



## Assessment of green biodiesel production based on Egyptian waste cooking oil using different porous membranes



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### Abstract

In this study, green biodiesel was produced from Egyptian waste cooking oil by trans-esterification reaction using membrane technology. The produced biodiesel was characterized by physicochemical properties, FTIR, and gas chromatography/mass spectrometry (GC/MS). It was found that it meets the specifications of the American standard test method (ASTM) D6751. Because glycerol was the only impurity that was difficult to separate from the prepared biodiesel by regular methods, polysulfone (PS) membrane and three hybrid membranes were prepared using the phase inversion method for the glycerol purification process. The hybrid membranes were prepared by mixing PS with different weight ratios of polyethylene glycol (PEG), polyvinyl pyrrolidone (PVP), and zinc oxide nanoparticles (ZnO NPs). The structure and surface morphology of the resulted membranes were characterized by scanning electron microscope (SEM), Fourier-transform infrared spectroscopy (FTIR), and thermal gravimetric analysis (TGA). The purification efficiency of these membranes was satisfied by high-performance liquid chromatography (HPLC) and weight loss ratio. The HPLC chromatogram showed that the membrane of the PS/ZnO NPs provided the highest separation rate of the biodiesel by-product glycerol compared to the other ones.

**Key words:** Waste cooking oil, biodiesel, polysulfone, hybrid membranes, trans-esterification process, phase inversion method.

### 1. Introduction

The increase in demand for fossil fuel in all human life like agriculture, transportation, human consumption, types of energy generation, industry, food and production of electricity [1] leads to rising the emission of CO<sub>2</sub> and greenhouse gases (GHG) like CO and methane that release to the atmosphere and cause some environmental problems like global warming, ozone depletion, acid precipitation, forest destruction, emissions of dangerous substances and air pollution. The amount of CO in the atmosphere increases due to fossil fuel combustion, the production of cement, green land removal and electricity production which is being the largest emission of CO. This problem must be taken into

consideration if we need to use renewable energy rather than fossil fuels in all human lives [2,3].

The major energy resources are petroleum, coal and natural gas that are non-renewable; these energy sources are decreasing day by day [4]. Due to the problems associated with using petroleum as a fuel and their higher cost; scientists are searching for alternative fuel without the previous problems and with the lowest cost such as solar energy, wind, hydroelectric energy, nuclear energy and biofuel energy. For developing countries, biofuel can provide a feasible solution to these problems.

The biofuel may be alcohol, vegetable oils, biomass, and biogas. Some of these fuels can be utilized directly while others need some processes

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to be fuel. The most common sources of biofuel are vegetable oil, fat, lard and tallow. Vegetable oil is the most preferable oil in the existing diesel engines due to it has good physico-chemical properties like octane number, cetane number, heat of vaporization, and stoichiometric air/fuel ratio with mineral diesel fuel [5]. In 1900, Rudolf Diesel used vegetable oil as a fuel in his engine [6] but his tries led to several engine problems due to its high viscosity, the chemical structure of triglycerides and incomplete combustion. Thus, one of the aims of this work is to prepare an alternative fuel for petroleum diesel derived from waste cooking oil by reducing its viscosity [7-9].

Vegetable oil consists of free fatty acids and triglycerides which is the feedstock of biofuel production [10]. Biodiesel is the most preferred biofuel because it is derived from vegetable oils or animal fats. So it is considered to be a green fuel, low toxicity, less effects on human health, higher flash point, lower emissions of pollutants such as CO, SO<sub>2</sub> and particulate matter such as polycyclic aromatic hydrocarbons, aldehydes and can be used in compression ignition engine(CIE) directly or blended with diesel fuel [11-14].

Biodiesel is a liquid biofuel and mono alkyl ester produced by trans-esterification of triglycerides and alcohols in the presence of homogeneous, heterogeneous or enzymatic catalyst [15]. The source of triglycerides is a vegetable oil such as palm oil (South-East Asia)[16], soybean oil (US)[17], *jatropha curcus* oil, rapeseed oil (Europe), and rice bran oil (India) and non-vegetable oil such as animal fats and waste cooking oil as a feedstock [18,19]. Alcohol such as methanol is used due to its lower cost compared to that of other alcohols [20]. Vegetable oil has a higher cost than petroleum diesel. So, biodiesel was prepared in this work from waste cooking oil owing to its lower cost [21].

At the end of trans-esterification, the glycerol was separated from the biodiesel by gravitational settling or centrifugation due to its higher density

## Materials and methods

### 1.1. Materials

Waste cooking oil (WCO) was collected from cafeterias, restaurants, and household kitchens, Cairo, Egypt. All solvents [e.g. methanol, N-methyl pyrrolidone (NMP)] and polymers [e.g. PS, PEG with molecular weight 8000, polyvinyl pyrrolidone (PVP)] were purchased from Sigma-Aldrich Company. Potassium hydroxide, zinc sulphate hepta-

hydrate and sodium hydroxide, were also procured from Sigma-Aldrich Company.

than biodiesel. Crude biodiesel is impure and contains several impurities such as soap, non-reacted triglycerides, alcohol and catalyst. It must be purified from impurities to increase its quality as a fuel in the CIE and to meet the severe international standard specification provided by EN14214 [22].

Purification of biodiesel is achieved by wet washing, dry washing or membrane. The wet washing has been used to separate impurities of biodiesel with several problems such as higher cost, purification time and wastewater production. On the other hand, dry washing technique (using magnesol powder and ion exchange resins) requires expensive raw materials, large particle size of magnesol or ion exchange powder grains making them very difficult to be removed and causing fuel contamination [23,24]. Due to the problems associated with dry and wet washing techniques, all eyes have turned on membrane purification.

Membranes are semi-permeable barriers homogenous or heterogeneous, solid or liquid, organic or inorganic, hydrophilic or hydrophobic nature and are used in the purification of biodiesel from impurities based on particle size, hydrophilic or hydrophobic nature [25,26]. In addition, they have several advantages such as simplicity, high yield, high purity and high quality of biodiesel with less energy consumption and lower cost [27-29].

This paper focus on the preparation of new membranes based on PS which are widely used as a polymer for commercial ultra-filtration and microfiltration membranes. PS as a thermoplastic polymer has been used as a support material for nano-filtration and reverse osmosis membranes, because it has high thermal (150–170°C) and chemical stability, mechanical strength and microorganism resistance [30-33]. Additives such as PEG, PVP and ZnO NPs were separately used with PS to produce composite membranes. Efficiency of the latter were evaluated for biodiesel purification and compared with that of PS-based membrane (traditional membrane).

hydrate and sodium hydroxide, were also procured from Sigma-Aldrich Company.

