Periodic mesoporous organosilica functionalized sulfonic acid as highly efficient and recyclable catalysts in biodiesel production

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1. Experimental Procedure

1-1. General

^{1}H NMR spectra were recorded on commercial instruments (250 MHz and 400 MHz). Chemical shifts were reported in ppm with the solvent resonance as the internal standard (CDCl3: δ= 7.26). Spectra are reported as follows: chemical shift (= ppm), multiplicity (s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet), coupling constants (Hz), integration. ^{13}C NMR spectra were collected on commercial instruments (62.90 MHz and 100.60 MHz) with complete proton decoupling. Reagents obtained from commercial sources were used without further purification. Thermal treatments were conducted from room temperature to 800 °C in argon flow using a Pheometric Scientific analyzer.

1-2. Chemicals

BTEB (1,4-bis(triethoxysilyl)benzene), BTEE (1,2-bis(triethoxysilyl)ethane), MPMDS (3-mercaptopropylmethyl dimethoxysilane), tetraethoxysilane (TEOS), 3-mercaptopropyl trimethoxysilane (MPTMS) and triblock co-polymer P123 (Eo_{70} Po_{20} Eo_{70}) were obtained from Aldrich and used as received.

1-3. Catalyst preparation

1-3-1. Synthesis of Et-PMO-Me-PrSO_3H (1b)

In this synthesis procedure, pluronic P123 (1.95 g) was added under vigorous stirring to 70 ml of HCl solution (2*N*). After complete dissolution of surfactant at 35 °C, BTEE (2.77 g) was added and the agitation was continued for 3h before the dropwise incorporation of MPMDS (0.478 g). The stirring was followed for 24 h at 35 °C. Then the suspension was aged for 24 h at 87 °C. The solid material were separated by filteration, washed with deionized water and dried at room temperature. The surfactant was removed by solvent extraction with anhydrous ethanol in a soxhlet apparatus for 24 h (Entry 1, Table 1). Typically, 0.2 g of extracted material was contacted with 8 g H_2O_2 (30 wt%) and the suspension was stirred at room temperature for 24 h. After filteration and washing with deionized water and warm ethanol separately, the oxidized samples were acidified in 100 ml 0.1 M H_2SO_4 solution during 2 h. Next, the samples were washed thoroughly with deionized water until neutral *p*H, filtered and vaccum dried at 60 °C overnight.

1-3-2. Synthesis of Ph-PMO-Me-PrSO_3H (1a)

In a typical one-step synthesis, 0.66 g pluronic P123 was dissolved in 23.6 g deionized water, 0.57 g H_2O_2 (30wt%), and 0.13 g of HCl (37wt%). Then 0.47 g BTEB and 0.0902 g (30 mol% in total silica precursors) of MPMDS were added to the solution. The resulting mixture was agitated for 2 h at 40 °C and thereafter aged for 24 h at 100 °C. The resulting solid material was filtered and air-dried. To extract the residual block co-polymer, the solid material (0.5 g) was stirred in acetone (60 ml) for 10 h at 56 °C, followed by washing with deionized water. The final products were obtained after drying the samples in oven for 1 day at 100 °C.

1-3-3. Preparation of SBA-15-Pr-SH

The synthesis of SBA-15-PrSH has been achieved using known procedure described by Stucky and his co-workers. [1] This procedure involved a synthetic strategy based on cocondensation of tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane

(MPTMS) in the presence of Pluronic P123 as structure directing agent. In a typical preparation procedure, 4.0 g of Pluronic P123 (Aldrich, average Mw =5800) was dissolved in 125 g of 1.9 M HCl solution with stirring at room temperature. The solution was heated to 40 °C before adding 6.83g TEOS. After 3 h pre-hydrolysis of TEOS, 1.6 g thiol precursor MPTMS was added. The resultant solution was stirred for 20 h at 40 °C, after which the mixture was aged at 100 °C for 24 h under static conditions. The solid was recovered by filtration and air dried at room temperature overnight. The template was removed from the as-synthesized material by washing with ethanol using a Soxhelet apparatus for 24 h.

1-3-4. Preparation of SBA-15-Ph-PrSH [2]

To a suspension of SBA-15-Pr-SH (3 g) in dry toluene $PhSi(OEt)_3$ (PTES, 4 mmol) was added. The resulting mixture was first stirred at room temperature for 1 h and then refluxed for further 24 h. The solid materials was filtered and successively washed with toluene, EtOH, and Et_2O and dried overnight at 120 °C to afford the corresponding SBA-15-Ph-PrSH.

1-3-5. Preparation of SBA-15-$PrSO_3H$

Typically, 0.3 g of SBA-15-Pr-SH was suspended in 10 g of aqueous 30 wt% H_2O_2. This suspension was stirred at room temperature in an Ar atmosphere for 24 h. After the oxidation treatment, the resulting solution was filtered and washed separately with water and ethanol. Finally the wet material was suspended in 1M H_2SO_4 solution for 2 h and then was washed several times with deionized water and ethanol and dried at 60 °C under vacuum overnight to give the corresponding catalyst.

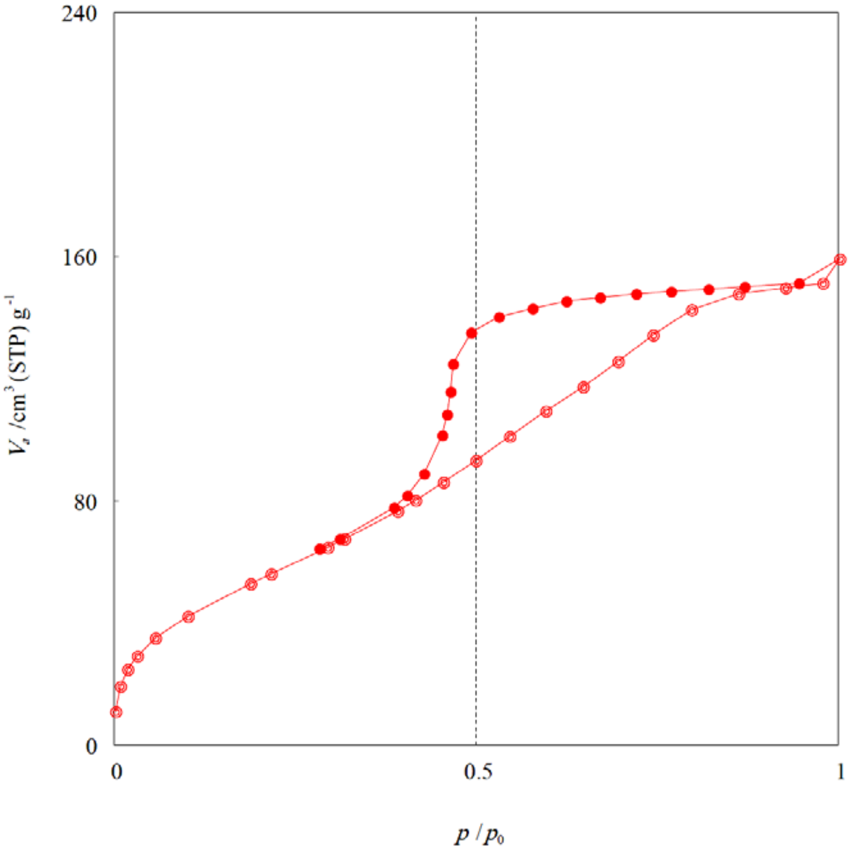
1-3-6. Preparation of SBA-15-Ph-$PrSO_3H$ [2]

Conversion of thiol groups of catalyst to sulfonic acid moiety was accomplished by hydrogen peroxide. Typically, 0.3 g of solid hodrophobic material was suspended in 10 g of aqueous 30 wt% H_2O_2. This suspension was stirred at room temperature in an Ar atmosphere for 24 h. After the oxidation treatment, the resulting solution was filtered and washed separately with water and ethanol. Finally the wet material was suspended in 1M H_2SO_4 solution for 2 h and then was washed several times with water and ethanol and dried at 60 °C under vacuum overnight to give the corresponding catalyst.

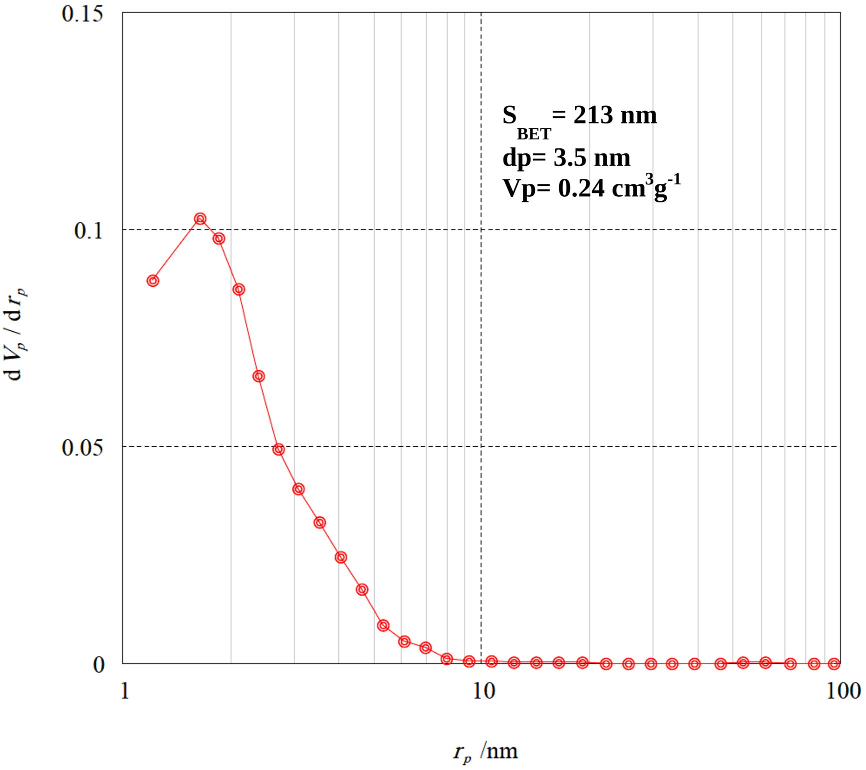
1-4. Characterization

The textural properties of the functionalized mesoporous organosilicas were measured from nitrogen adsorption-desorption isotherms at 77 k with a BELSORB max system. The surface area and pore size distribution were calculated with the BET and BJH methods, respectively. Organic material present in the solids was determined by elemental analysis and the organic composition of the modified mesoporous materials was determined by thermogravimetric analysis (TGA) and differential thermoanalysis (DTA), with heating from room temperature to 800 °C under Argon flow. The ion exchange capacities of the sulfonic acid functionalized mesoporous organosilicas were determined by acid-base titration and *p*H metery. The TEM image also demonstrate that the mesostructure Et-PMO-Me-$PrSO_3H$ (1b) exhibit ordered 2D-hexagonal (p6mm) patterns.

1-4-1. Et-PMO-Me-PrSH analysis data

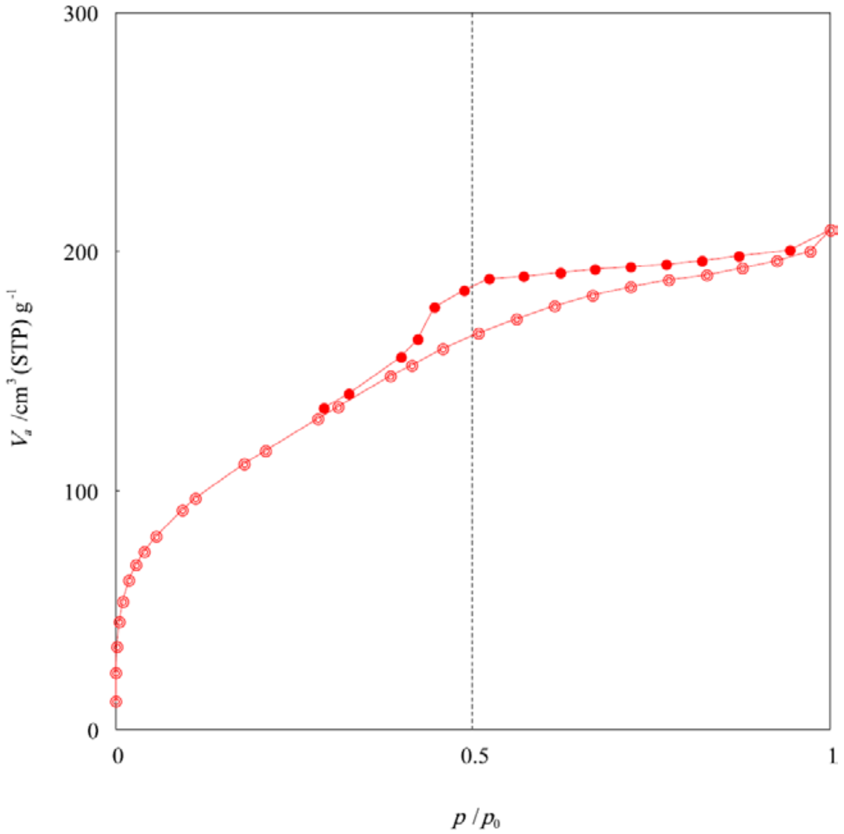


N_2 adsorption-desorption of Et-PMO-Me-PrSH

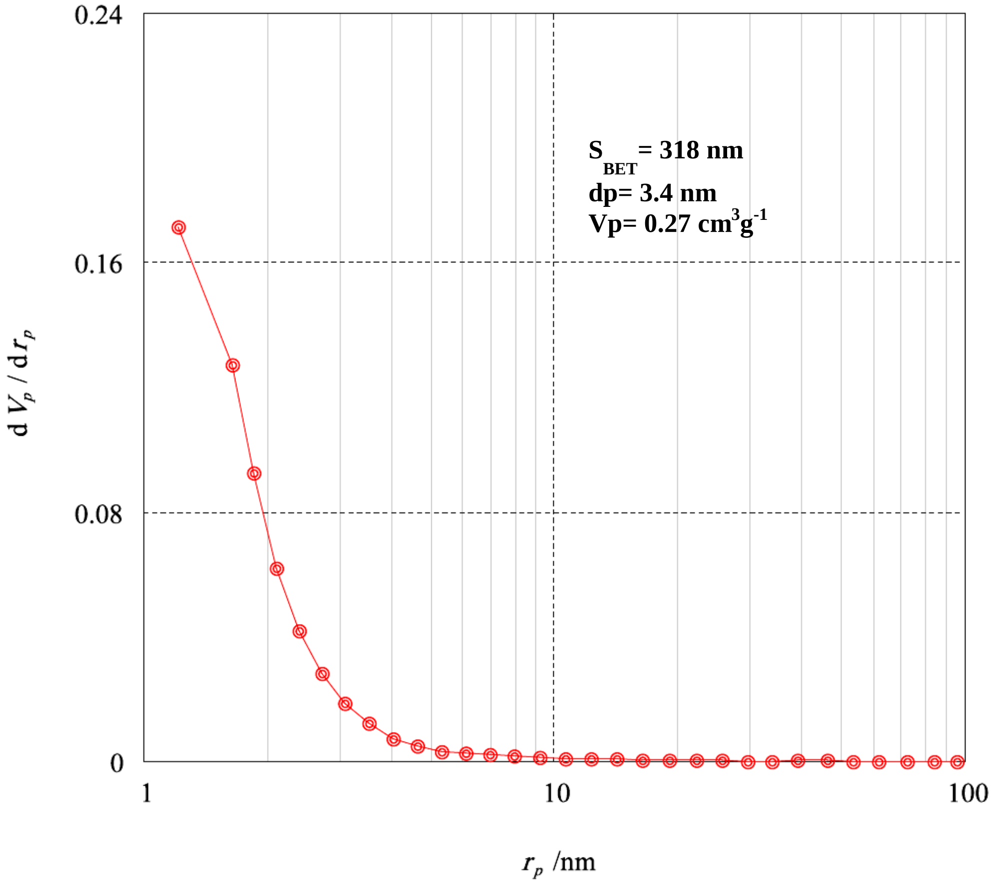


BJH analysis of Et-PMO-Me-PrSH

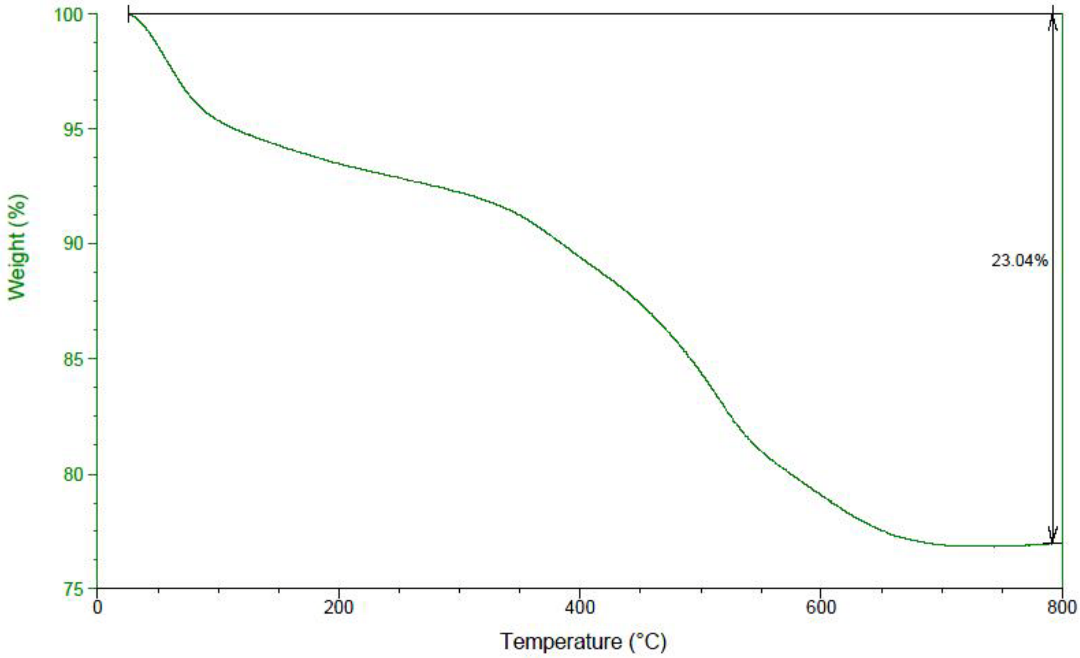
1-4-2. Et-PMO-Me-PrSO$_3$H (1b) analysis data



