



## Research article

# Preparation and characterization of biodiesel from waste cooking oils using heterogeneous Catalyst(Cat.TS-7) based on natural zeolite

Mayas Saad<sup>\*</sup>, Baraa Siyo, Hussam Alrakkad*Department of Chemistry, Faculty of Science, Tishreen University, Lattakia, Syria*

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## ABSTRACT

Biodiesel is known as renewable biodegradable and less polluting material. It is produced by transesterification of triglycerides found in vegetable oil or animal fats. Many studies have been conducted on biodiesel production using homogeneous catalysts, but they are very expensive and not environmentally friendly. On the other hand, heterogeneous catalysts are cost-effective from the production process and ecofriendly. In this study, zeolite ore was used as a solid heterogeneous catalyst for the production of biodiesel by the transesterification reaction of waste cooking oils and studying the possibility of reusing it for several cycles under optimal reaction conditions. The catalyst was characterized by different techniques, such as TG-DTA, FTIR, XRD and TPD methods. High-quality biodiesel with 93% yield was obtained under optimal reaction conditions with the ratio of oil to methanol (1:9) mol, amount of catalyst (1.5% by weight of oil), at temperature (60 °C), and reaction time of 2 h. Biodiesel has been characterized using infrared spectroscopy, GC/MS, its physical and chemical specifications have been studied and compared with the American (ASTM) and European (EN) standards.

## 1. Introduction

The increase in world population and rapid demographic growth as well as technological development in recent years; impose an increase in demand for energy at a rapid pace. Since the extraction of oil from the ground is limited. In addition, petroleum fuels have significant damage to the environment and humans health, due to the emission of toxic gases into the atmosphere [1]. Therefore, it is necessary to find other resources for energy production. The provision of renewable energy sources is still one of the most important challenges in the twenty-first century. Despite the research to develop renewable energy sources, the scale of technical, and engineering challenges are still constitute as an obstacle [2]. In industrialized countries the scientific research is dedicated to provide green fuel to vehicles as an alternative to the petroleum fuels [3]. Biodiesel is very similar to petroleum diesel, and it is biodegradable, has a favourable combustion emission profile and a high flash point, and produces less amounts of carbon monoxide, sulfur dioxide and unburned hydrocarbons compared to petroleum-based diesel fuel [4]. In the industrialized countries of the world, the most productive countries are led by Germany and France [5]. The oil crops that start growing from seed to oil production take only several months. This promised energy (vegetable oil) can produce liquid biofuel, which is an alternative renewable energy, environmentally friendly to a degree [6]. Biodiesel is an alternative fuel for diesel engines that is gaining interest in the United States of America [7], having

<sup>\*</sup> Corresponding author.

E-mail address: [Mayas.saad@hotmail.com](mailto:Mayas.saad@hotmail.com) (M. Saad).

## Nomenclature

ASTM	American Society for Testing Materials
FFA	Free Fatty Acid
EN	European Standards
WCO	Waste Cooking Oil
CTMABr	Cetyl tri Methyl Ammonium Bromide
B	Biodiesel
FAME	Fatty Acid Methyl Ester

reached a significant success level in Europe [8].

Biodiesel produced from edible oil is currently more expensive than petroleum fuels; causing a food-for-fuel problem around the world. Therefore, the idea of using inedible oils and waste vegetable oil was presented as an economical solution and also gives a waste management solution [9]. Some edible oil resources such as coconut, soybean, and palm oil have also been used to produce biodiesel due to their ready availability and lower free fatty acid (FFA) content than non-edible oils [10–12].

*Trans*-esterification is one of the most important and most common methods used in biodiesel production [13], which is the reaction of triglycerides with alcohol (methanol or ethanol) in the presence of an acidic, basic or enzymatic homogeneous catalyst to produce an alkyl ester (biodiesel) [14]. In this process glycerol emerges as a by-product [15]. Methanol is the most common type of alcohol used in biodiesel production because of its physical and chemical advantages, besides, its reaction with triglycerides is fast and gives a better and fast conversion rate due to the short chain [16], and other alcohols can also be used such as ethanol, propanol and butanol [17].