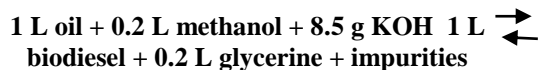
### 1.2. Methods

#### 1.2.1. Pretreatment of waste cooking oil

Waste cooking oil was filtered using wool fibre to eliminate any indiscernible impurities and then heated up to 100°C to remove moisture.

### 1.2.2. Trans-esterification of waste cooking oil (biodiesel production)

Process of biodiesel production is a reversible reaction (reaction 1). Therefore, an excess of alcohol was added (1:5 oil: alcohol ratio) to shift the reaction direction towards the biodiesel formation [34].

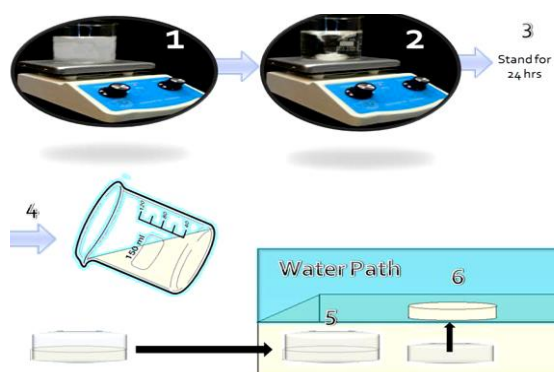


**Reaction 1.** Production of biodiesel via trans-esterification reaction [35].

Methoxide solution was primarily prepared by mixing methanol with potassium hydroxide (KOH). A half quantity of methoxide solution was added to treat waste cooking oil and stirred for 10 min with heating up to 60°C. The remaining quantity of methoxide was added to the mixture with continuous stirring at 1000 rpm and heating up to 60°C for 1 hour. The brown solution product was left to stand for 1 day. After that, it separated into two phases according to density, the upper phase was biodiesel and the lower one was glycerol [36].

### 1.2.3. Preparation of membranes

The pure PS and PS hybrid membranes were selected according to their compatibility with the solvents and commercial availability. These membranes were prepared via phase inversion method as is shown in **Figure 1**. The phase inversion method is the process of preparing asymmetric membranes and plays an important role in membrane structure formations. It is not only a thermodynamically process but a kinetic process as well.



**Fig.1.** Graphical representation of membrane preparation by phase inversion method.

The process of inversion involved a two-phase conversion of the homogeneous PS solution, one of which is a solid phase; it was rich in the polymer and formed the membrane. A liquid phase is another one; it produced pores [37-43].

### 1.2.3.1. Preparation of polysulfone membrane without additives

1 gm of PS was placed in a bottle with 20 ml of N-methyl pyrrolidone (NMP). The solution mixture was stirred at 300 rpm up to 6 hours for complete miscibility and to produce a homogenous polymer solution. It was left at room temperature for 24 hours to remove bubbles and then poured into a glass plate using a hand-casting knife with a knife gap set at 200µm followed by immediately immersing the glass plate into de-ionized water at room temperature to solidify the solution in the form of membrane sheet which stored between two filter papers (**Fig. 1**) [44].

### 1.2.3.2. Preparation of ZnO nanoparticles

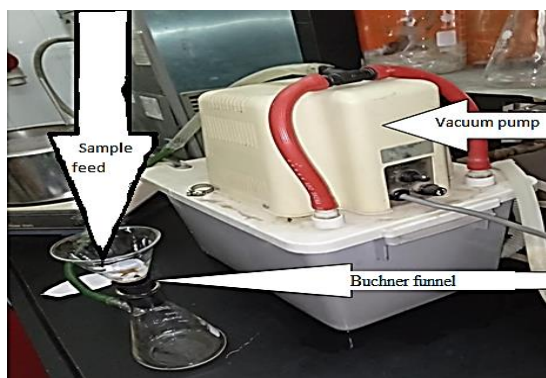
ZnO<sub>2</sub> NPs were prepared according to [45] as follows: To the aqueous solution of zinc sulphate heptahydrate, sodium hydroxide was added drop wise in a molar ratio of 1:2, under vigorous stirring, and the stirring action is continued for almost 18 hours and large amount of white precipitate was formed, this precipitate was filtered and washed with distilled water and dried using a muffle furnace at a temperature of 100°C and it is ground to fine powders.

### 1.2.3.3. Modification of polysulfone membrane

The PS membrane was modified separately with PEG, PVP and ZnO NPs to produce hybrid membranes. One gm of PS and 0.4, 0.6 or 1.2 gm of PEG, PVP and ZnO NPs were singly placed in a bottle containing 20 ml of NMP. The solution mixture was stirred at 300 rpm up to 6 hours for complete miscibility and a homogenous polymer solution is formed, then left at room temperature for 24 hours to remove any bubbles. After that, it was poured into the glass plate by means of a hand-casting knife with a knife gap set at 200µm followed by immediately immersing the glass plate into the de-ionized water at room temperature to solidify the solution. The prepared membrane sheets were stored between two filter papers (**Fig. 1**) [46].

### 1.2.4. Application of the prepared membranes in purification of biodiesel from glycerol

Purification of biodiesel with membranes was done using a Buchner funnel and driving force such as oil pump or vacuum pump (**Fig. 2**). The prepared membranes were used in the filtration process by separating crude biodiesel into two phases. The upper phase glycerol was located on the surface of the membrane and the lower phase biodiesel was located at the bottom of the Buchner.



**Fig. 2.** Biodiesel purification technique

### 1.3. Characterization of biodiesel and membranes

The produced biodiesel was characterized using Fourier-transform infrared spectroscopy (FTIR) (Instrument Model Spectrum Two, Detector MIR TGS) in order to recognize the functional groups in this biodiesel and their structure. In addition, physico-chemical tests were done at the Egyptian Petroleum Research Institute (EPRI) on the produced biodiesel (**Tables 1&2**) to satisfy it as a fuel.