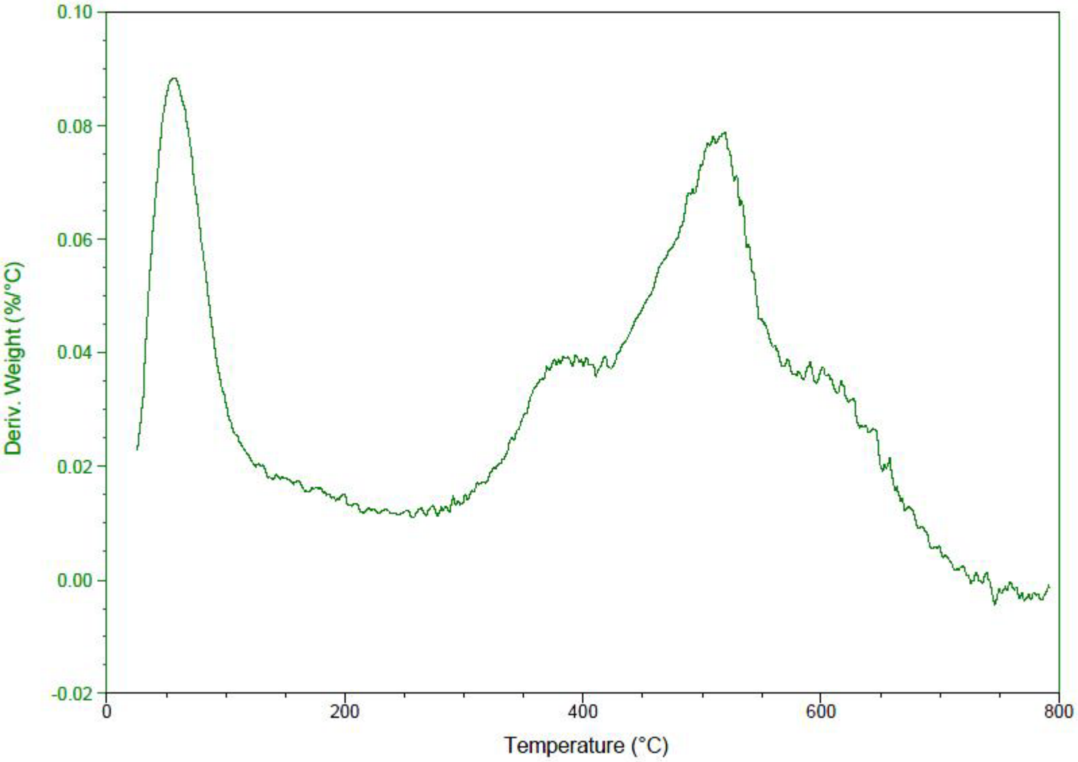
N$_2$ adsorption-desorption of Et-PMO-Me-PrSO$_3$H catalyst



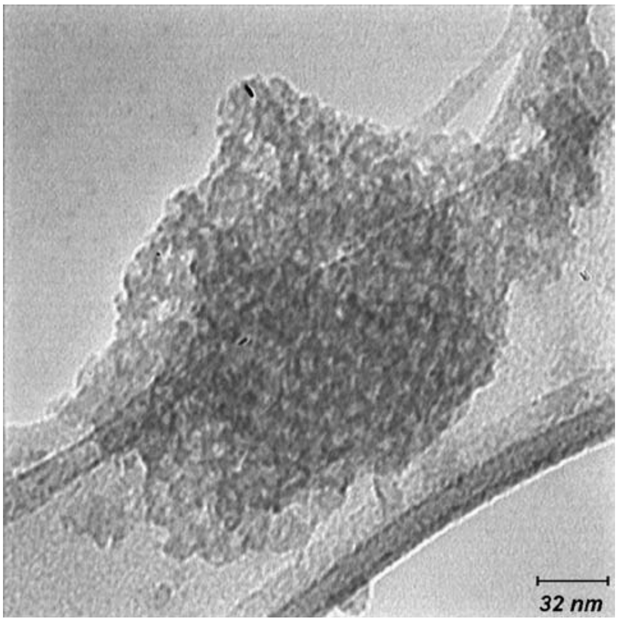
BJH analysis of Et-PMO-Me-PrSO$_3$H catalyst



TGA analysis of Et-PMO-Me-PrSO$_3$H catalyst

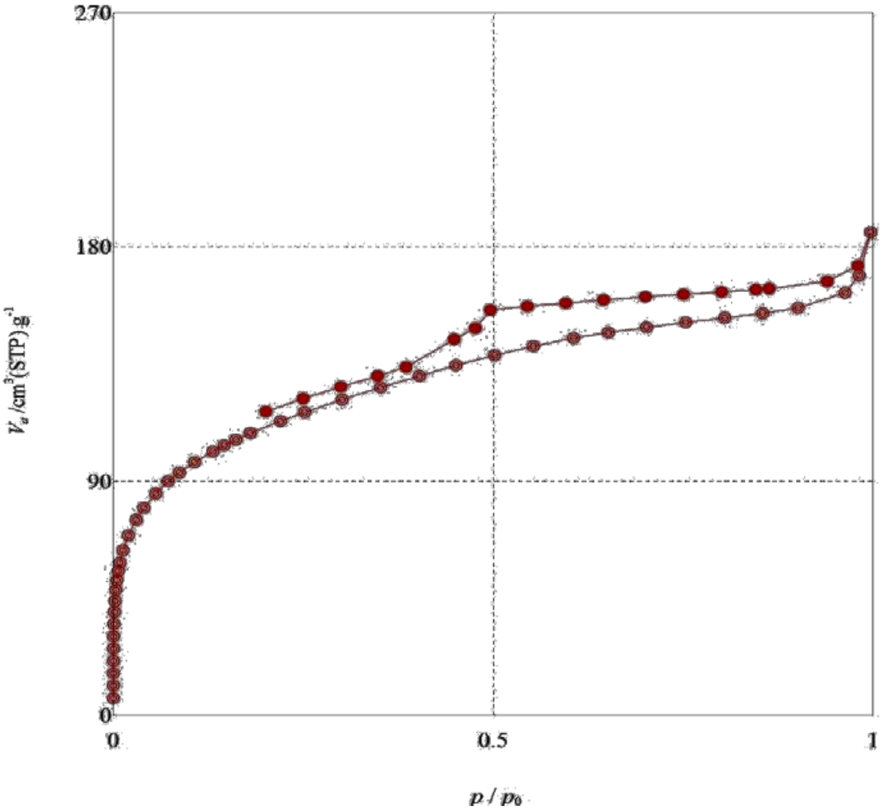


DTA diagram for Et-PMO-Me-PrSO$_3$H catalyst

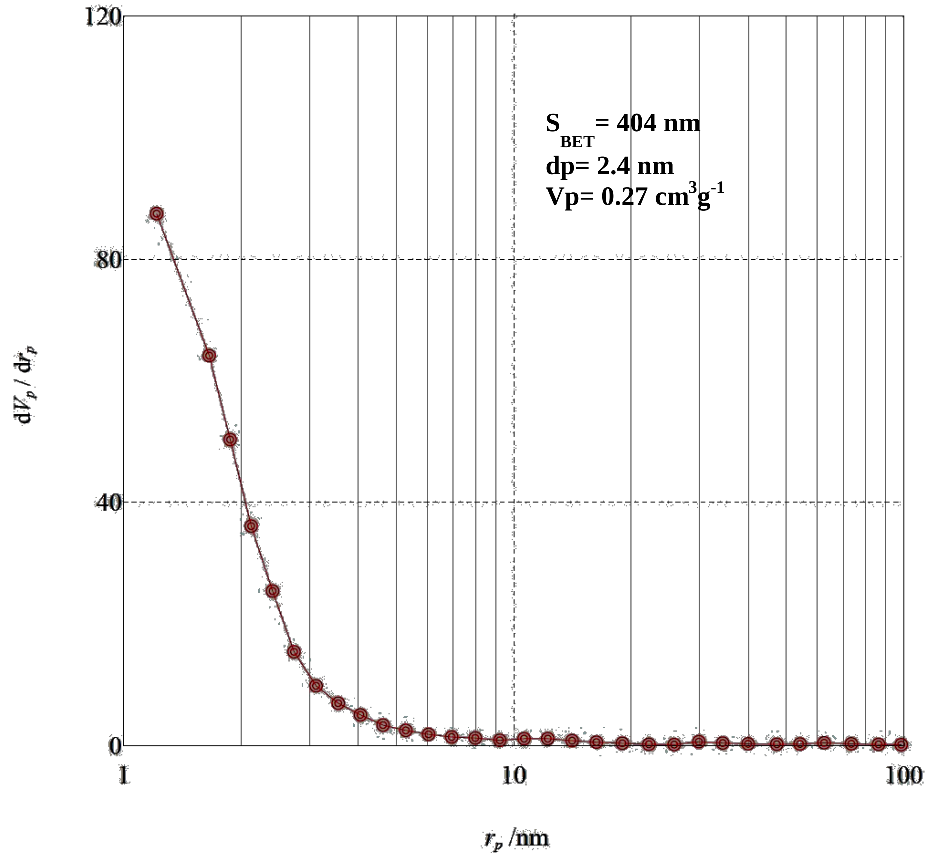


TEM image of Et-PMO-Me-PrSO$_3$H catalyst

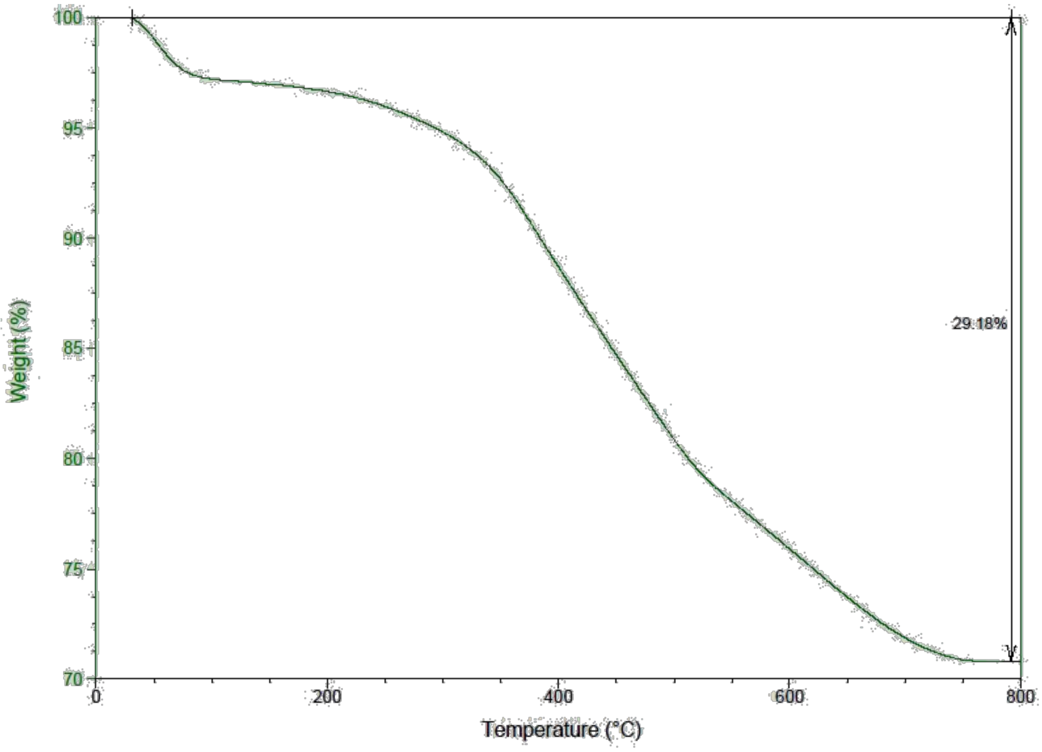
1-4-3. Ph-PMO-Me-PrSO$_3$H (1a) analysis data



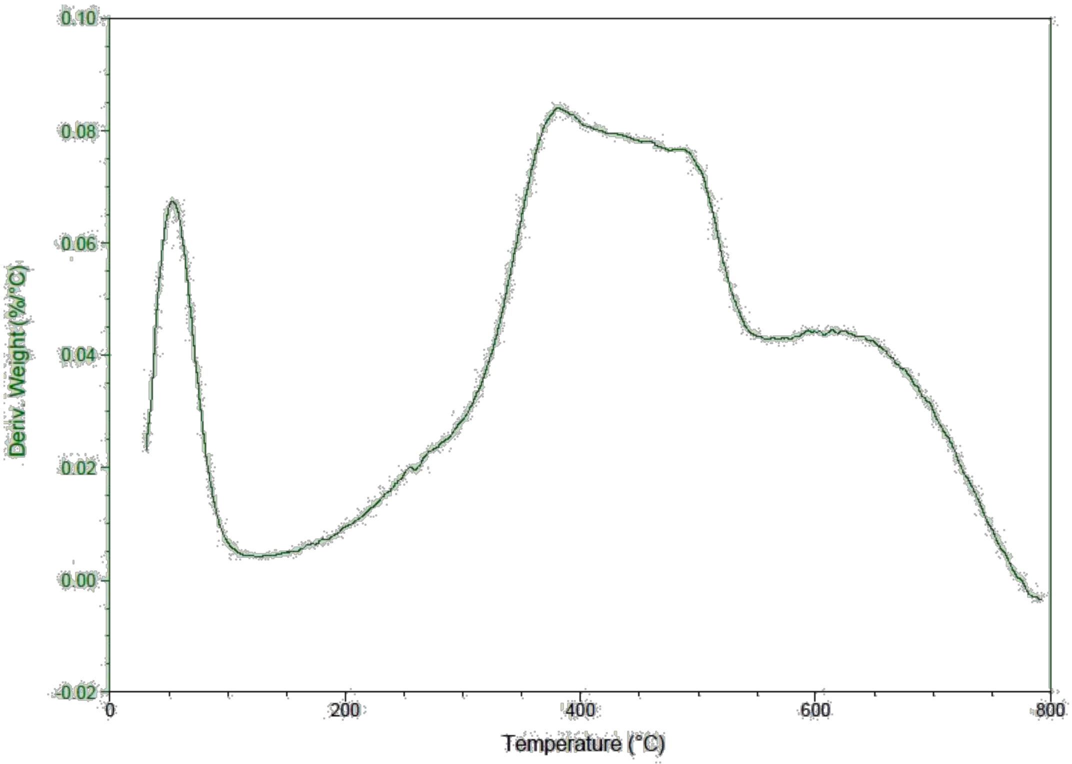
N$_2$ adsorption-desorption of Ph-PMO-Me-PrSO$_3$H catalyst