Various types of homogeneous and heterogeneous catalysts are used in the transesterification reaction to produce biodiesel, with homogeneous catalysts being the most common. Although homogeneously catalyzed reactions occur faster compared to heterogeneously catalyzed reactions [18]. However, it faces a number of drawbacks. A high level of free fatty acids are usually found in animal fats or waste cooking oil. This can be converted into soap by reaction with a homogeneous alkaline catalyst through the saponification reaction, which leads to a reduction in biodiesel yield and difficulty in separation and purification process. In addition, the use of homogeneous acid catalysts in the transesterification reaction faces some technical drawbacks such as (relatively slow reaction rate, equipment corrosion, and requires multiple purification steps in the final stages) [19]. Therefore, research has turned to the use of heterogeneous catalysts in biodiesel synthesis, where it is possible to recover solid catalysts in an easy way and reuse for several cycles with constant catalytic activity and can reduce the cost of biodiesel production [20]. The purification process is also simple, which leads to reduced energy consumption and waste [21].

Many solid catalysts like alumina, silica, zeolites, clay and MCM structures are used in several industries. Several studies have also been indicated to use some low-cost natural raw materials as zeolites, clays and phosphates as catalysts for some reactions or in the purification processes of industrial water and air. These raw materials have low efficiency compared to industrial materials because they contain high percentages of impurities due to its uncontrolled conditions such as temperature, pressure and ratios of components ... etc. which hinder their use in many fields [22].

The main aim of the present study is to produce and characterize biodiesel through transesterification process using low value triglyceride resources such as waste edible oils in the presence of a low cost solid base catalyst prepared from Syrian natural zeolite ore TS-7 that can be reused for several production cycles. After the preparation and characterization of the biodiesel, it was mixed with petroleum diesel produced in Syria in different ratios. The physical properties of the mixtures, such as density, kinematic viscosity, flash point, and pour point are measured according to international standards and these properties compared to standard conditions. Finally, the best ratio of biodiesel/diesel is obtained.

## 2. Experimental

### 2.1. Materials

The materials used in this study were: Waste cooking oil (WCO) collected from nearby restaurants from Tishreen university, methanol (anhydrous, 99.6%), distilled water, Syrian natural zeolite TS-7, hydrochloric acid (37%wt%), ammonium hydroxide, (25% w/v), Cetyl tri methyl ammonium bromide (CTMABr). All the chemicals were used as analytical reagent grade.

### 2.2. Catalyst preparation and characterization

#### 2.2.1. Preparing method of Cat.TS-7

In this study the Syrian natural zeolite was used as initial material. The natural or rock was crushed and a part of 0.1–0.3 dimension was taken and washed with distilled water several times to remove dissolution material, dried at 105 °C for 6 h and treated with hydrochloric acid (20%) with stirring at 160 r.t./min for 24 h. The resulting was filtrated. Ammonium hydroxide (25%) was added to filtrate gradually until pH ~ 9, then 0.1g of cetyltrimethyl ammonium bromide (CTMABr) to form a gel. The product from previous process was placed in Teflon reactor within tightly closed stainless steel container, and the reactor was heated in drying oven at 135 °C

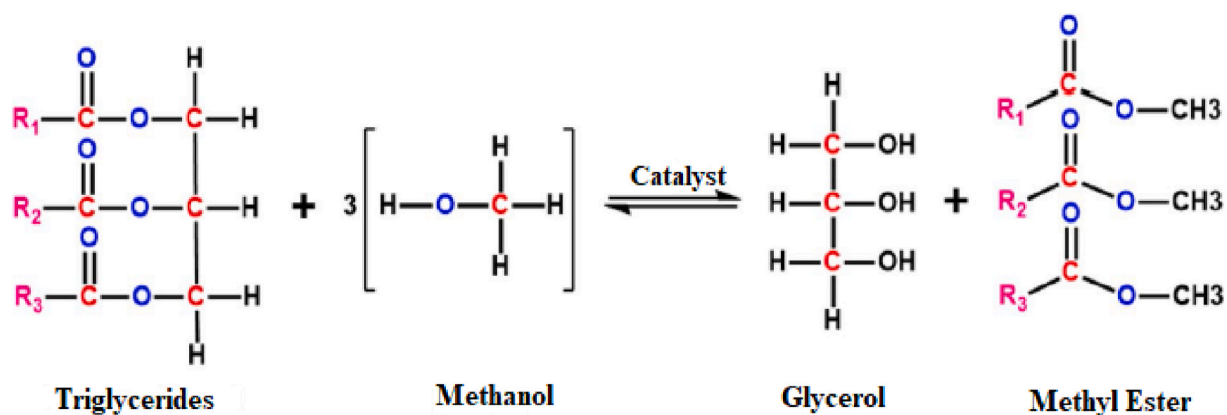


Fig. 1. The transesterification of vegetable oil or fat with methanol alcohol.



