is no need to use dry methanol for high voltage esterification.

In this new reaction, there is not any direct relationship between the voltage and yield of biodiesel (Fig4). In fact, the high voltage condition imposes polarization or ionization phenomena on reagents molecules, which speeds up the esterificative reaction rate and reduces the reaction time.

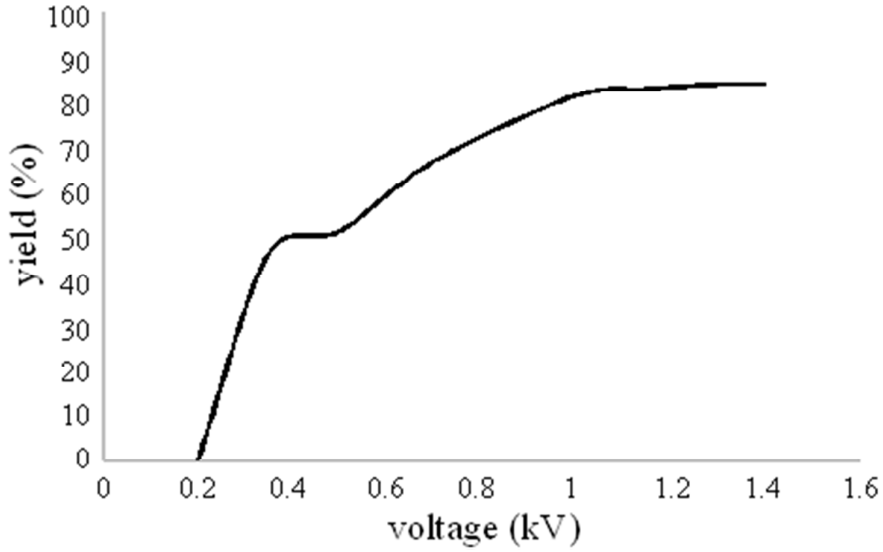



Figure 4. The yield of biodiesel synthesis versus the applied voltage.

Performing the reactions under high voltage and nano-catalytic procedure, considered environmentally benign, are some of the important features of this protocol. The increase in temperature increases the mobility of the ions. These factors promote the accessibility of

substrate molecules on the catalyst surface. Moreover the water of the esterification process has no considerable effect on reaction yield and this by-product disperses in methanol media. So it is not necessary to use dry methanol in the reaction. It seems that the water by-product has no effect on the catalyst.

## 3. Experimental

### 3.1. Chemicals and apparatus

For elemental analysis, a X-ray fluorescence analyzer, Bruker, S4 PIONEER was used. For phase analysis, X-ray diffraction study of the precursor powder was carried out in a Philips Xpert pro diffractometer over 2θ range from 10 to 80°. The Brunauer-Emmett-Teller (BET) surface areas measured using (Quantachrome Nova 4200e). The morphology and particle size was observed using field emission scanning electron microscopy (FESEM JEOL J XA A-840). The fourier transform infrared spectroscopy (FTIR JASCO 680) was done using the KBr pellet method. The gas chromatography analysis was done using the GC-clarus 580, Perkin Elmer USA. The rapeseed oil and methanol were purchased from industrial sources. The purity of rapeseed oil was verified by random checks using gas chromatography. The quality parameters of rapeseed oil (oleic acid) were presented in the table 4.

Table 4. The quality parameters of rapeseed oil (oleic acid)

| Features | Test result | Standard |
|---|---|---|
| FFA (%) | 2.58 | Max 0.1 |
| Peroxide (PV) | 1.71 | Max 1meq/kg |
| Moisture (%) | 0.02 | 0.1 % |
| Insoluble impurities | 0.6 | Max 0.05% |
| Iodine number | 106 | 105-126 |
| Refract index | 1.4657 | 1.465-1.467 |
| Color | 1.6-16 | 1.5 red-15yellow |

The fatty acids weight percent in rapeseed oil (oleic acid) and conversion percent of oleic acid to methyl ester (FAME) were calculated by equation 1, according to the GC chromatograms data.

$$C\ (\%) = = (\sum(A) - Ais) / Ais) * (wis / m) * 100 \qquad \text{Eq. 1}$$

C (%) = Conversion percent

∑ (A) = The surface area for all couriers

Ais = Surface area of the internal standard

Wis (mg) = Weight of the internal standard (methyl ester)

m (mg) = Weight of rapeseed oil or fatty acid to methyl ester

### 3.2. Preparation of $ZrO_2/Al_2O_3$ nano-catalyst by sol-gel method

Analytical grade $Al(NO_3).9H_2O$, $ZrOCl_2.8H_2O$ and citric acid $C_6H_8O_7$ (Sigma-Aldrich, USA) was used as raw material to prepare nano-catalyst. The starting solution was prepared by dissolving 16.71 g aluminum nitrate into distilled water. 1.45 g of zirconium oxychloride was added into aluminum nitrate such that the final composition contained 20 wt% zirconia. 15.07 g citric acid was dissolved into deionised water and then was added to the mixed solution. The solution was continuously stirred for 5 hr and kept at 85°C until turned into a transparent gel. Then the stabilized nitrate-citrate gel was heated to 85°C. Then the gel was placed into a furnace at 1100°C for in time 120 minute. After cooling the catalyst was crushed by a mortar to fine particles[23].