BJH analysis of Ph-PMO-Me-$PrSO_3H$ catalyst

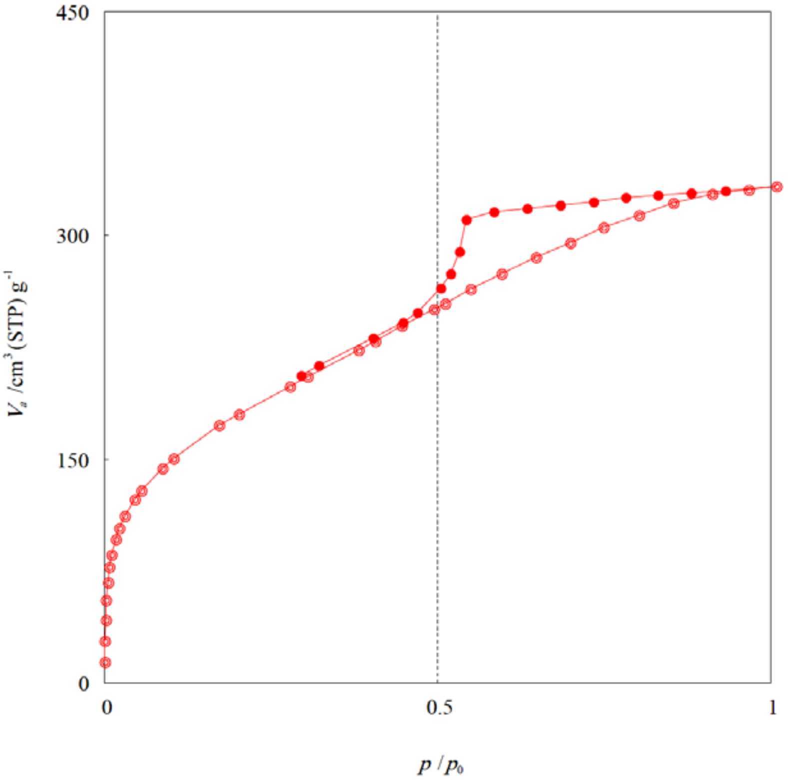


TGA analysis of Ph-PMO-Me-$PrSO_3H$ catalyst

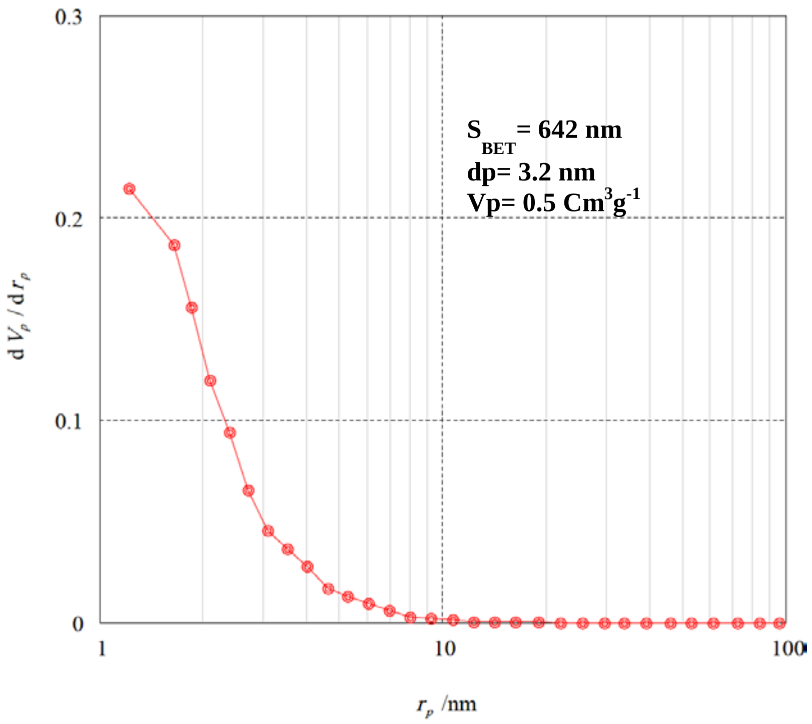


DTA diagram for Ph-PMO-Me-PrSO$_3$H catalyst

1-4-4. Reused Et-PMO-Me-PrSO$_3$H catalyst data at 150 °c

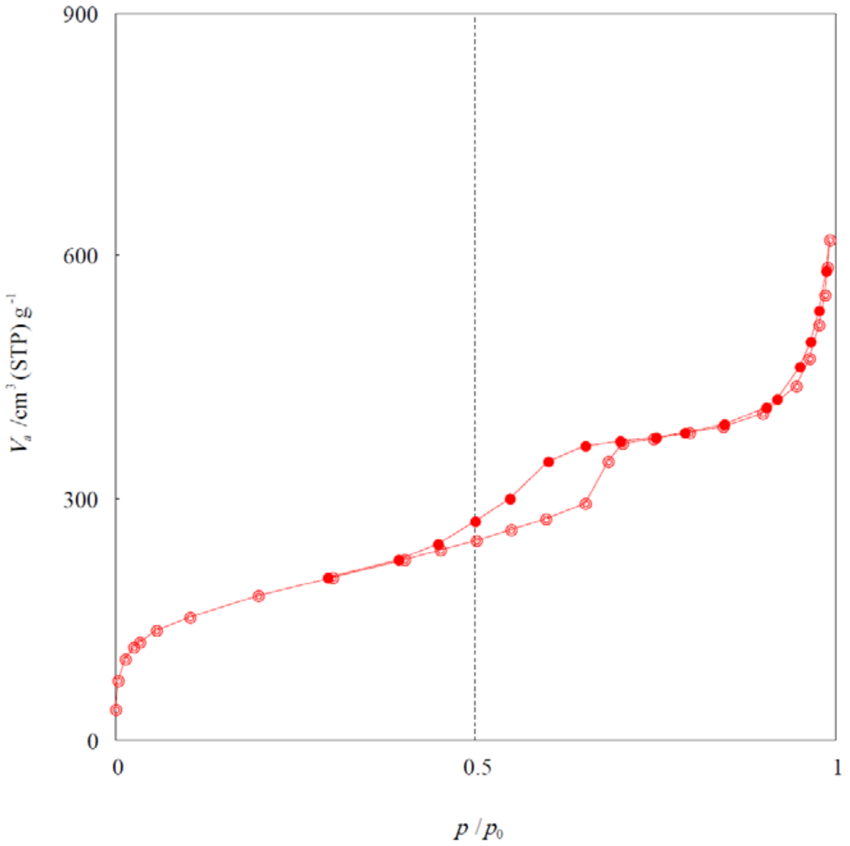


N2 adsorption-desorption of 3rd reused Et-PMO-Me-PrSO$_3$H catalyst in conditions: T=150 °c, Molar ratio Canola oil/methanol= 1/100, time= 4 h

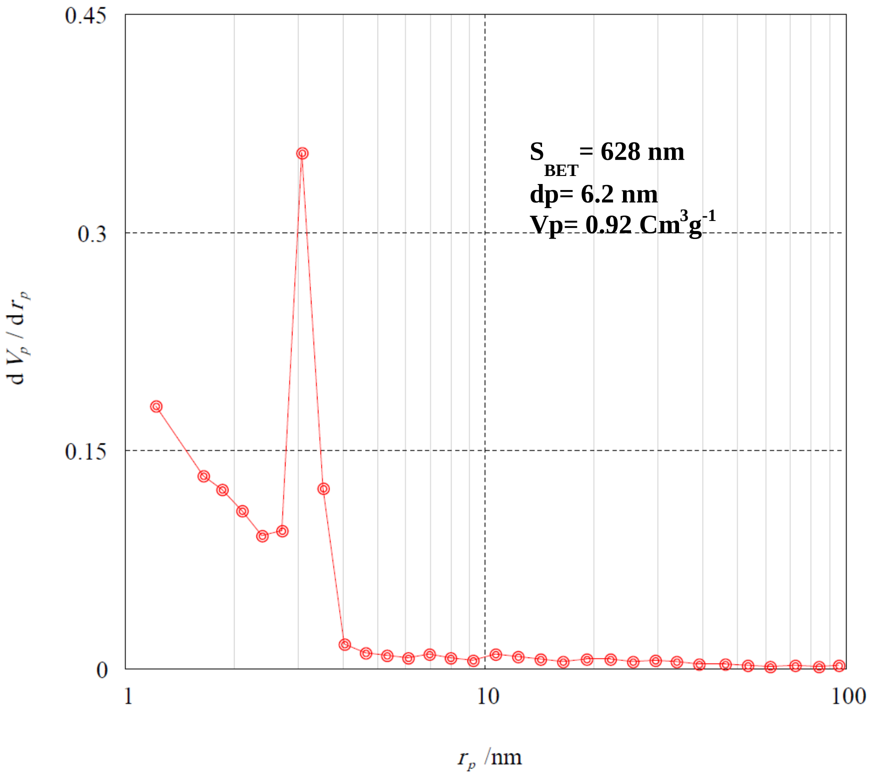


BJH analysis of 3rd reused Et-PMO-Me-$PrSO_3H$ catalyst in conditions: T=150 °c, Molar ratio Canola oil/methanol= 1/100, time= 4 h

1-4-5. SBA-15-$PrSO_3H$ porosimetry data

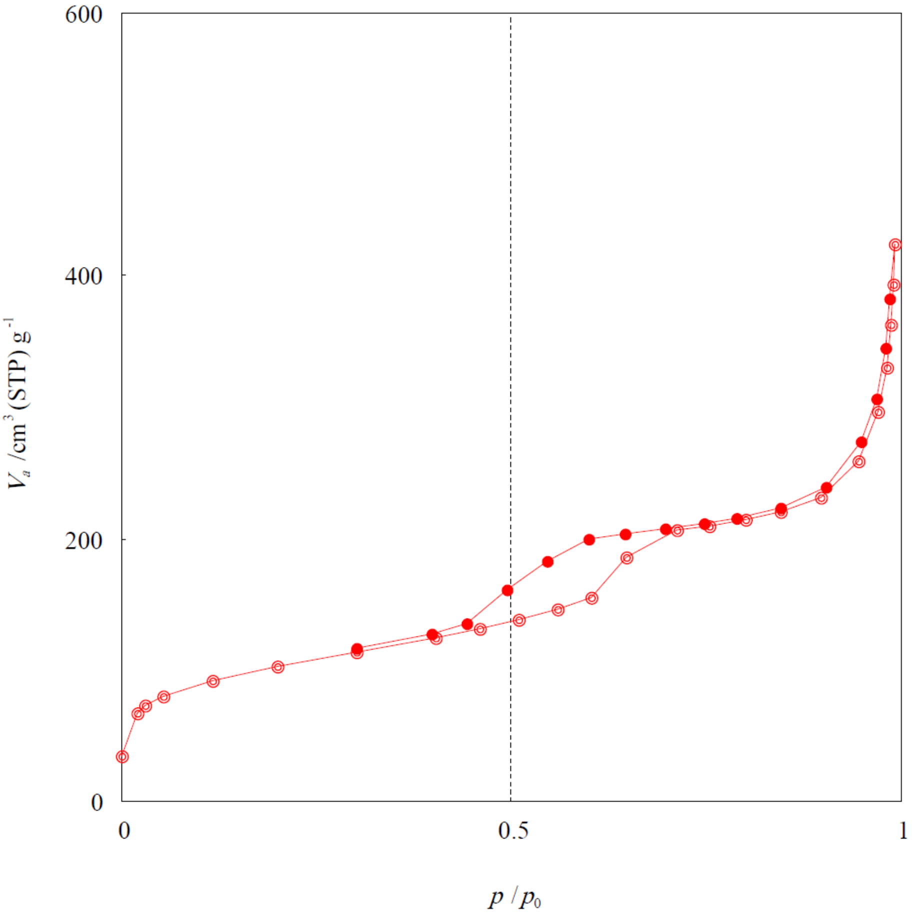


N_2 adsorption-desorption of SBA-15-$PrSO_3H$ catalyst

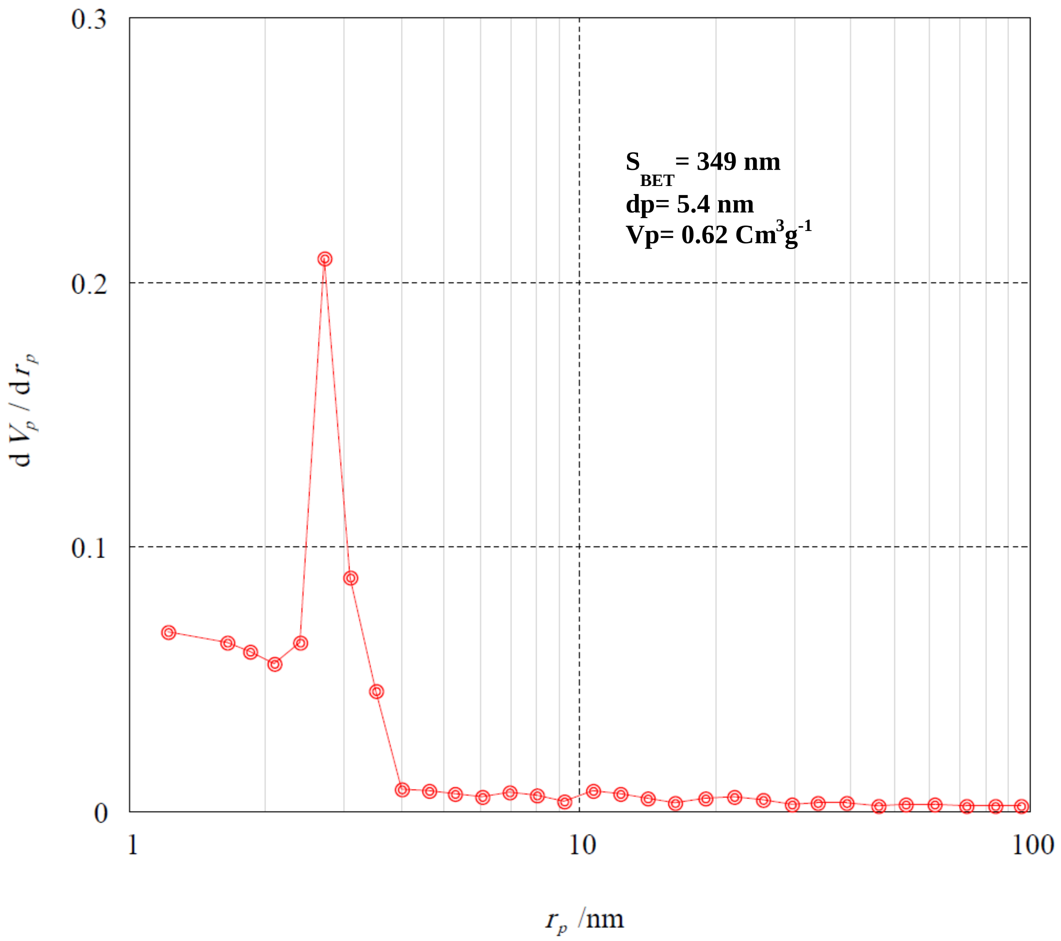


BJH analysis of SBA-15-PrSO$_3$H catalyst

1-4-6. SBA-15-Ph-PrSO$_3$H porosimetry data



N$_2$ adsorption-desorption of SBA-15-Ph-PrSO$_3$H catalyst



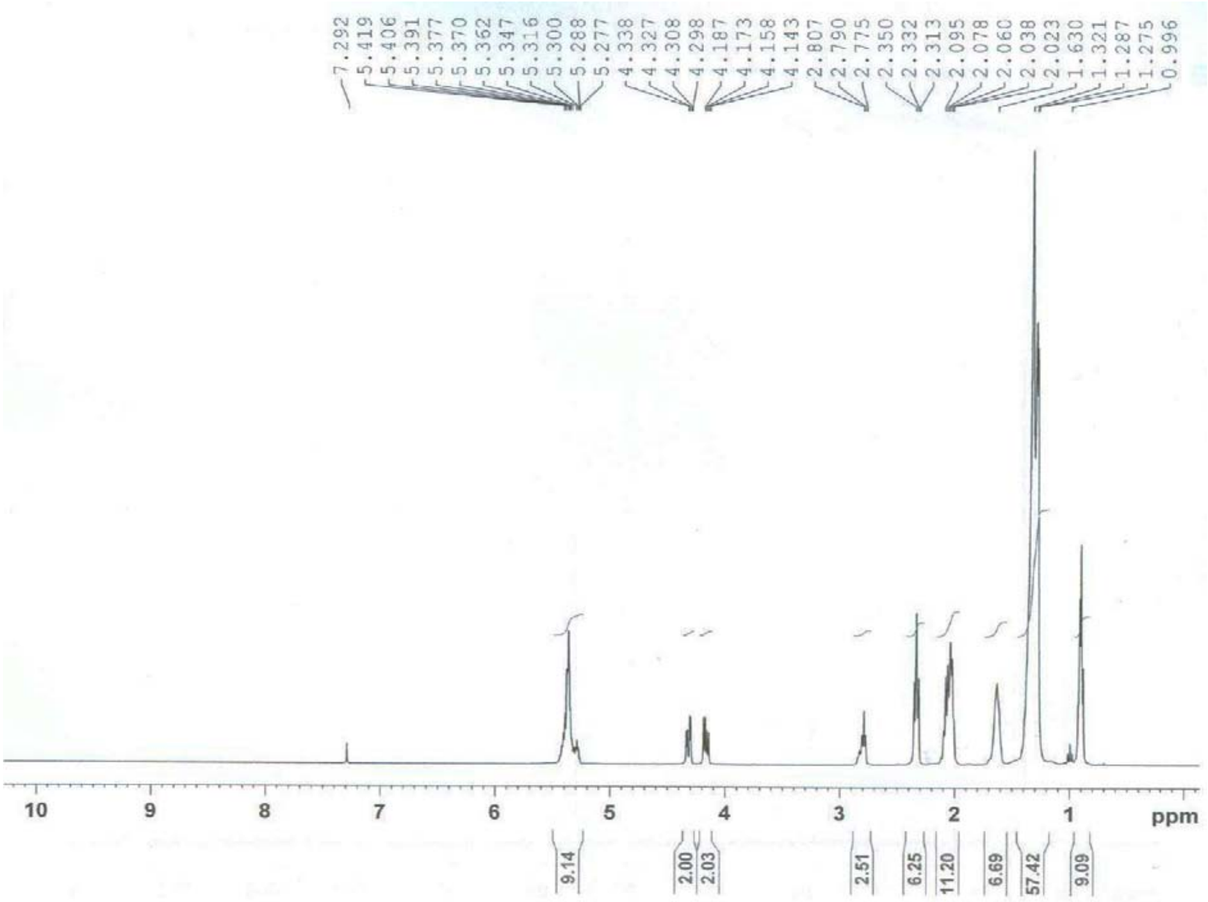
BJH analysis of SBA-15-Ph-PrSO$_3$H catalyst