Fig. 2. Zeolite catalyst used in the present study (Cat.TS-7).

for 8 h. Then, the reactor was cooled down suddenly using a stream of water to room temperature and the resulting precipitate was filtered, washed with distilled water several times, dried at 110 °C for 24 h and calcined at 750 °C for 4 h. The resulting product named Cat.TS-7 (see Fig. 2).

#### 2.2.2. TG-DTA analysis of uncalcined Cat.TS-7

The amount of uncalcined Cat.TS-7 was taken after drying and Thermogravimetric analysis (TGA) was conducting at a heating rate of 10 °C/min from 25 to 900 °C under atmospheric air.

#### 2.2.3. Characterization

The prepared solid base was explored X-ray (Cu K $\alpha$  irradiation,  $\lambda = 0.154$  nm, in the 2 $\theta$  range of 10–80) and FTIR spectrometer using KBr disk technique with wavenumber ranged from 400 to 4000  $\text{cm}^{-1}$ , Temperature programmed desorption CO<sub>2</sub>-TPD was performed to determine the basic properties, Chemical composition of catalyst was determined by chemical.

### 2.3. Transesterification reactions

Biodiesel was prepared by the transesterification reaction of cooking oil shown in Figure (1) using (Cat.TS-7) as a heterogeneous catalyst was performed using a three-necked flask (250 mL) connected with a magnetic stirrer, digital heater, and a water-cooling condenser. Waste cooking oil (15g) was stirred with different amounts of prepared catalyst (0.5–2.5% by weight of oil) for different reaction time intervals (1,2,3 h) and reaction temperature range of (30 °C–75 °C) and using different oil/Methanol ratios 1:6, 1:9, 1:12. After each experiment, the catalyst was removed from the reaction medium by centrifugation and the residual liquid was retained in separating funnel for 24 h, where the mixture is separated into two layers (top layer is biodiesel, and bottom layer is

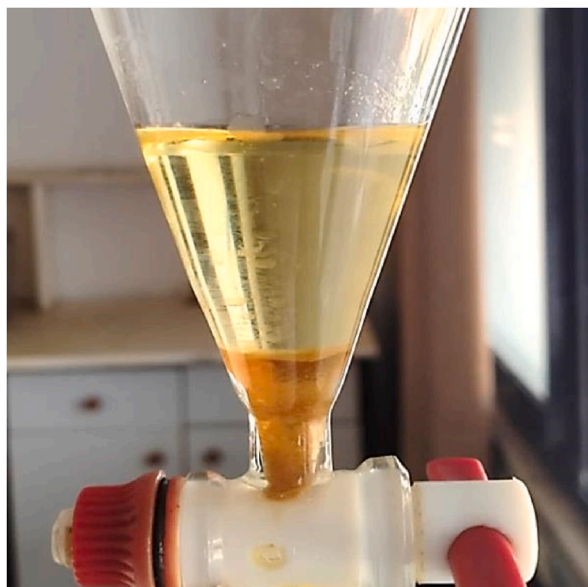


Fig. 3. Separation of glycerol phase (bottom) from biodiesel phase (upper) in a lab separating funnel.