Chromatographic analysis using gas chromatography/mass spectrometry (GC/MS) was performed (Agilent Technologies 7890B GC Systems combined with 5977A Mass Selective Detector). Capillary column was used (HP-5MS Capillary; 30.0 m  $\times$  0.25 mm ID  $\times$  0.25  $\mu$ m film) and the carrier gas was helium at a pressure of 7.5 psi with 1  $\mu$ l injection). The constituents were determined by mass fragmentations with the NIST mass spectral search program for the NIST/EPA/NIH mass spectral library Version 2.2 (Jun 2014). The sample was analysed with the column held initially for 3 min at 60°C after injection, then the temperature was increased to 275°C with a 15°C/min heating ramp, with a 3.0 min hold. The injection was carried out in split mode (10:1) at 300°C. MS scan range was ( $m/z$ ): 30–450 atomic mass units (AMU) under electron impact (EI) ionization (70 eV).

High performance liquid chromatography (HPLC) (HPLC Agilent 1100 with quaternary pump, the mobile phase is water with flow rate 1 ml /min, Agilent XDBC 18 column 4.6\*150 mm, diode array detector at wavelength 190 nm) to identify the

**Table 1:** Properties of waste cooking oil.

Property	ASTM Standard Method	Result
Density at 15.56°C, kg m <sup>-3</sup>	D-4052	911
Specific gravity		0.9126
API gravity at 60 °F		23.56
Total acid number, mg KOH/ gm	D-664	0.98
Free fatty acid		0.98/1.989= 0.49
Kinematic viscosity at 40°C (cSt)	D-445	3.321

chemical components of the biodiesel. The prepared membranes were characterized using FTIR.

Scanning electron microscope (SEM) (using SEM model Quanta FEG EMRA1n) to identify the morphology of membranes. The membranes were coated with gold by (K550X sputter coater, England) then scanned by scanning electron microscope.

Thermal gravimetric analysis (TGA) of pure and hybrid PS membranes was done by means of LINSEIS (STA PT1600 each powdered sample was heated by 10°C/min up to 1000°C temperature, weight, change in Wt. and thermal behaviour of the samples are recorded in the charts).

### 1.4. Evaluation of the prepared membranes for biodiesel purification

Evaluation of the prepared membranes towards biodiesel purification was done using weight loss (difference in weight between biodiesel before and after purification) and HPLC.

All characterizations cited above were conducted based on international standards.

## 2. Result and discussions

### 2.1. Characterization of waste cooking oil and biodiesel

Waste cooking oil (WCO) and the produced biodiesel were characterized by several physico-chemical tests (**Table 1**) and FTIR to satisfy the conversion of WCO to biodiesel (**Fig. 3**). Viscosity and free fatty acid (FFA) were measured to determine the availability of WCO for using it as a fuel or in trans-esterification directly. If the acid value is very high, WCO requires a pre-treatment to decrease its fatty acid content before the conversion to biodiesel to prevent saponification reaction. Previous studies [47-49] have suggested that, feedstock FFA content before trans-esterification should be 0.5-1% and higher than 0.5% content of FFA in WCO must be reduced. Table 1 shows that, the waste cooking oil used in the current work had a density of 911 kg m<sup>-3</sup> at 15.56°C, kinematic viscosity of 3.321 cSt (centistokes) (1 cSt = 1 mm<sup>2</sup>·s<sup>-1</sup> = 10<sup>-6</sup> m<sup>2</sup>·s<sup>-1</sup>.) at 40°C and FFA of 0.49. These data show that this feedstock is appropriate to obtain high ester yields.

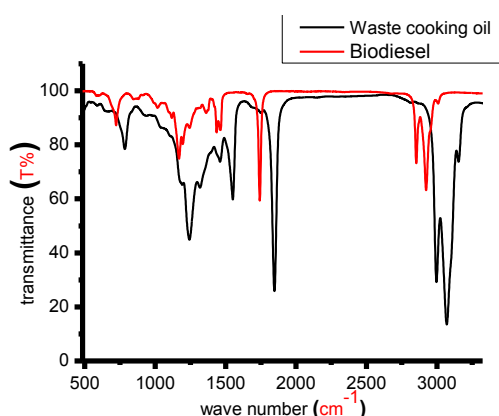
#### 2.1.1. Physico-chemical tests

**Table 2:** Properties of biodiesel and diesel and ASTM of biodiesel

Experiment	ASTM Standard Method	Result of biodiesel	Diesel	Biodiesel (ASTM)
Density @15.56°C, kg m <sup>-3</sup>		0.9045		
Specific gravity	D-4052	0.9054	0.855	0.86-0.90
API gravity @60 °F		24.79		
Total acid number, mg KOH/ gm	D-664	0.323	0.062	Max 0.50
Kinematic viscosity @40°C (cSt)	D-445	2.389	2.6	1.9 - 6
Total Sulfur, wt %	D-4294	Not detected	0.0-0.0024	0.0015 max
Cloud point, °C	D-97	9	-35 to 5	-3 to 15
Flash point, °C	D-92	175	60-80	100-170
Fire point, °C	D-92	195		
BS and W, vol. %	D-96	Nil		
Cetane index	D-976	44.11		
Cetane number	D-613	41.76	40 -55	48 – 65

### 2.1.2. Fourier-transform infrared spectroscopy of biodiesel and waste cooking oil

In **Figure 3**, the FTIR spectrum showed stretching absorption band in the region of 1743.33 cm<sup>-1</sup> due to C=O of the formed ester. Four bands in the region of 1000–1300 cm<sup>-1</sup> are assigned to the asymmetric and symmetric vibration modes of methyl groups and ethylene groups, respectively. Stretching band at 2927 cm<sup>-1</sup> was the characteristic of sp<sup>3</sup> C-H aliphatic group.

**Fig. 3.** FTIR of waste cooking oil and biodiesel.

### 2.1.3. Biodiesel analysis

Physico-chemical and thermal properties of the produced biodiesel were measured according to the American Society for Testing and Materials (ASTM) D6751 for evaluating the quality standards of biodiesel (**Table 2**).

#### 2.1.3.1. Physico-chemical properties of biodiesel

##### 2.1.3.1.1. Yield of biodiesel

Biodiesel yield was calculated using the following equations

$$\text{Yield (\%)} = \frac{\text{Amount of biodiesel produced}}{\text{Amount of oil used}} * 100$$

In this work, the yield was recorded up to 98%

##### 2.1.3.1.2. Biodiesel density

The density of biodiesel depended on the feedstock used in the production process. Measurements of biodiesel density was done based on pycnometer cup. As the chain length of fatty acid methyl esters (FAMES) increases, the density increases. So, The biodiesel produced from saturated fats is denser; it contains more energy than biodiesel produced from unsaturated fats. The measured biodiesel density was found to be 0.9045; it was under the ASTM standards [50,51].