1-5. Characterization of the product

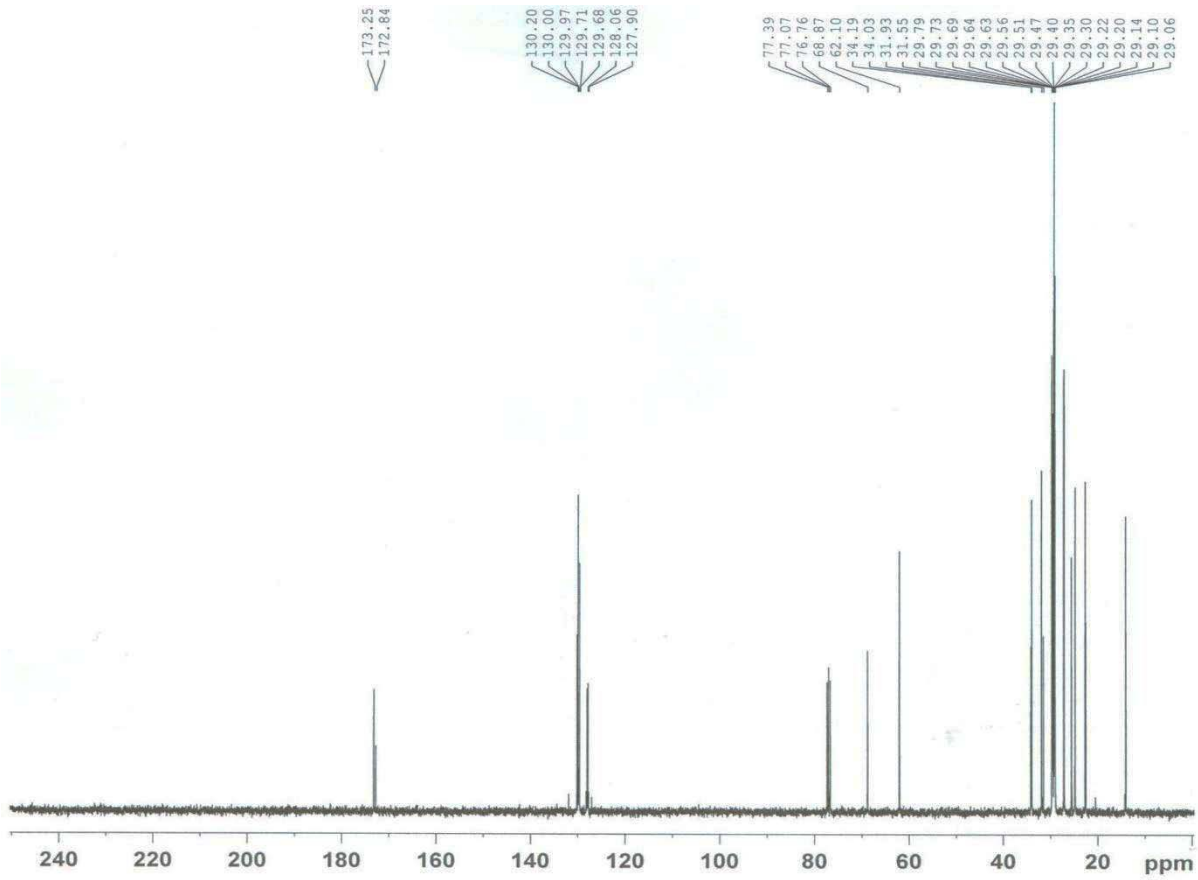
1 Canola oil

^{1}H NMR (400 MHz; $CDCl_3$): δ_H= 5.27-5.41 (m, 9H), 4.25-4.31 (dd, J_1= 4.4 Hz, J_2= 12 Hz, 2H), 4.14-4.18 (dd, J_1= 5.6 Hz, J_2= 12.00 Hz, 2H), 2.79 (t, 2H), 2.33 (t, J= 7.5 Hz, 6H), 2.02-2.09 (m, 11H), 1.63 (brs, 6H), 1.27-1.32 (brs, 57H), 0.99 (t, J= 7.5 Hz, 9H); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ_C= 173.2, 172.8, 130.2, 130.0, 129.9, 129.7, 129.6, 128.0, 127.9, 68.8, 62.1, 34.1, 34.0, 31.9, 31.5, 29.7, 29.7, 29.6, 29.6, 29.6, 29.5, 29.5, 29.4, 29.4, 29.3, 29.3, 29.2, 29.2, 29.1, 29.1, 29.0, 27.2, 25.6, 24.8, 22.6, 22.6, 14.1

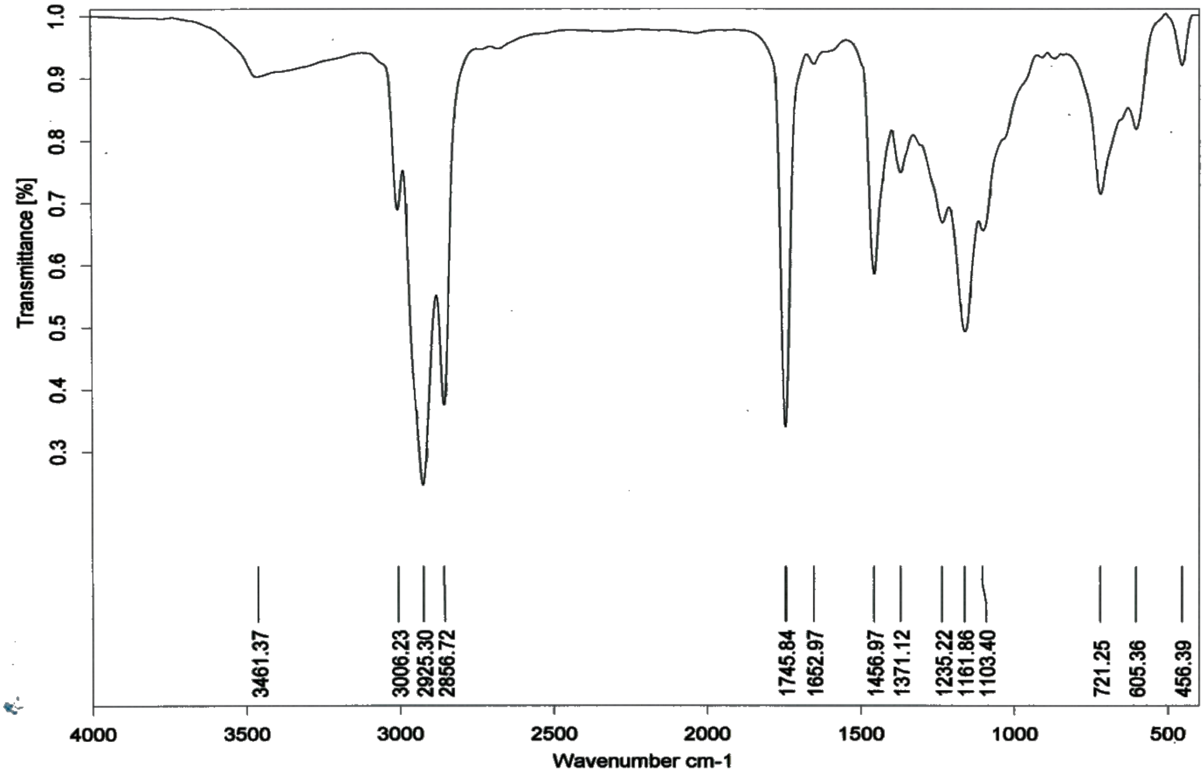
IR (neat): 456, 605, 721, 1103, 1161, 1235, 1371, 1456, 1652, 1745, 2925, 3006, 3461



^{1}HNMR (400 MHz) of Canola oil



^{13}CNMR (400 MHz) of Canola oil

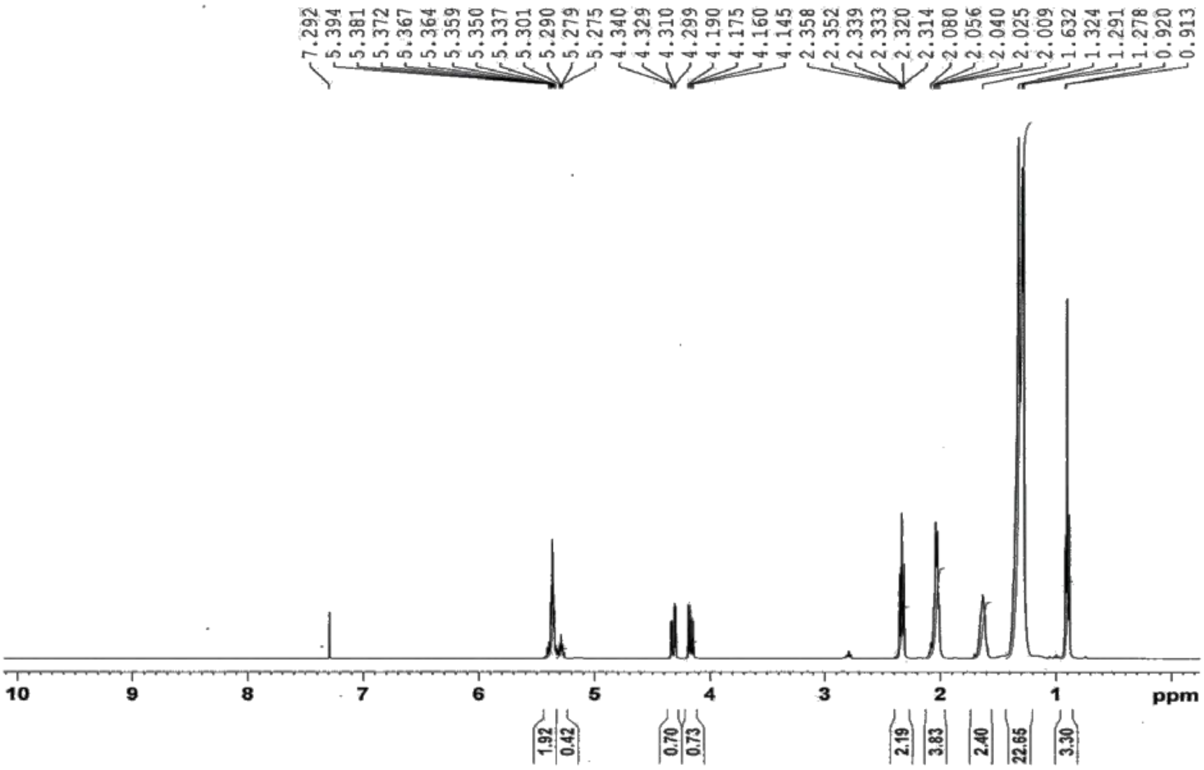


IR spectrum of Canola oil (neat)

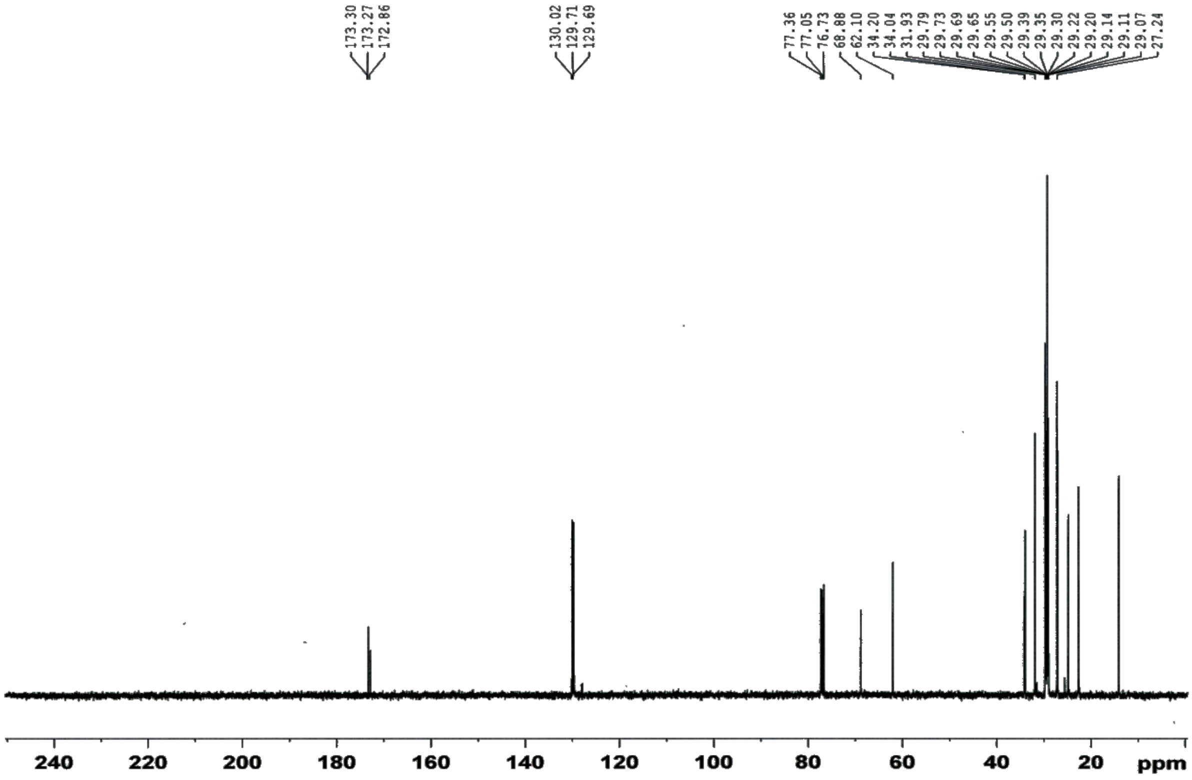
2 Olive oil

^{1}H NMR (400 MHz; CDCl$_3$): δ_H= 5.20-5.40 (m, 7H), 4.25-4.31 (dd, J_1= 4.2 Hz, J_2= 11.7 Hz, 2H), 4.09-4.16 (dd, J_1= 5.8 Hz, J_2= 12.0 Hz, 2H), 2.72-2.80 (m, 1H), 2.30 (t, J= 7.8 Hz, 8H), 1.95-2.10 (m, 12H), 1.55-1.70 (m, 8H), 1.25 (brs, 72H), 0.86 (t, J= 6.0 Hz, 12H); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ_C= 173.2, 172.8, 130.2, 129.9, 129.6, 128.0, 127.8, 68.8, 62.0, 34.1, 34.0, 33.9, 31.8, 31.5, 29.7, 29.6, 29.5, 29.3, 29.1, 27.2, 27.1, 25.6, 24.8, 24.6, 14.1