### 3.3. Esterification of oleic acid by $ZrO_2/Al_2O_3$ nano-catalyst under high voltage conditions

Esterrification of oleic acid were carried out in a three necked round bottom containing the catalyst, methanol and oleic acid at 340 K included condenser and two graphite electrodes connected to high voltage DC device (Fig. 5). The result product of high voltage process was purified with 10% $Na_2CO_3$ solution, to eliminate unreacted free fatty acids. After the reaction, the solution was analyzed by high performance gas chromatography and fourier transform infrared spectroscopy.

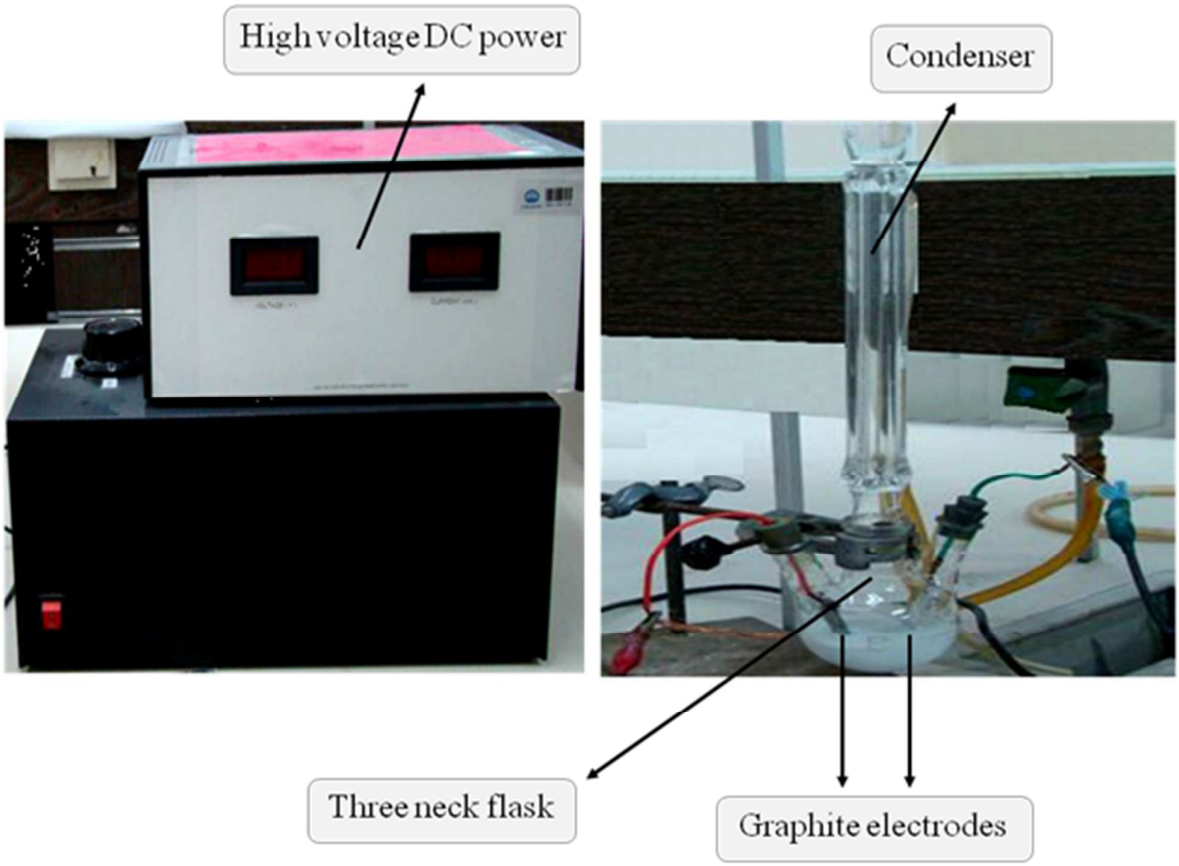



Figure 5. The High voltage esterification apparatus.

The total weight percent of fatty acids in rapeseed oil was 84.72% (Fig. 6).