##### 2.1.3.1.3. Total acid number

It is described as the amount of KOH per mg used to neutralize the acid content in a fuel. The acid value was measured using the acid base titration method in presence of phenolphthalein as an indicator. The acid value and viscosity of biodiesel may be increased with increasing storage time and the higher content of acid in fuel caused corrosion problems in the fuel supply system. Pure biodiesel is not acidic with a maximum of 0.5mg KOH/g. The total acid number of biodiesel was found to be 0.323; which was under the ASTM standards [52,53].

$$\text{Acid value} = \text{FFA (free fatty acid) \%} \times 1.989$$

$$\text{FFA (free fatty acid)} = \frac{\text{acid value}}{1.989} = \frac{0.323}{1.989} = 0.1623$$

##### 2.1.3.1.4. Kinematic viscosity

The Kinematic viscosity is the resistance of a liquid to flow. It is used as an indicator to measure the completeness and effectiveness of biodiesel. Fuel with high viscosity leads to forming large droplets on the injection pump, causing high smoke emission and poor combustion. The fuel with low viscosity contains high fatty acid methyl ester (FAME) and good combustion with low smoke and emissions. So, trans-esterification was prior. It was used to decrease

the viscosity of the fuel. The viscosity of the prepared biodiesel was found to be 2.389; it was under the ASTM standards [54-55].

#### 2.1.3.1.5. Sulfur content

Sulfur content is undesirable in fuel; it causes harmful corrosion in the engine and has a negative effect on human health. Biodiesel produced from fresh vegetable oil had no sulfur content. On the other hand, biodiesel produced from waste vegetable oil might contain traces of sulfur. The sulfur content of the prepared biodiesel was not detected and this is fitted with the ASTM standards [54]

#### 2.1.3.1.6. Cloud point and pour point

Cloud point is the temperature at which the crystal formation starts to form precipitates. Pour point is the temperature at which the fuel begins to flow. Below the cloud point, the crystal drop at the bottom of the tank. The cloud and pour point give a minimum temperature at which fuel ignites efficiently. At cloud point, the biodiesel cannot be used, but at pour point, biodiesel can be used. The cloud point of biodiesel was found to be 9; and this is according to the ASTM standards [56].

#### 2.1.3.1.7. Flash point and fire point

The flash point is the temperature at which the fuel inflames, but forms spark due to the formation of a homogeneous mixture of fuel vapour and the air above the fuel surface. The fire point is the temperature at which fuel ignites. The fire point of biodiesel was found to be 195; which was under the ASTM standards.

The flash point is an important test for biodiesel, which determines the ability of fuel to storage and handling. The flash point of biodiesel was found to be 175 and it was under the ASTM standards and higher than diesel [57]. The high flash point makes fuel less volatile fuel and safer to transport than petroleum diesel [53-55].

#### 2.1.3.1.8. Cetane number

The cetane number is the ability of fuel to ignite quickly after being injected. The ignition quality of the fuel become better as the cetane number increase[58]. The cetane number of the prepared WCO biodiesel was 41.76, which is within the recommended range for diesel.

#### 2.1.3.1.9. Bottom sediments and water

Bottom sediment and water (BS and W) test method cover the centrifuge method for determining sediment and water in crude oil. It is not the most accurate, but the most practical method for field

determination. The BS and W of the prepared biodiesel were not detected.

#### 2.1.4. Gas chromatography - mass spectrometry

The prepared biodiesel was characterized by GC-MS techniques as shown in **Figure 4**. The fatty acid content of the waste cooking oil is completely converted into the respective fatty acid methyl esters. Four esters were identified in the GC-MS analysis and recorded with their retention times (RT) in **Table 3**. The mass spectrometry for each peak of these esters is shown in **Figures 4a-d**. The constituents were determined by mass fragmentations with the NIST mass spectral search program for the NIST/EPA/NIH mass spectral library Version 2.2 (Jun 2014).

**Table 3**

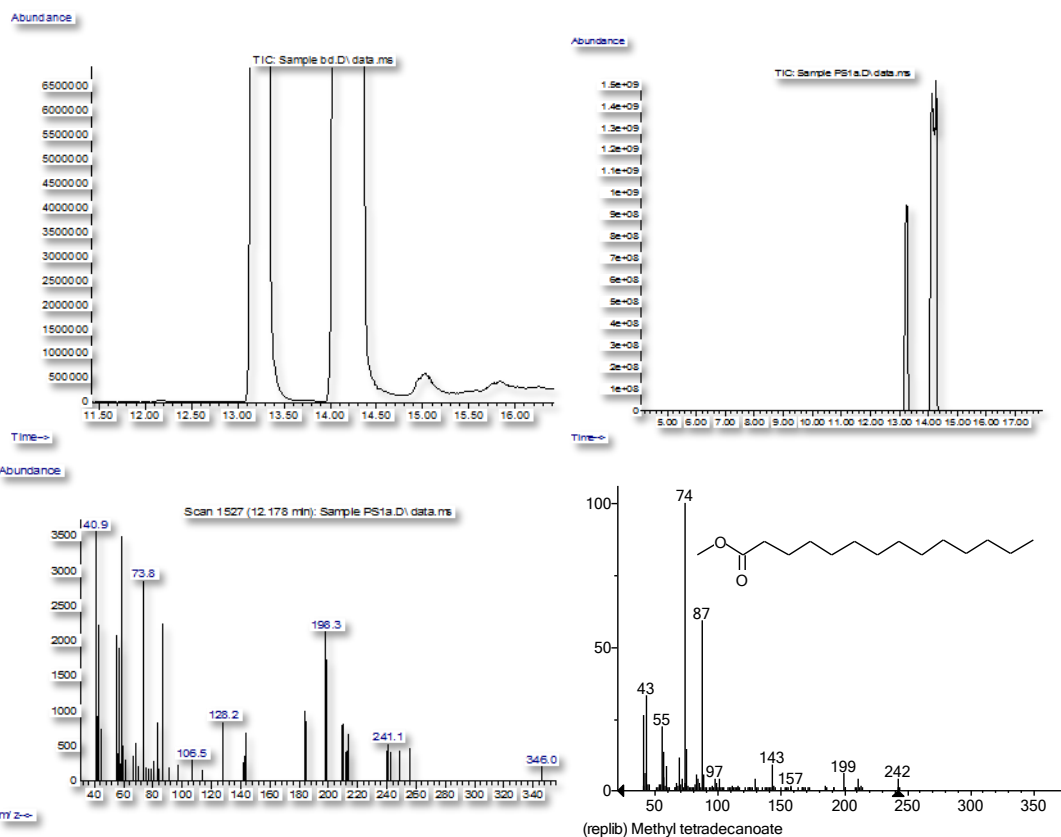
Biodiesel components with their retention times