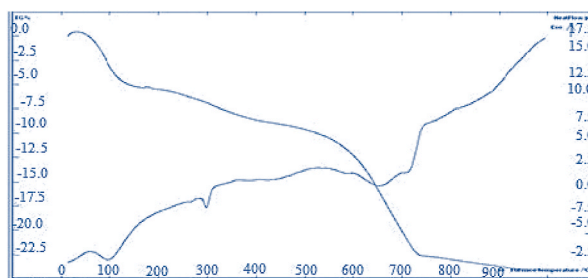


Fig. 4. TG-DTA spectrum of un calcined Cat.Ts-7.

glycerol (see Fig. 3)). The top layer is taken and washed with hot distilled water to remove alcohol, glycerine and catalyst residues, then filtered to get rid of glycerol residue, then dried at 110 °C for 2 h to get rid of water residue. The efficiency of conversion reaction (biodiesel yield%) was estimated using the following equation [23].

$$\text{Biodiesel yield (\%)} = \frac{\text{Volume of biodiesel}}{\text{Volume of waste cooking oil}} \times 100 \quad (1)$$

### 3. Results and discussion

#### 3.1. TG-DTA analysis of uncalcined Cat.TS-7

As shown in Fig. 4 mass losses were observed from 25 to 750 °C corresponding to the dehydration and dehydroxlation processes. The peak corresponding to dehydration were centered at 100 °C (endothermic) with loss of 5, 12 wt%. Another endothermic peaks appear at 300 °C attributed to the loss of hydroxyl groups –OH accompanying the  $M(\text{OH}) \rightarrow \text{MOOH}$  transformation, while the endothermic peak at 660 °C due to the  $\text{MOOH} \rightarrow \text{M}_2\text{O}_3$  transition [24,25]. After that no thermal effect appears indicating a change in the structure of the prepared solid base, so the dried precipitate was calcined at 750 °C for 4 h.

#### 3.2. Catalyst characterization

##### 3.2.1. Chemical analysis

Chemical analysis of Cat.TS-7 showed that the catalyst consists mainly of Ferric oxide  $\text{Fe}_2\text{O}_3$ (59.55)and Aluminum oxide  $\text{Al}_2\text{O}_3$  (40.45).

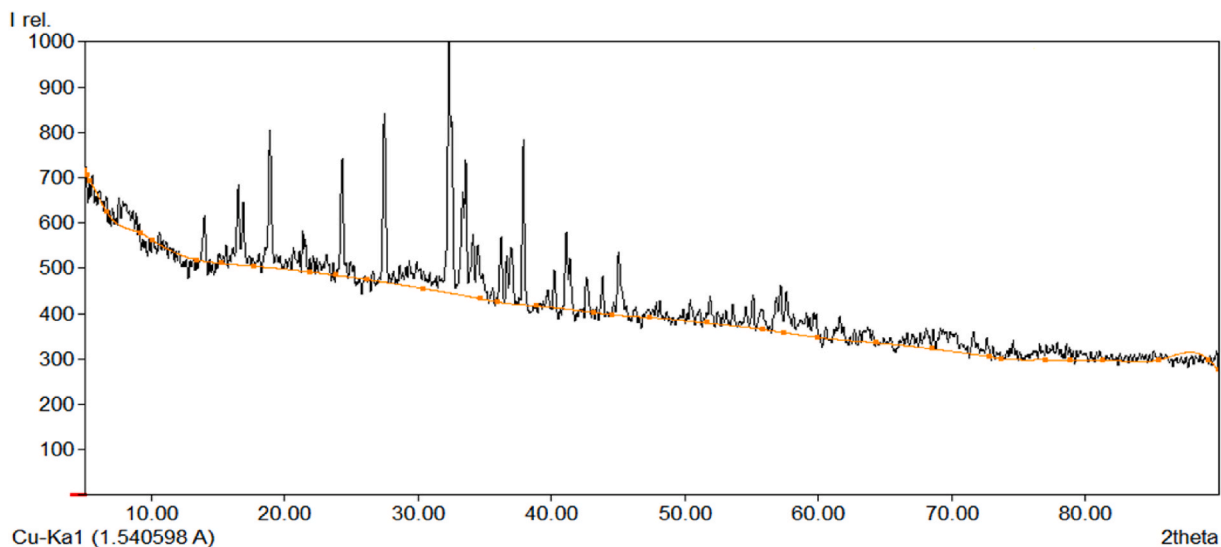


Fig. 5. XRD patterns of Cat.TS-7.