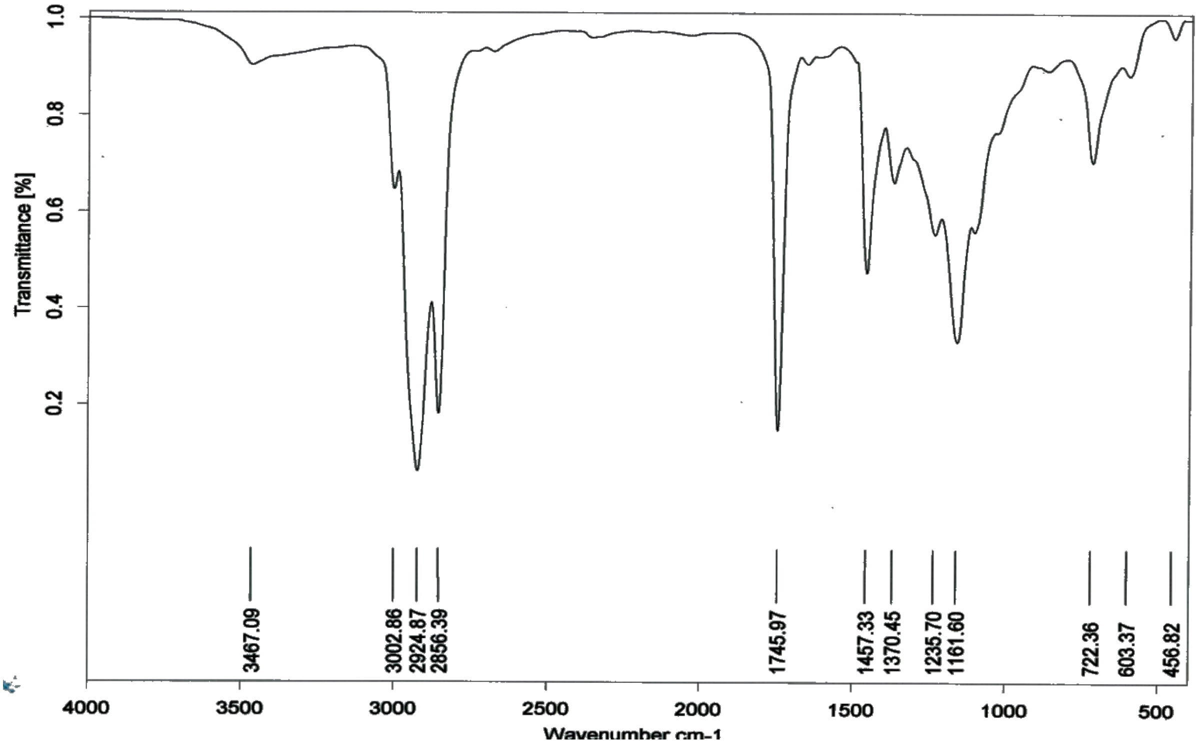
IR (neat): 456, 603, 722, 1161, 1235, 1370, 1457, 1745, 2924, 3002, 3467



^{1}HNMR (400 MHz) of refined olive oil

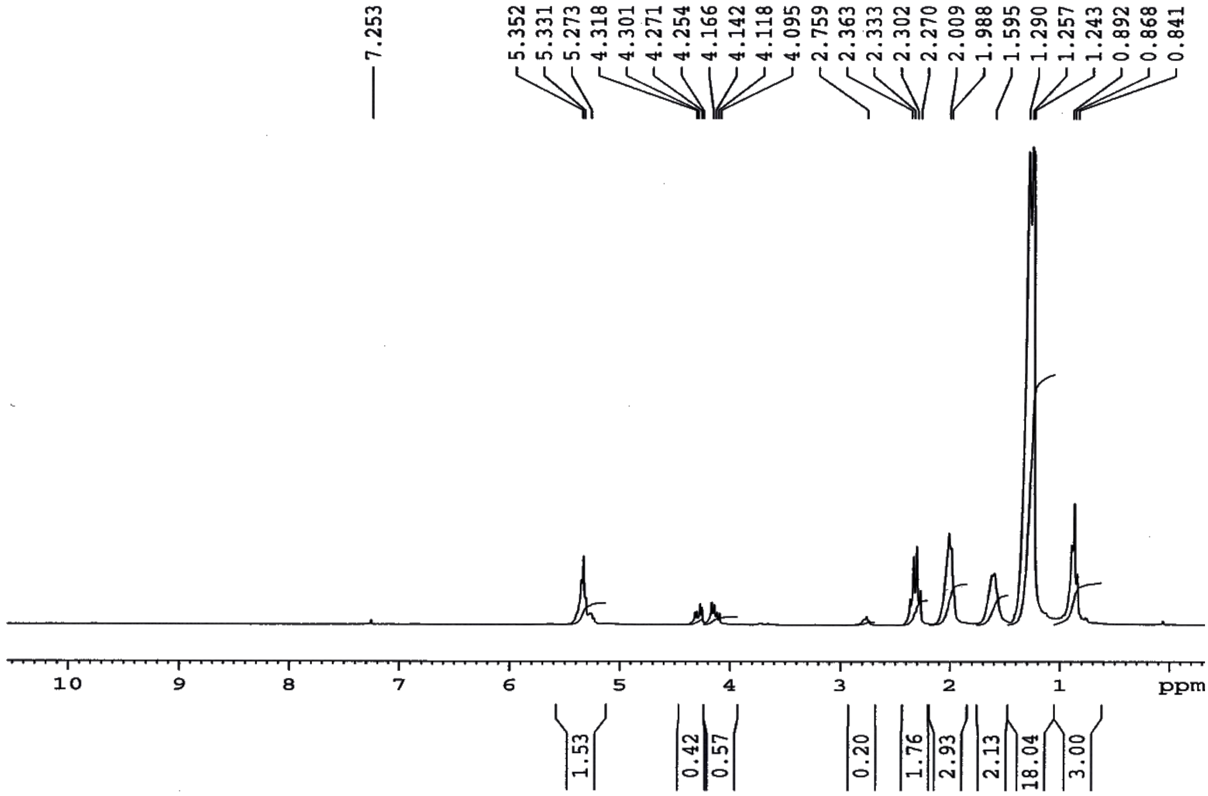


^{13}CNMR (100.6 MHz) of refined olive oil

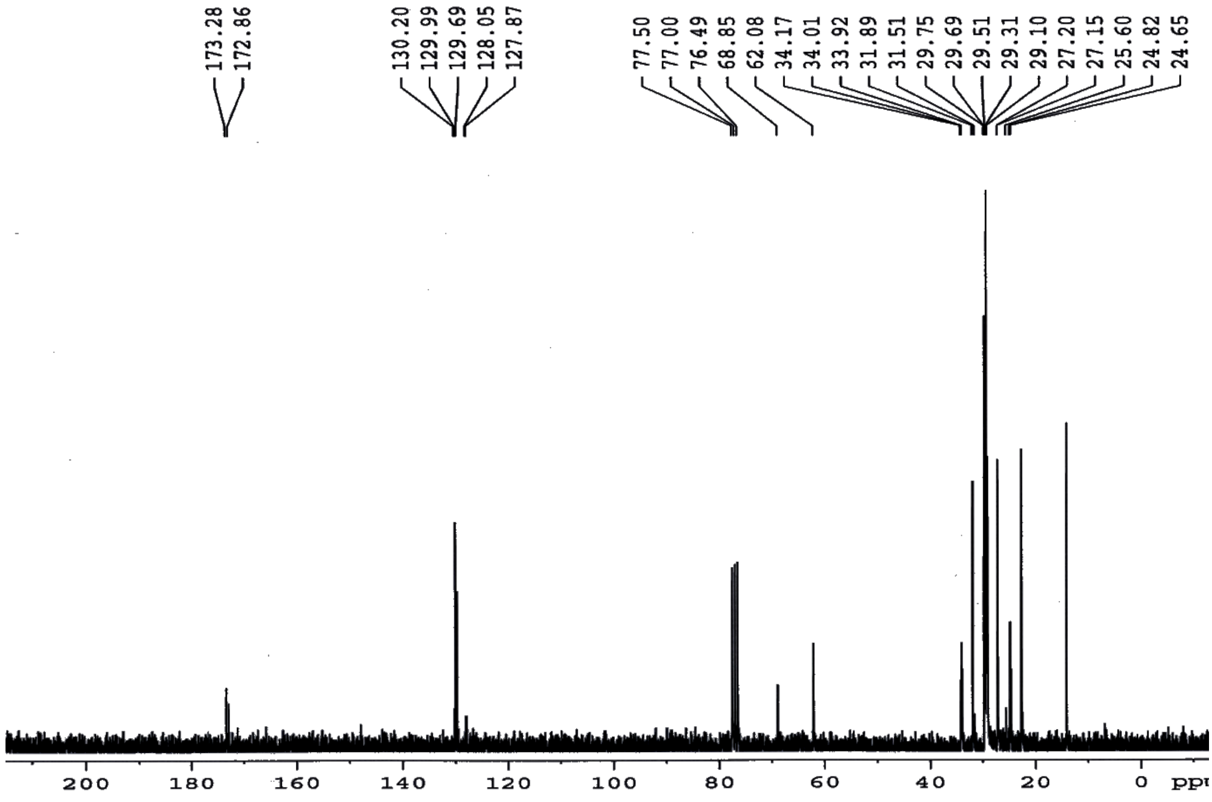


IR spectrum of Olive oil (neat)

3 Extracted oil from olive sludge



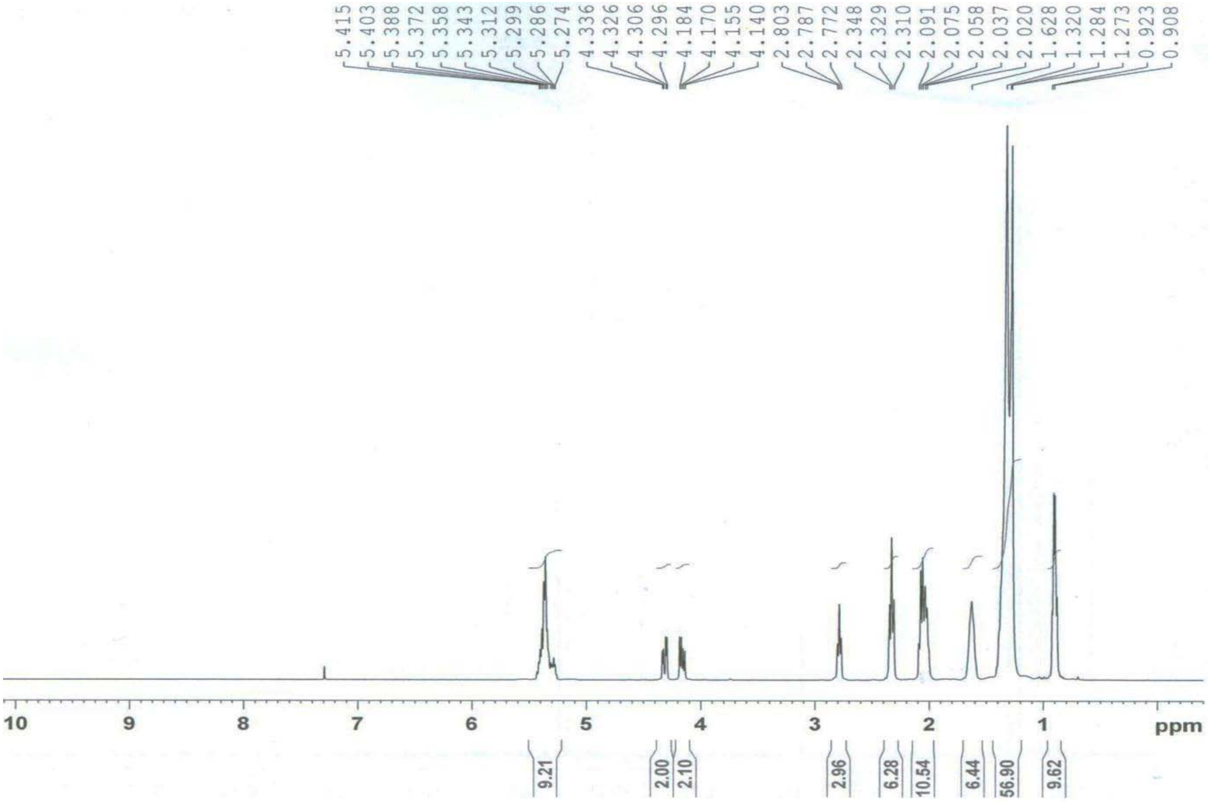
^{1}HNMR (250 MHz) of Extracted oil from olive sludge



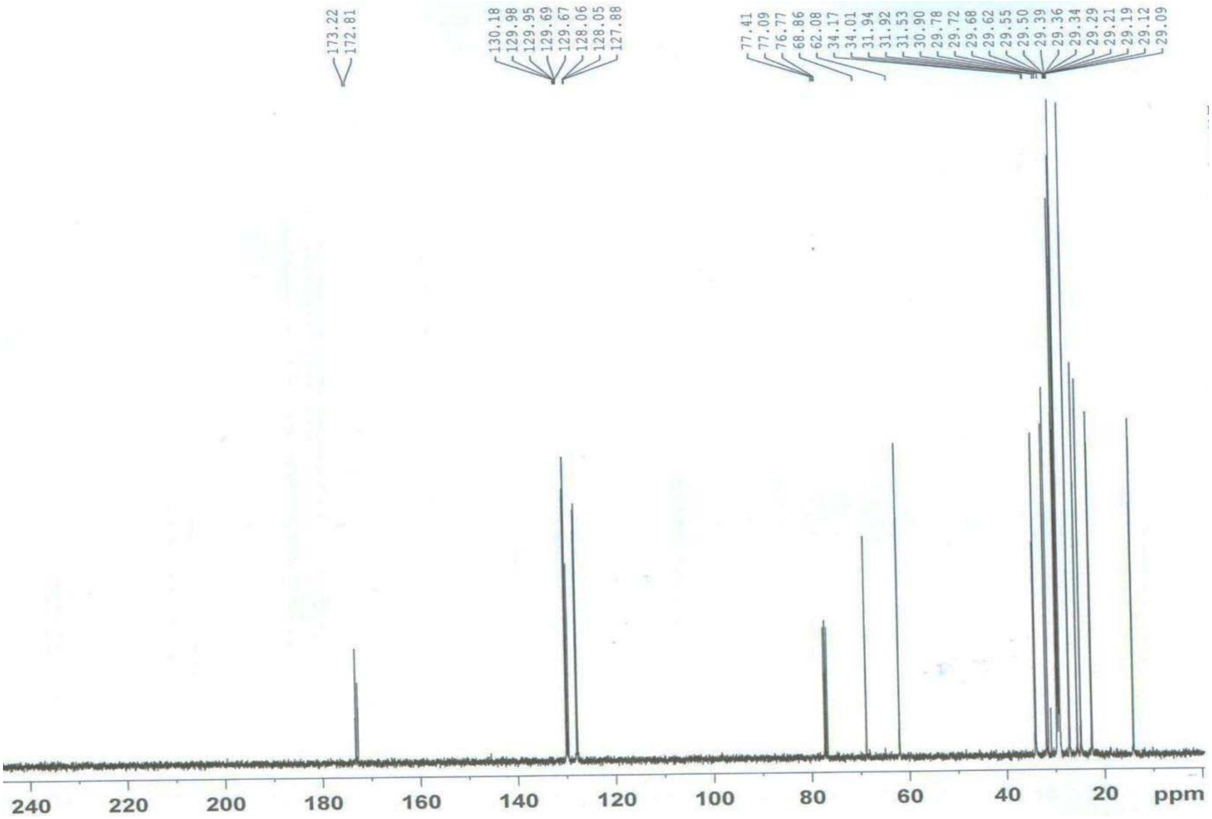
^{13}CNMR (62.9 MHz) of Extracted oil from olive sludge