RT	Name of ester	Figure number
12.30	1) Methyl tetra decanoate	4a
13.30	2) Palmitic acid methyl ester	4b
14.06	3) Linoleic acid methyl ester	4c
15.00	4) 11-Eicosenoic acid methyl ester	4d

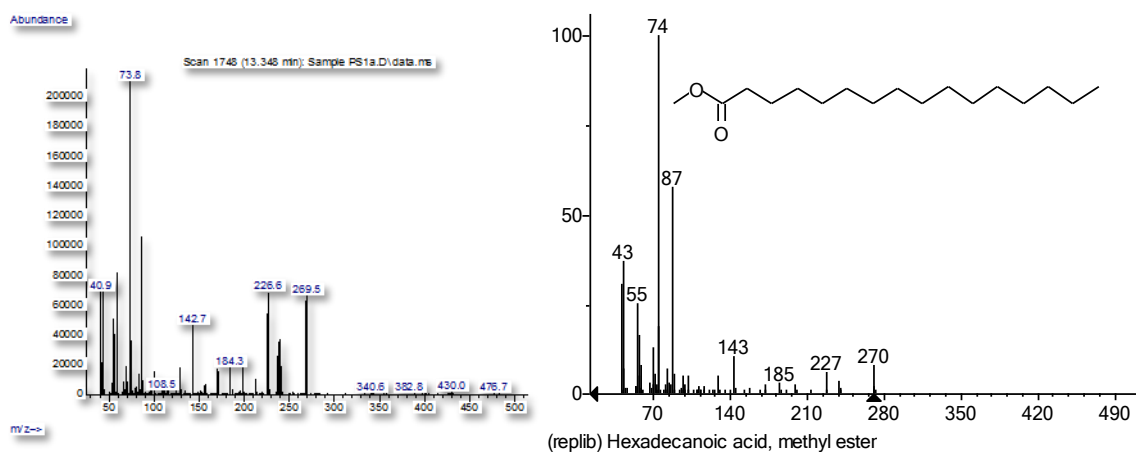
#### 2.2. Characterization of the prepared membranes

##### 2.2.3. Fourier-transform infrared spectroscopy

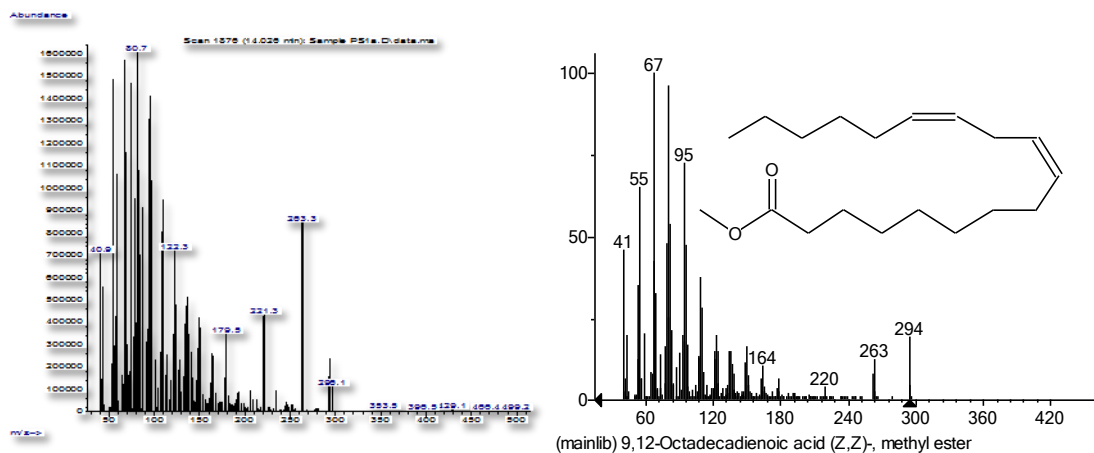
FTIR spectrum of pure PS and PS/PEG, PS/PVP and PS/ZnO NPs hybrid membranes are shown in **Figures 5a-c**, respectively. It is evident (**Fig. 5a**) that, FT-IR spectrum of PS showed two bands at 1500 and 1600  $\text{cm}^{-1}$  due to C-C stretching vibrations in the aromatic ring; stretching band at 2924  $\text{cm}^{-1}$  can be attributed to C-H and two strong bands at 1160-1120  $\text{cm}^{-1}$  and 1350-1300  $\text{cm}^{-1}$  are related to S=O group. On the other hand, the stretching band at 3362  $\text{cm}^{-1}$  (**Fig. 5a**) denotes the presence of hydroxyl groups (OH) in the structure of PS/PEG membrane, whereas the stretching band at 1080  $\text{cm}^{-1}$  suggests the presence of C-O group. The spectrum of the PS/PVP membrane (**Fig. 5b**) discloses stretching bands at 1647  $\text{cm}^{-1}$ , 2900  $\text{cm}^{-1}$  and 1300-1400  $\text{cm}^{-1}$  due to C=O,  $\text{CH}_2$  of acyclic and cyclic structures, respectively. The spectrum of PS/ZnO NPs membrane (**Fig. 5c**) shows that the band of zinc with carbon disappeared in the FT-IR spectrum and this proves that ZnO NPs not bonded with PS but deposited on it.