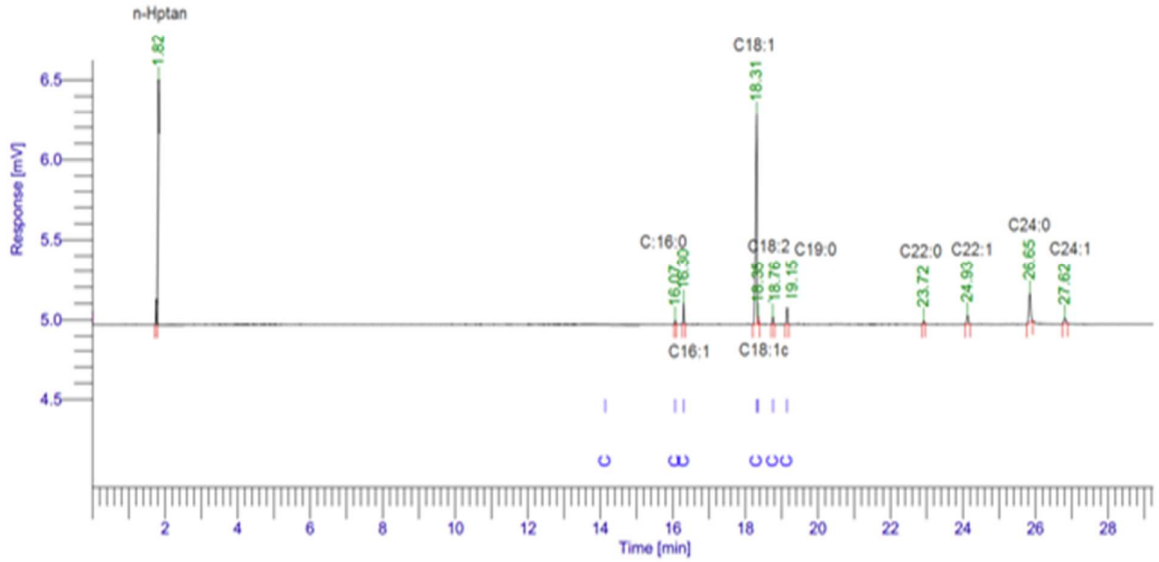



Figure 6. The gas chromatogram of rapeseed oil (oleic acid)

[C (%) = (4714-47-206.91/206.91)*(4.06/104.4)*100=84.72%]

The conversion percent of fatty acids to methyl esters (FAME) in biodiesel was 76.65% (Fig. 7). So, the total conversion was 90.47% (76.65/84.72*100= 90.47).

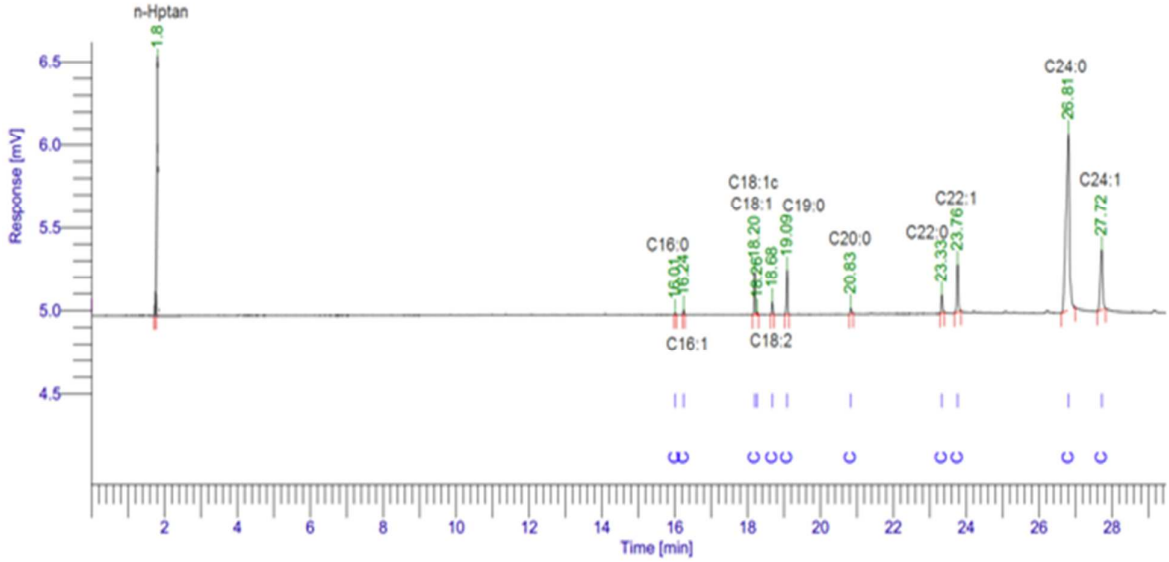



Figure 7. The gas chromatogram of biodiesel (FAME,)

[C (%) = (12762.41-611.02/611.02)*(4.02/104.3)*100=76.65%]

## 4. Conclusions

In conclusion, we described the synthesis and catalytic activity of ZrO2/Al2O3 nano-catalyst as a highly effective heterogeneous and active catalyst that converts oleic acid and

methanol into fatty acid esters under high voltage conditions. The procedure offers several advantages including clean reaction profiles, environmentally benign, simple, cheap, economical, easily available raw materials, high yields, short reaction times, reusability of the catalyst and the little catalyst loading. This green nano-catalyst could be used for other significant organic reactions and transformations. Further explorations of similar protocols are underway in our laboratory.

## 5. Acknowledgments

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