4 Corn oil

^{1}H NMR (400 MHz; CDCl$_3$): δ_H= 5.27-5.41 (m, 9H), 4.29-4.33 (dd, J_1= 4.0 Hz, J_2= 12 Hz, 2H), 4.14-4.18 (dd, J_1= 5.6 Hz, J_2= 12.00 Hz, 2H), 2.78 (t, J= 6 Hz, 3H), 2.32 (t, J= 7.6 Hz, 6H), 2.02-2.09 (m, 10H), 1.62 (brs, 6H), 1.27-1.32 (brs, 57H), 0.92 (m, 9H); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ_C= 173.2, 172.8, 130.2, 130.0, 129.9, 129.9, 129.6, 129.6, 128.0, 128.0, 127.8, 68.8, 62.0, 34.1, 34.0, 31.9, 31.9, 31.5, 30.9, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.3, 29.3, 29.3, 29.2, 29.2, 29.1, 29.1, 29.0, 27.2, 25.6, 24.8, 22.6, 22.6, 14.1



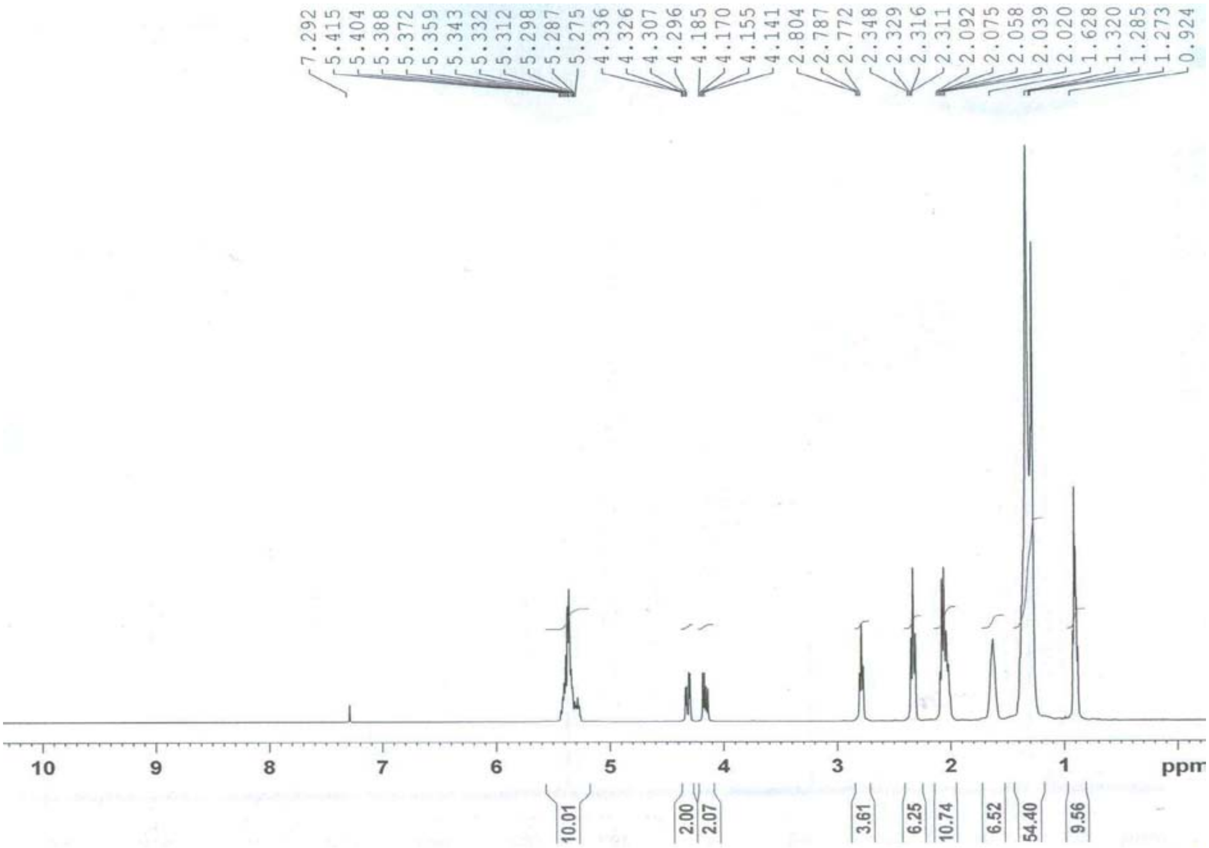
^{1}HNMR (400 MHz) of Corn oil



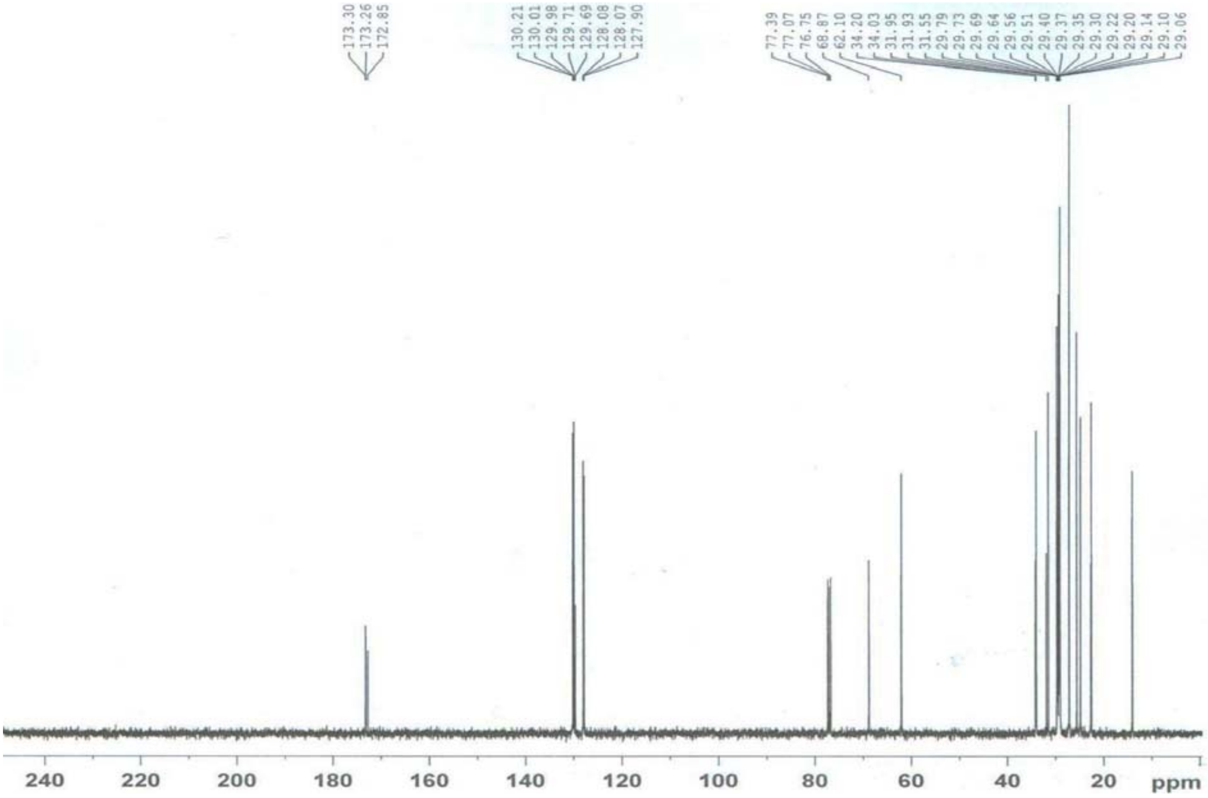
^{13}CNMR (100.6 MHz) of Corn oil

5 Sunflower oil

^{1}H NMR (400 MHz; CDCl$_3$): δ_H= 5.27-5.41 (m, 10H), 4.29-4.33 (dd, J_1= 4.0 Hz, J_2= 12 Hz, 2H), 4.14-4.18 (dd, J_1= 5.6 Hz, J_2= 12.00 Hz, 2H), 2.78 (t, J= 6 Hz, 3H), 2.32 (t, J= 7.6 Hz, 6H), 2.02-2.09 (m, 10H), 1.62 (brs, 6H), 1.27-1.32 (brs, 54H), 0.92 (m, 9H); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ_C= 173.2, 172.8, 130.2, 130.0, 129.9, 129.7, 129.6, 128.0, 128.0, 127.9, 68.8, 62.1, 34.2, 34.0, 31.9, 31.9, 31.5, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.3, 29.3, 29.3, 29.2, 29.2, 29.1, 29.1, 29.0, 27.2, 25.6, 24.8, 22.6, 22.6, 14.1



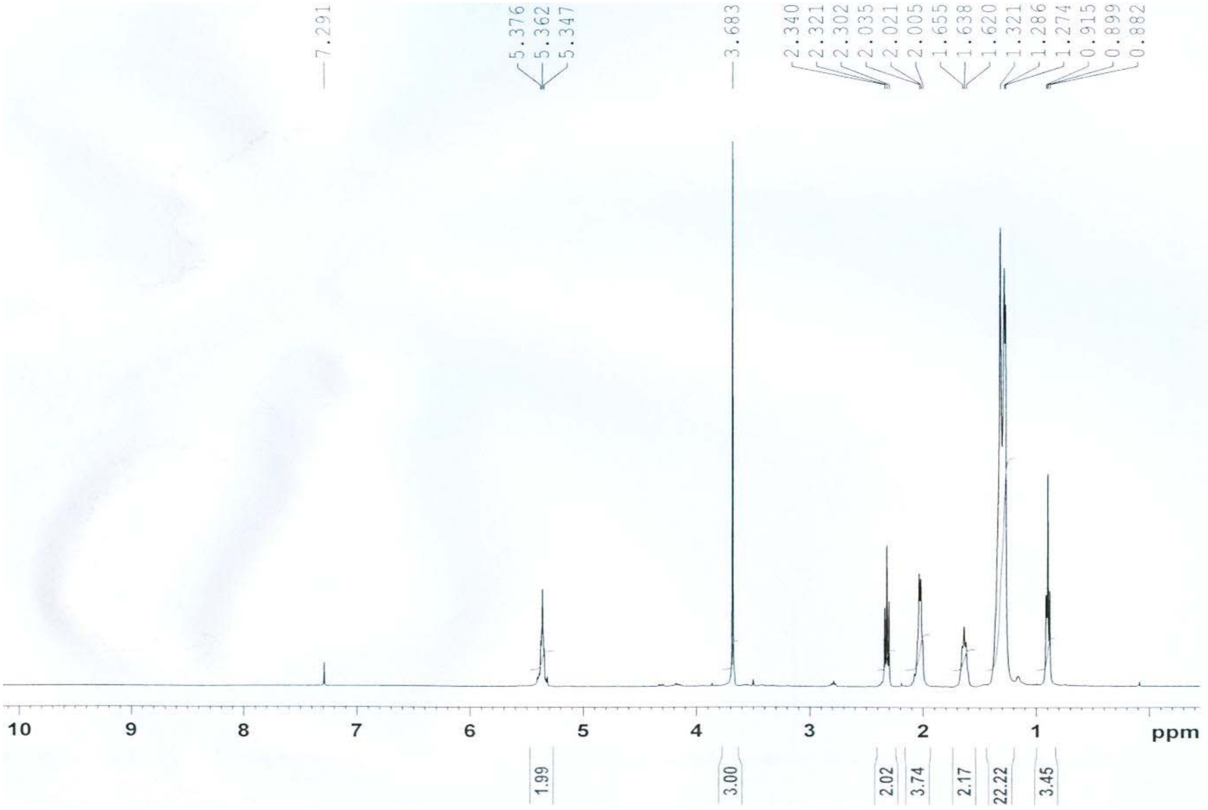
^{1}HNMR (400 MHz) of Sunflower oil



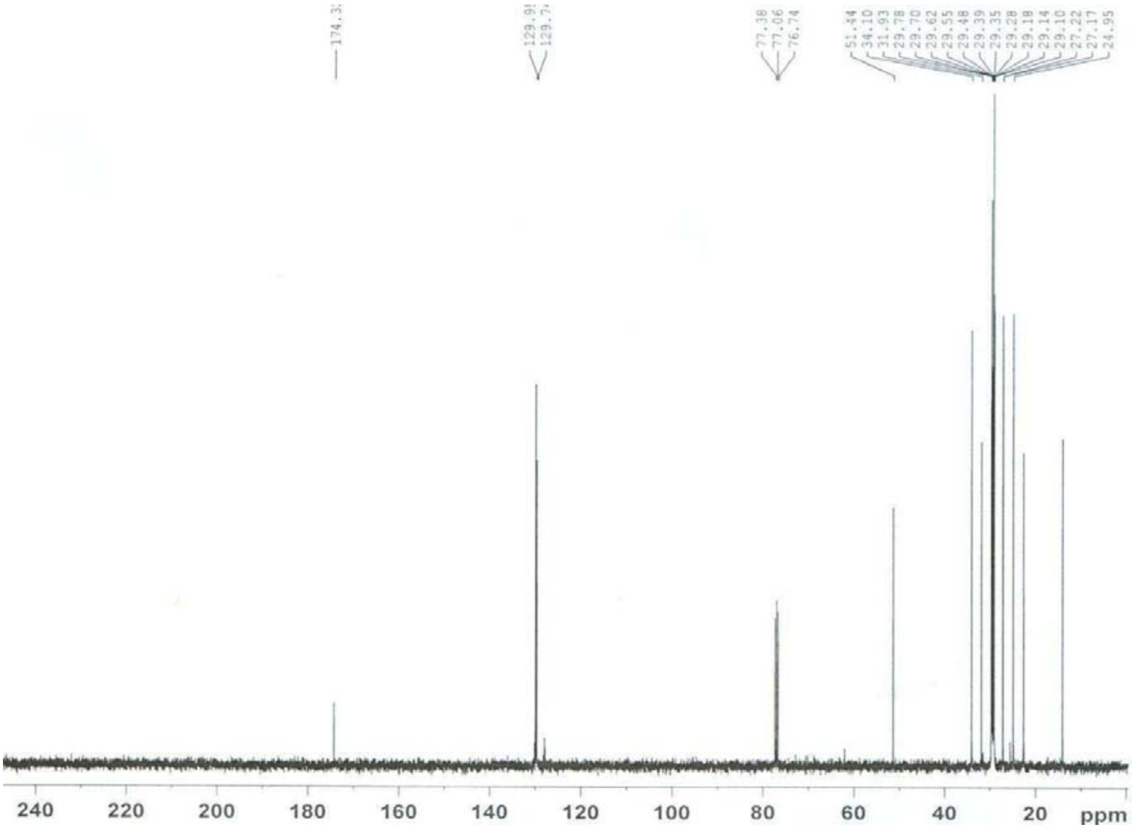
^{13}CNMR (100.6 MHz) of Sunflower oil

6 Biodiesel 99% from refined olive oil

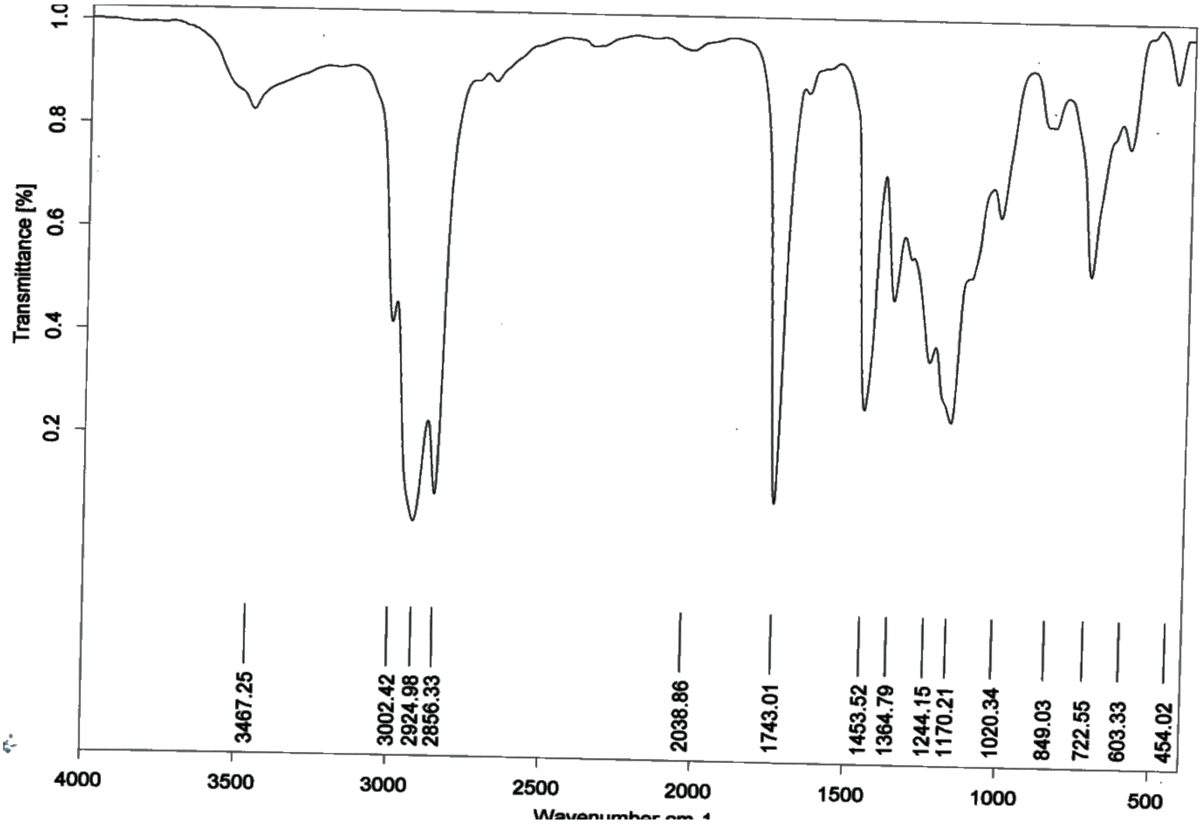
^{1}H NMR (400 MHz; CDCl$_3$): δ_H= 5.33-5.40 (m, 2H), 3.68 (s, 3H), 2.32 (t, J= 7.6 Hz, 2H), 2.00-2.03 (m, 4H), 1.62-1.65 (quin, J= 6.8 Hz, 2H), 1.27-1.32 (brs, 22H), 0.89 (m, 3H); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ_C= 174.3, 129.9, 129.7, 51.4, 34.0, 31.9, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.3, 29.2, 29.1, 29.1, 29.1, 27.2, 27.1, 24.9, 14.0