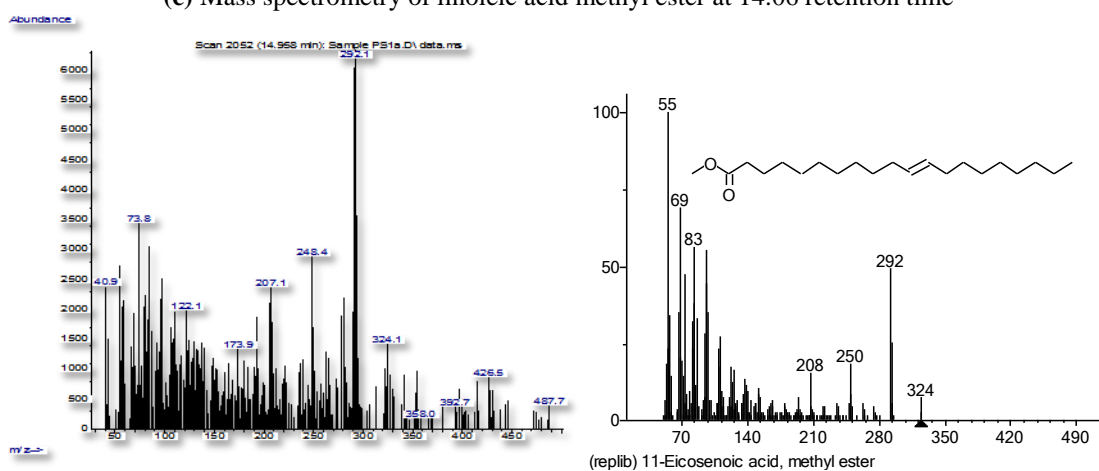
(a) Mass spectrometry of methyl tetra decanoate at 12.3 retention time



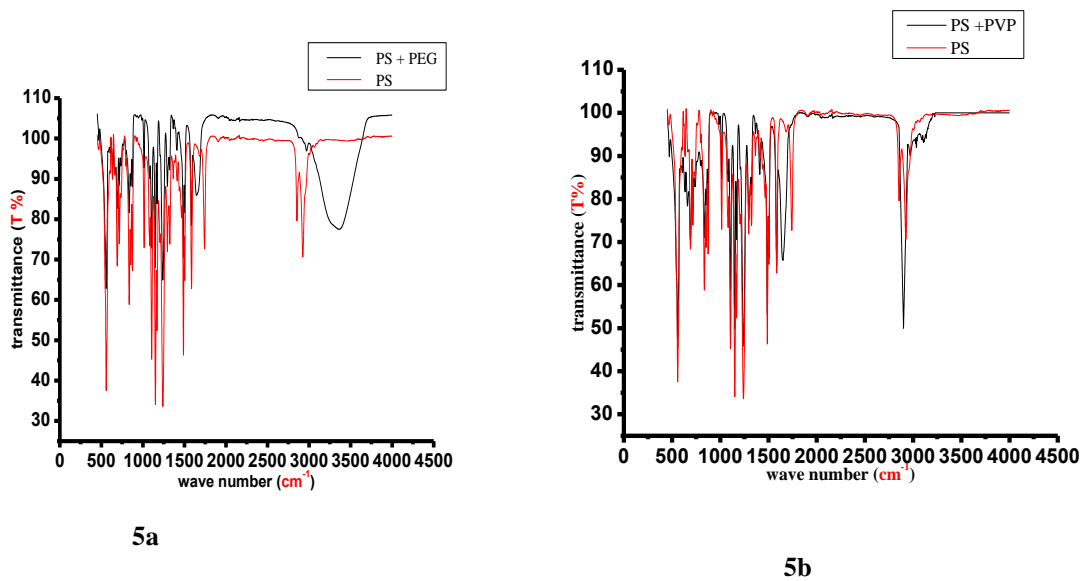
(b) Mass spectrometry of palmitic acid methyl ester at 13.3 retention time



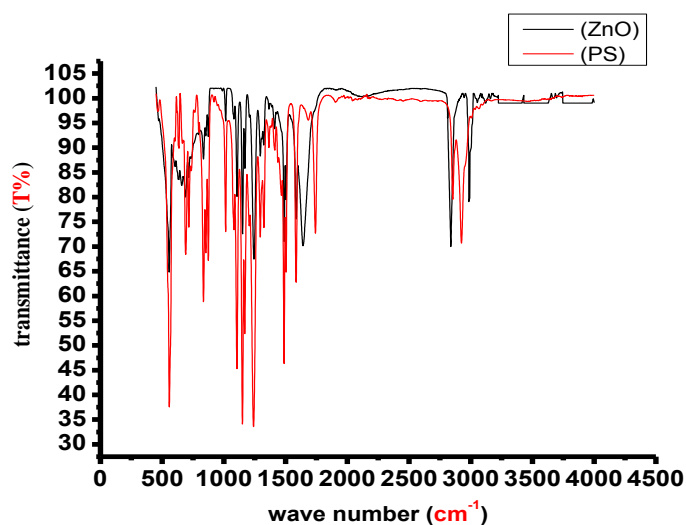
(c) Mass spectrometry of linoleic acid methyl ester at 14.06 retention time



(d) Mass spectrometry of 11-eicosenoic acid methyl ester at 15 retention time

**Fig. 4.** Chromatogram of gas chromatography of biodiesel: the right-hand chromatogram for higher concentrations and the left-hand chromatogram for lower concentrations.





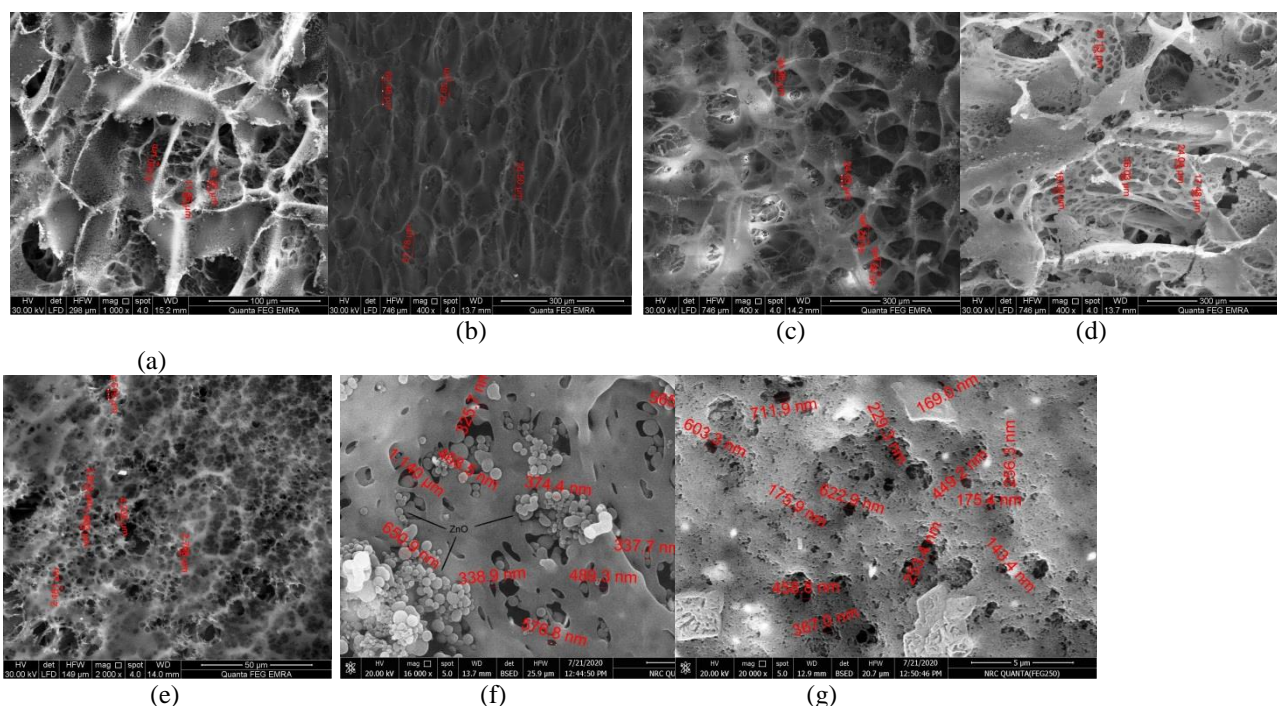
5c

**Fig.5.** FTIR of the prepared membranes : (a) PS/PEG; (b) PS/PVP; (c) PS/ZnONPs.

#### 2.2.4. Morphological characterization

The outer surface and morphology of the prepared membranes were investigated by SEM and the recorded images are illustrated in **Figures 6a-g**. Images of membranes in this figure clearly indicated that, PS/ZnO NPs composite membrane (**Fig. 6f&g**), have many nano-scale pores on the surface as compared to ZnO NPs-free membranes. This renders it more efficient towards separating impurities from biodiesel. PS/PVP composite membrane (**Fig. 6d&e**)

is the second-best membrane in its ability to separate impurities from biodiesel. This is valid with its pore size ranged from 3.9- 8 $\mu$ m and 2-4 $\mu$ m for [PVP] of 4% and 6%, respectively. On the other hand, the PS/PEG membrane respectively (**Fig. 6b&c**) keeps the biggest in term of pore size and this gives less efficiency. This holds true with its pore size ranged from 11-28 $\mu$ m and 24-45 $\mu$ m for [PEG] corresponds to 4% and 6%.



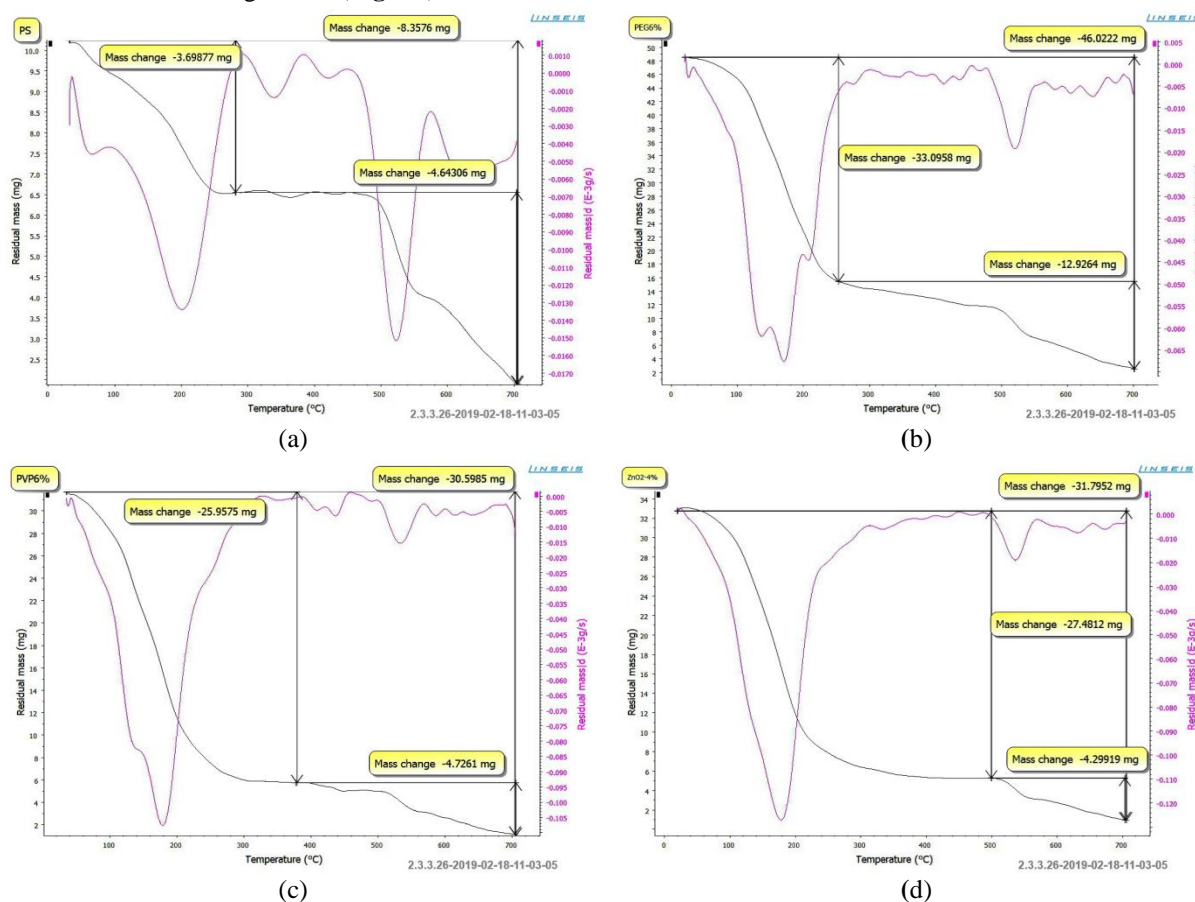
**Fig. 6.** Scanning electron microscope images of the prepared membranes : (a) unmodified PS; (b) PS/PEG 4%;(c) PS/PEG 6%;(d) PS/PVP 4% ; (e) PS/PVP 6%; (f) PS/ZnO NPs 4%; (g) PS/ZnO NPs 6%.