^{1}HNMR (400 MHz) of biodiesel 99% from refined olive oil



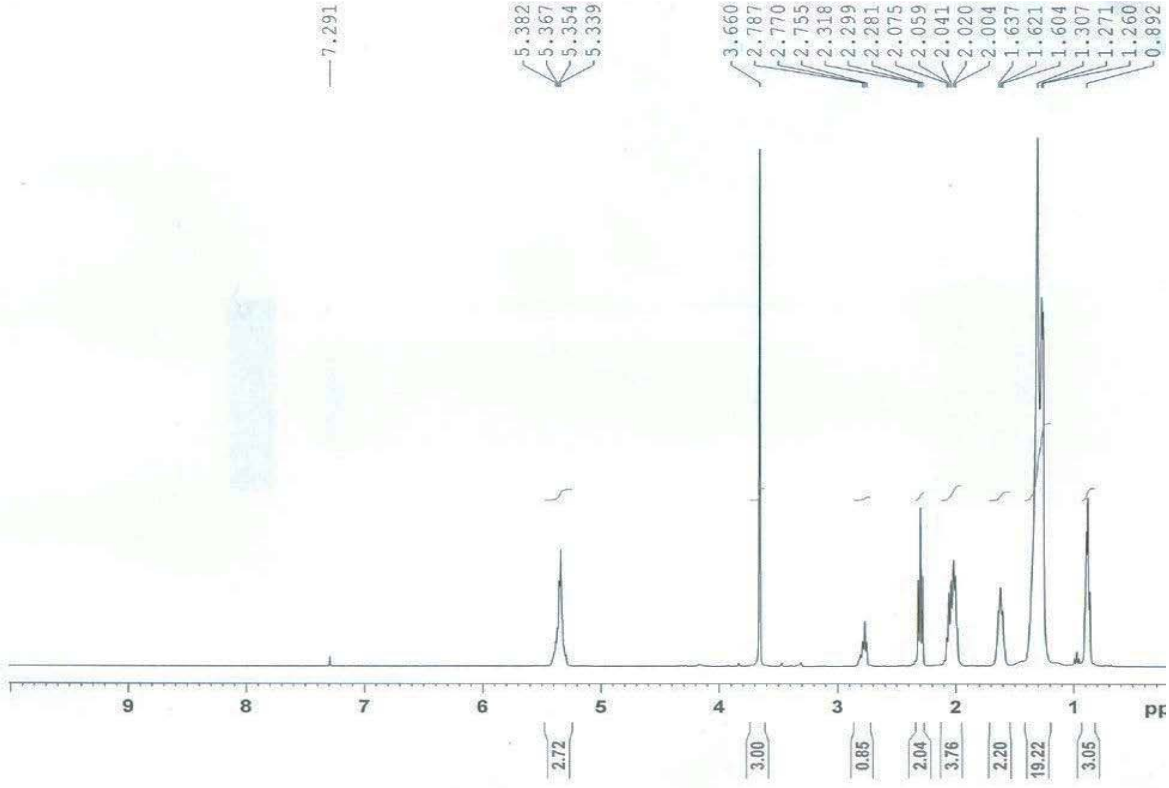
^{13}CNMR (100.6 MHz) of biodiesel 99% from refined olive oil



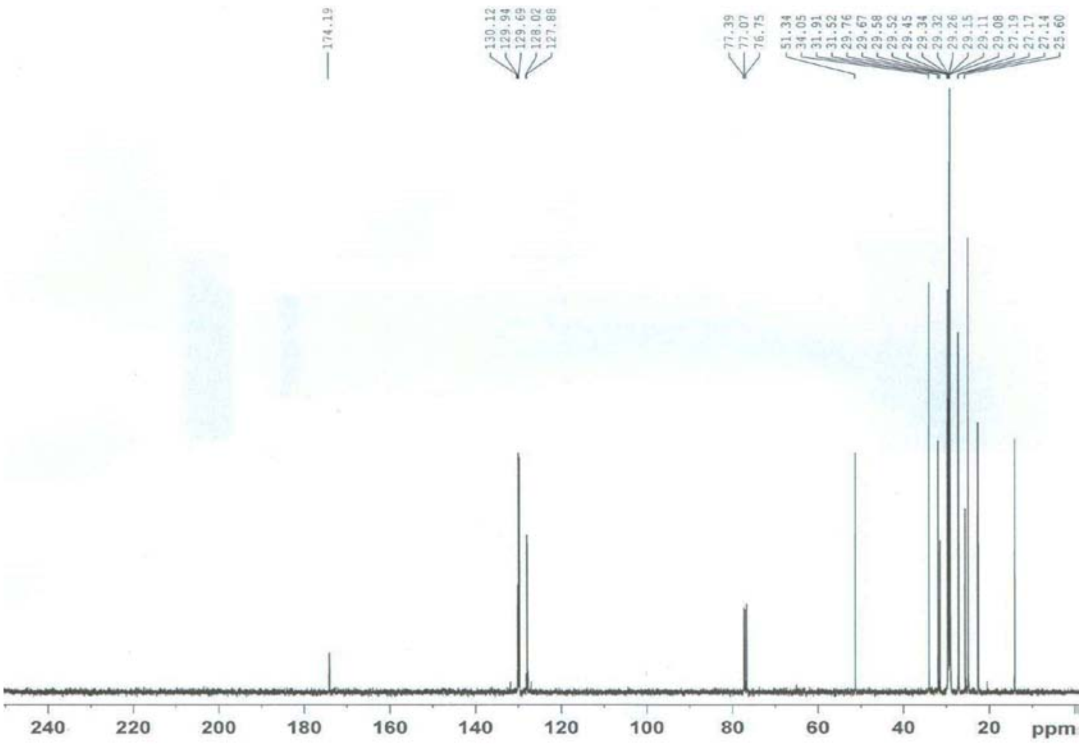
IR spectrum of biodiesel 99% from refined olive oil

7 Biodiesel 98% from Canola oil

^{1}H NMR (400 MHz; CDCl$_3$): δ_H= 5.34-5.38 (m, 3H), 3.66 (s, 3H), 2.77 (t, J=6 Hz, 1H), 2.30 (t, J= 7.6 Hz, 2H), 2.00-2.07 (m, 4H), 1.60-1.63 (t, J= 6.4 Hz, 2H), 1.31 (brs, 19H), 0.89 (m, 3H); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ_C= 174.2, 130.1, 129.9, 129.7, 128.0, 127.9, 51.3, 34.0, 31.9, 31.5, 29.7, 29.6, 29.5, 29.5, 29.4, 29.3, 29.3, 29.2, 29.1, 29.1, 29.1, 27.2, 27.2, 27.1, 25.6, 24.9, 14.0



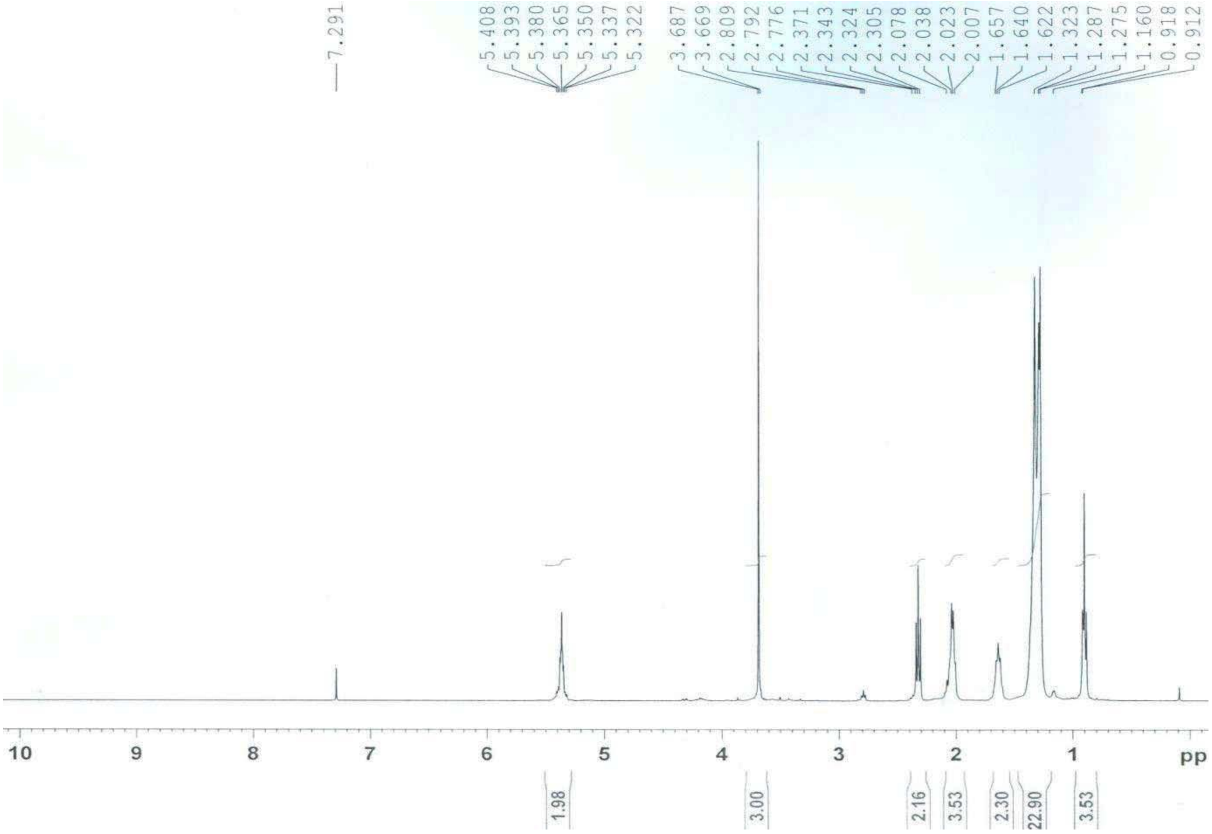
^{1}HNMR (400 MHz) of canola biodiesel (98%)



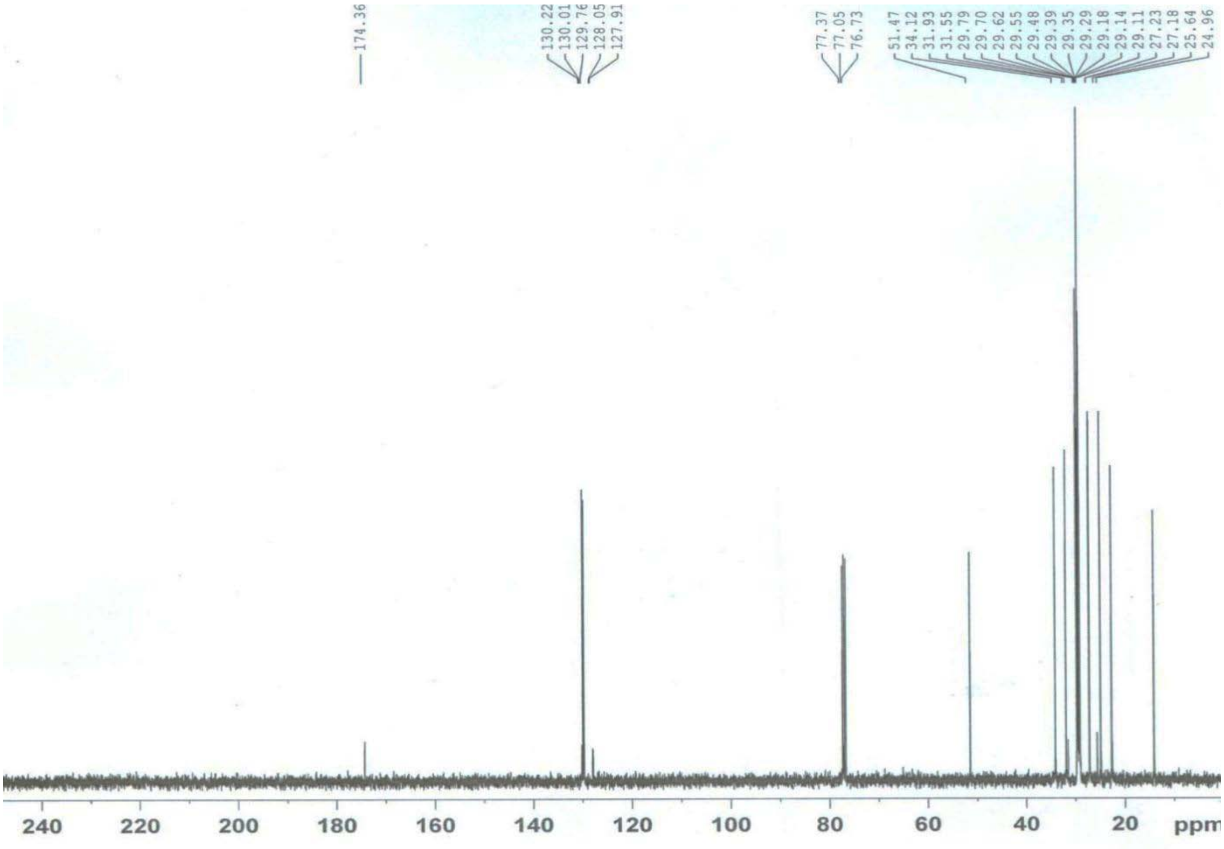
^{13}CNMR (100.6 MHz) of Canola biodiesel (98%)

8 biodiesel 93% from olive sludge extracted oil

^{1}H NMR (400 MHz; CDCl$_3$): δ_H= 5.32-5.40 (m, 2H), 3.68 (s, 3H), 2.32 (t, J= 7.6 Hz, 2H), 2.00-2.03 (m, 4H), 1.62-1.65 (quin, J= 6.8 Hz, 2H), 1.27-1.32 (brs, 23H), 0.91 (m, 3H); ^{13}C NMR (100.6 MHz, CDCl$_3$): δ_C= 174.3, 130.2, 130.0, 129.7, 128.0, 127.9, 51.4, 34.1, 31.9, 31.5, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.3, 29.2, 29.1, 29.1, 29.1, 27.2, 27.1, 25.6, 24.9, 14.0