### 2.2.5. Thermal gravimetric analysis

Thermal properties of the pure PS and the PS hybrid membranes were evaluated using TGA. A known weight of each membrane was placed in aluminium balance then heated from 25°C up to 1000°C at a rate of 10°C/min under a constant nitrogen gas flow rate of 50 ml min<sup>-1</sup>. Temperature, weight, change in Wt. and thermal behaviour of the samples are recorded in the thermo-gram as shown in **Figures 7a-d**. This figure shows variation in temperature for all tested membranes in a dry air atmospheric heating as well as the decomposition and weight loss of these membranes with the corresponding temperature. The weight loss of these membranes occurred in the temperature range 30°C ≤ T ≤ 200°C due to evaporation of the water and solvent absorbed on their surfaces, and above that range due to membrane decomposition. For the PS membrane (**Fig. 7a**); weight loss (%) occurred in the range of 500–700°C as a consequence of the degradation of PS to H<sub>2</sub>O and CO<sub>2</sub> (membrane-restricted moisture) resulting in the decomposition of the polymeric PS chain. On the other hand, the PS/PEG membrane weight loss (**Fig. 7b**) occurred at

two stages of thermal reduction from 200–500°C and 500–700°C, due to the degradation of the PS and PEG polymeric chains [59][60], whereas the weight loss (%) in the PS/PVP membrane (**Fig. 7c**) took place in the range of 200–510°C due to the decomposition of the aromatic backbone of PS and PVP polymers [61].

The TGA results of PS/ZnO NPs (**Fig. 7-d**) show a major weight loss tape in the range of 200–518°C. A significant weight loss occurred in the temperature range of 518–550°C due to polysulfone degradation accompanied by a sluggish rate of decomposition up to 700°C. It could also be observed (**Fig. 7-d**) that there are two endothermic peaks based on differential calorimetry scanning curves and with apparent weight loss stages based on TGA curves. The first peak showed the evaporation of the water absorbed on the surface of the membrane and the solvent, while the second peak occurred in the region of 518–550°C suggesting the depletion of OH-which is present with ZnO as Zn(OH)<sub>2</sub>. This may be demonstrated by the fact that PS/ZnO NPs have a better thermal stability relative to PS itself [62] [63].



**Fig. 7.** Thermo-gram Curves of the prepared membranes : (a) Pure PS; (b) PS/PEG ;( c) PS/PVP ;(d) PS/ZnO NPs.

### 2.3. Evaluation of the prepared membranes for the biodiesel purification

Efficiency of the prepared membranes for biodiesel purification is shown in **Table 4**. It is evident that the PS/PEG membrane brought about no improvement in the separation capacity of biodiesel impurities relative to the pure PS membrane, while the PS/PVP membrane produced modest separation efficiency improvements that corresponded to 85%

and 86% when 2% and 4% of PVP concentrations were used. The PS/ZnO NPs hybrid membrane has the highest separating performance of impurities (90%) when compared with the PS membrane, which can be due to an improvement in surface area, hydrophilicity and a good combination of permeability, selectivity and a relatively fast recovery rate, which contribute to an improved glycerol removal.

**Table 4:** The efficiency of membranes in the purification of biodiesel\*

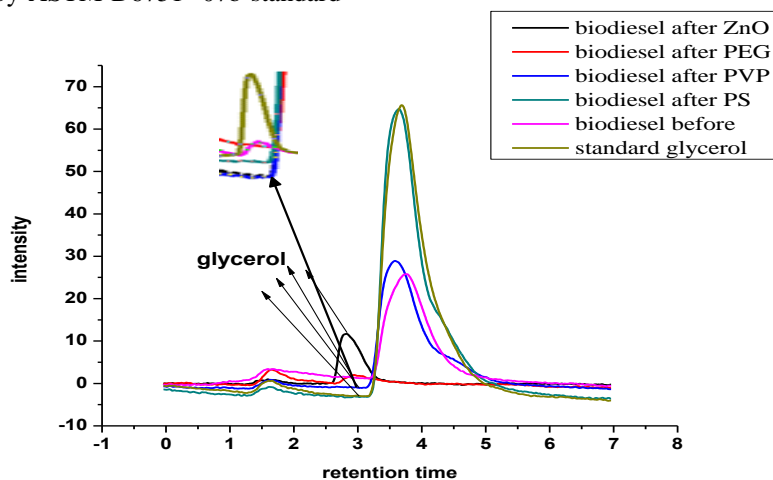
Type of membrane	Weight loss	Efficiency (%)
PS (control)	4.20	84
PEG 2%	4.05	81
PS+ PEG 4%	4.15	83
PEG 6%	4.20	84
PVP 2%	3.55	71
PS+ PVP 4%	4.25	85
PVP 6%	4.30	86
ZnO <sub>2</sub> 2%	4.15	83
PS+ ZnO <sub>2</sub> 4%	4.25	85
ZnO <sub>2</sub> 6%	4.50	90

\* Weight of sample = 5.

### 2.4. HPLC (high-performance liquid chromatography)

HPLC was used to ensure the absence or presence of glycerol in the purified biodiesel. The analysis of biodiesel using HPLC was done based on glycerol 0.1% standard with a peak at retention time 2.8, followed by the permeate part from PS, PS/PEG 4%, PS/PVP 6%, and PS/ZnO NPs membranes at the same conditions (**Fig. 8**). The initial concentration of glycerol in biodiesel sample (0.02 wt.%) was close to the values permitted by ASTM D6751- 07b standard

(<0.02%) [64]. The best permeation performance was obtained with PS/PVP (6%) and PS/ZnO NPs membranes, at 5.5 bar and 25°C. Almost no residual glycerol is present in the prepared biodiesel purified by these two membranes. This is due to that ZnO NPs membrane has many nano-scale pores on the surface and large surface area, which led to good permeability and selectivity for removing glycerol. Thus, more glycerol particles are adsorbed and attached to the membrane surface.



**Fig. 8.** Chromatogram of biodiesel samples and the glycerol standard

#### 4. Conclusion

Green biodiesel was produced from Egyptian waste cooking oil by trans-esterification reaction using membrane technology and characterized by different physico-chemical properties, FTIR and gas chromatography/mass spectrometry (GC/MS). It was found that, this biodiesel meets the specifications of American standard test method (ASTM) D6751. For comparative purposes, four membranes were prepared to evaluate their efficiencies for removal of the only impurity, glycerol, from the prepared biodiesel. These membranes included PS, PS/PEG, PS/PVP and PS/ZnO NPs. Structure and surface morphology of these membranes were characterized by scanning electron microscope (SEM), fourier-transform infrared spectroscopy (FTIR) and thermal gravimetric analysis (TGA). The HPLC chromatogram showed that the membrane of the PS/ZnO NPs provided the highest separation rate of the biodiesel by-product glycerol compared to the other ones.

#### Conflict of interest statement

#### Nothing declared

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