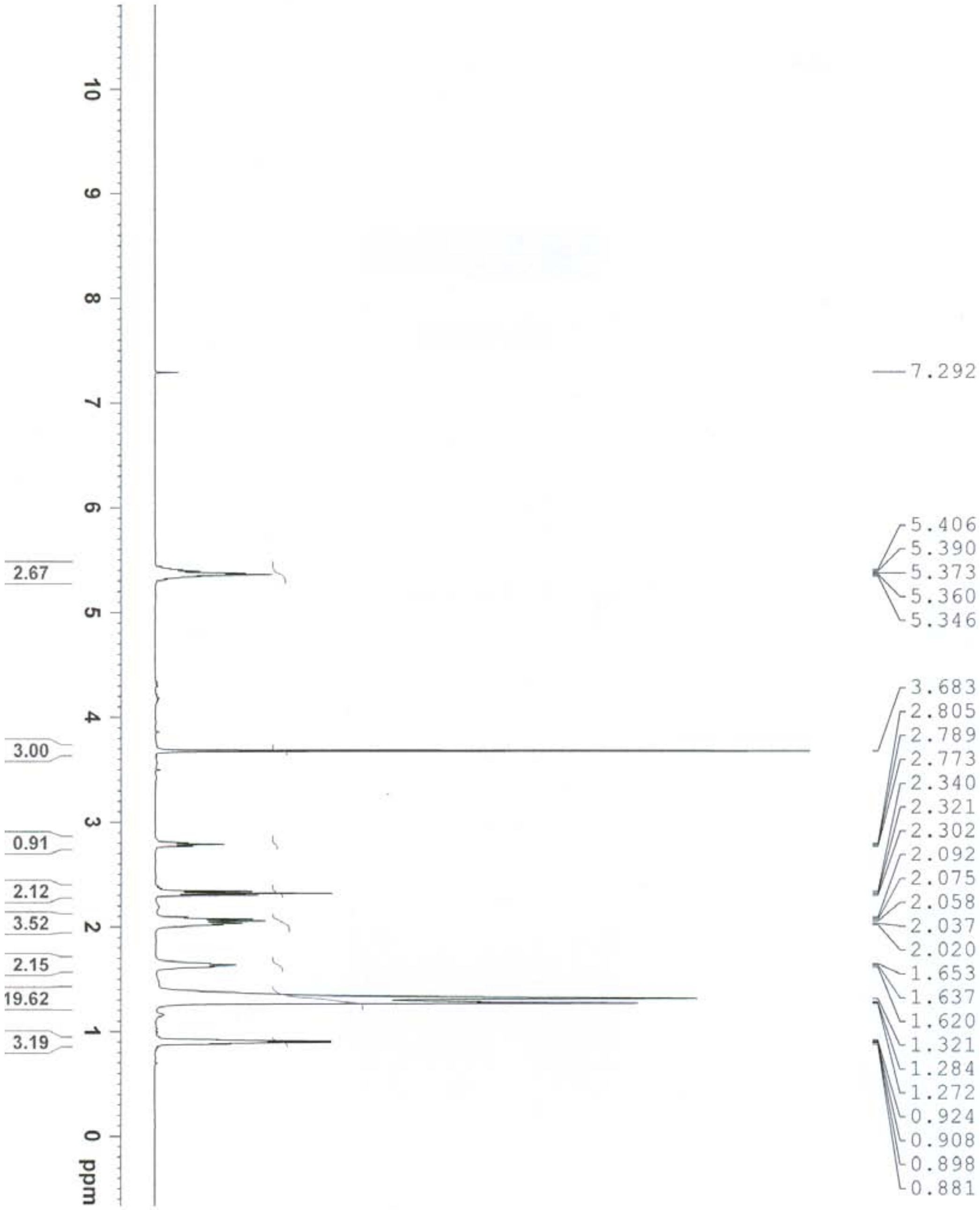


^{1}HNMR (400 MHz) of biodiesel (93%) from olive sludge extracted oil



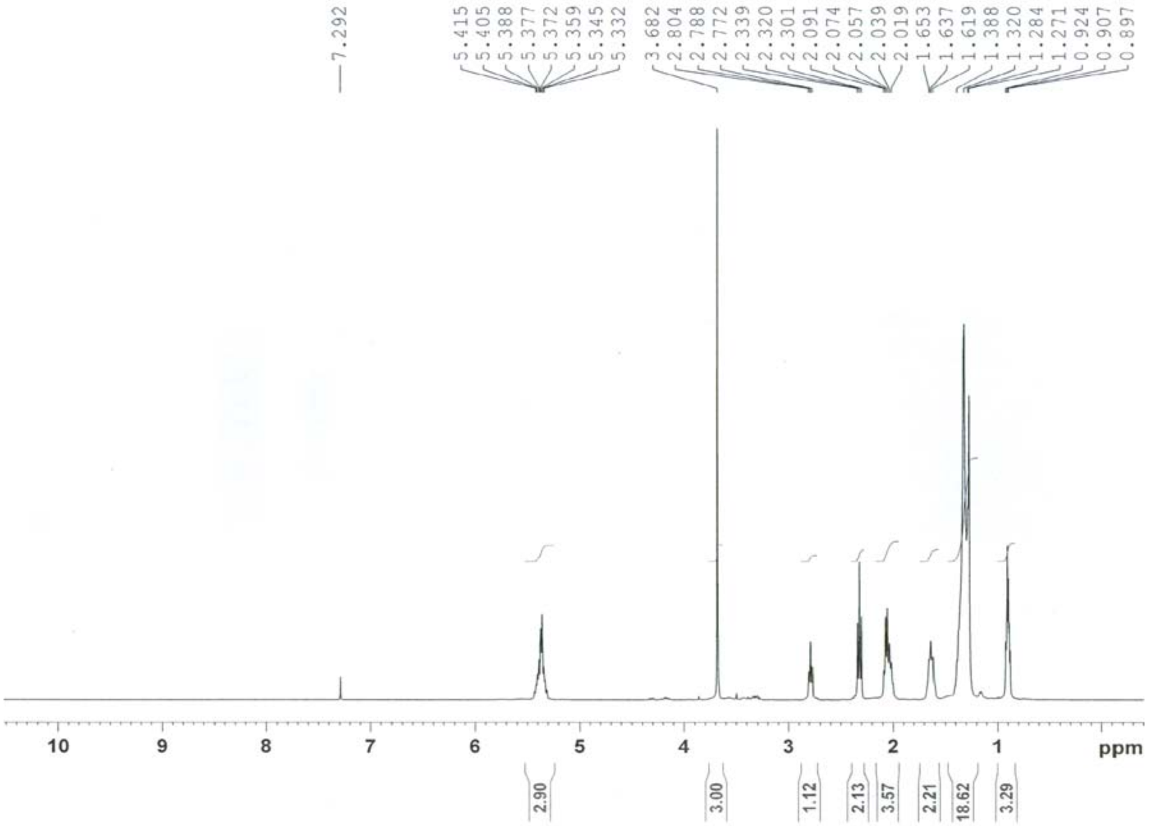
^{13}CNMR (100.6 MHz) of biodiesel (93%) from olive sludge extracted oil

9 Biodiesel from Corn Oil



^{1}HNMR (100.6 MHz) of Corn biodiesel (95%)

10 Biodiesel of sunflower oil

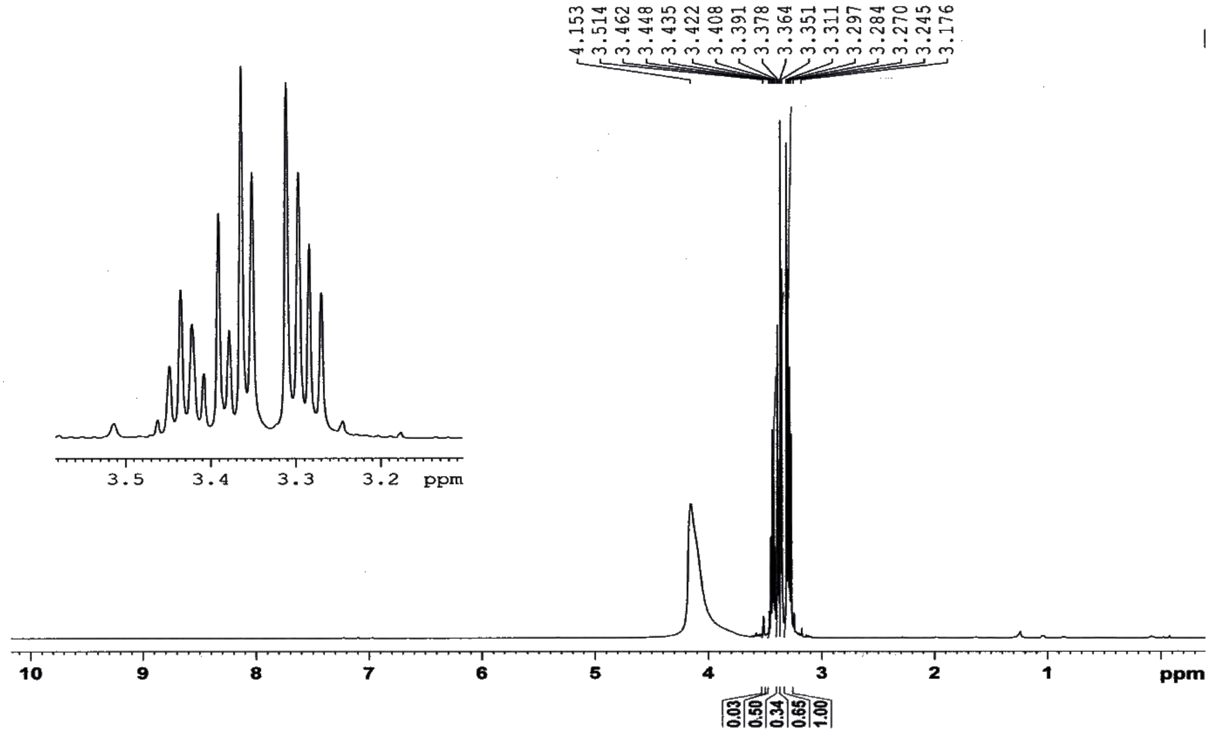


^{1}HNMR (100.6 MHz) of Sunflower biodiesel (94%)

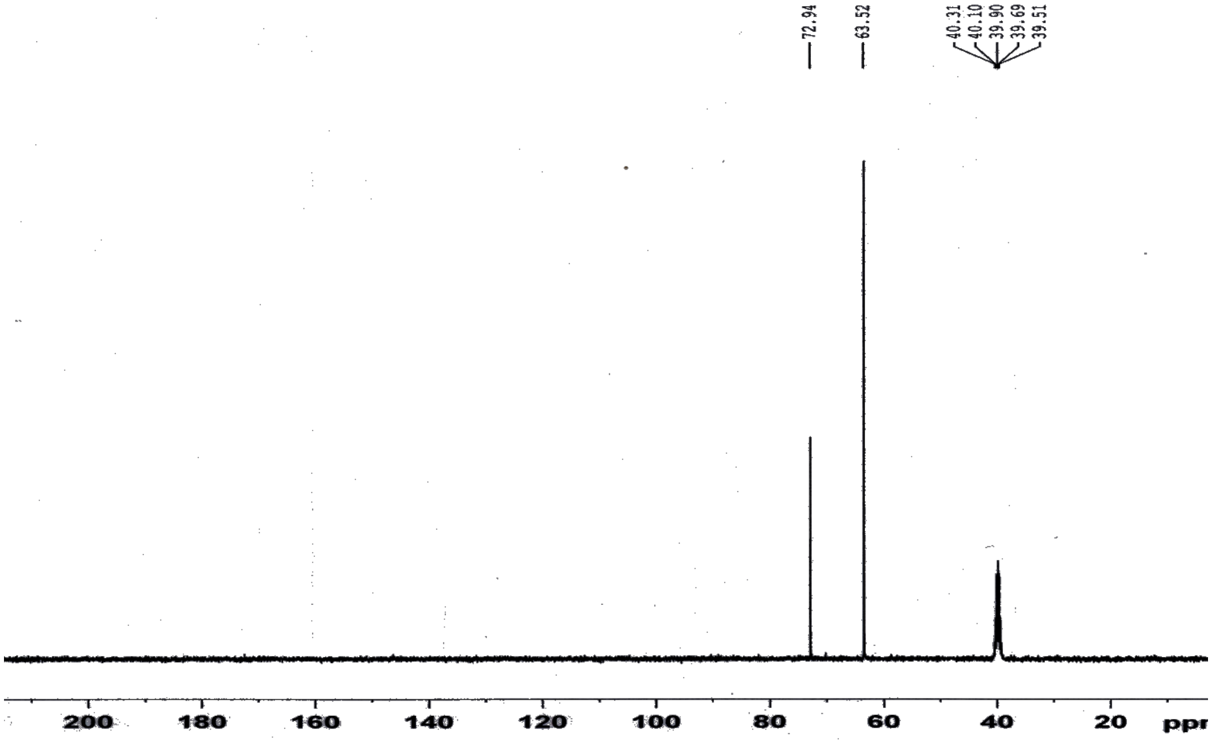
11 Glycerol

^{1}H NMR (400 MHz; DMSO): δ_H= 3.27-3.31 (dd, J_1= 5.6 Hz, J_2= 10.8 Hz, 2H), 3.35-3.39 (dd, J_1= 5.6, J_2= 10.8 Hz, 2H), 3.40-3.46 (quin, J= 5.6 Hz, 1H); ^{13}C NMR (100.6 MHz, DMSO): δ_C= 72.9, 63.5

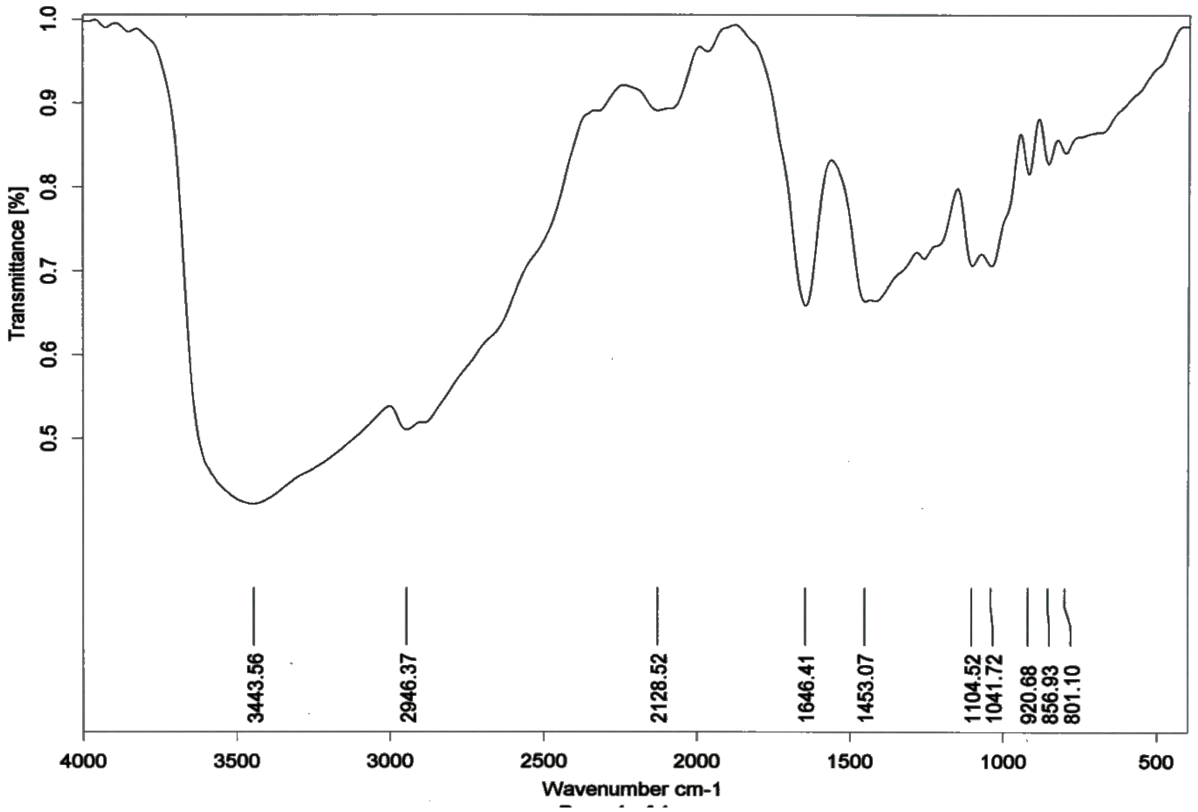
IR (neat): 801, 856, 920, 1041, 1104, 1453, 1646, 2128, 2500-3800 (broad)



^{1}HNMR (400 MHz) of Glycerol (by-product of biodiesel production)



^{13}CNMR (1006 MHz) of Glycerol (by-product of biodiesel production)



IR spectrum of Glycerol (by-product of biodiesel production)

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[2] B. Karimi and D. Zareyee, Design of a Highly Efficient and Water-Tolerant Sulfonic Acid Nanoreactor Based on Tunable Ordered Porous Silica for the von Pechmann Reaction, Org. Lett., 2008, **10**, 3989-3992.