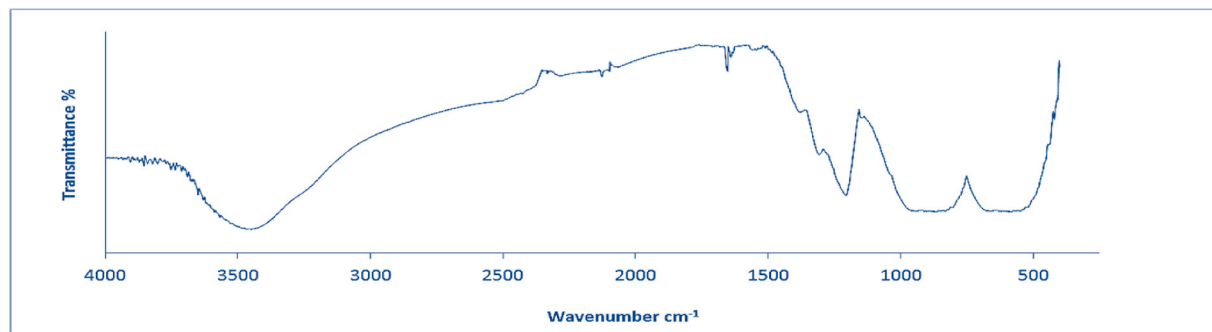


Fig. 6. IR spectrum of Cat.Ts-7.

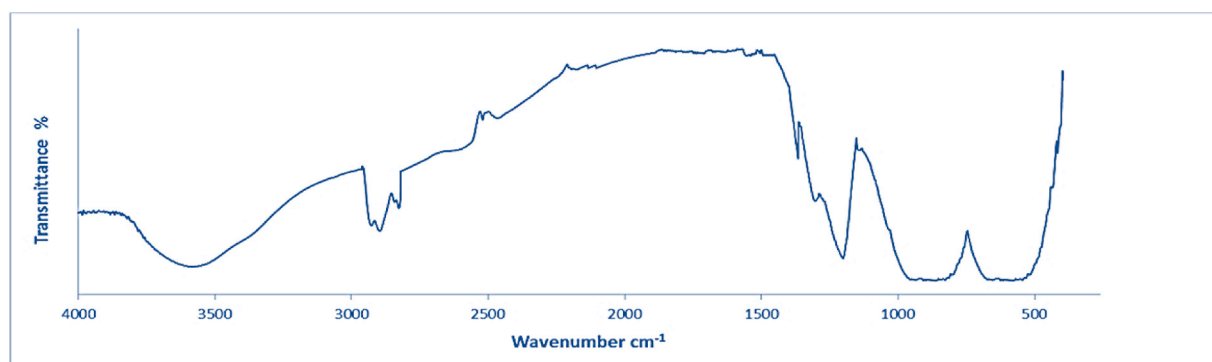


Fig. 7. IR spectrum of Cat.Ts-7 with methanol.

### 3.2.2. XRD patterns

The XRD spectrum showed a clear crystal structure of Cat.TS-7 as showed in Fig. 5, the reflexes at the value of  $2\Theta = 37.5, 24.4, 45.6$  attributed to the presence of  $\gamma\text{-Al}_2\text{O}_3$  phase, while at  $2\Theta = 24.2, 33.1, 36.7, 40.9, 49.4, 53.9, 57.6$  attributed to  $\alpha\text{-Fe}_2\text{O}_3$  crystalline phase. Also, reflections at  $2\Theta = 17.7, 21.2, 34.7, 36.7, 39.9, 47.3, 59.1$ , attributed to  $\alpha\text{-FeOOH}$  phase [26–28]. It is concluded from XRD spectrum that iron hydroxide did not fully crystallize.

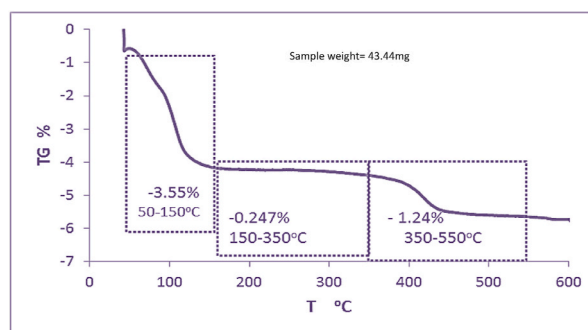


Fig. 8. CO<sub>2</sub>-TPD profile of Cat.Ts-7.

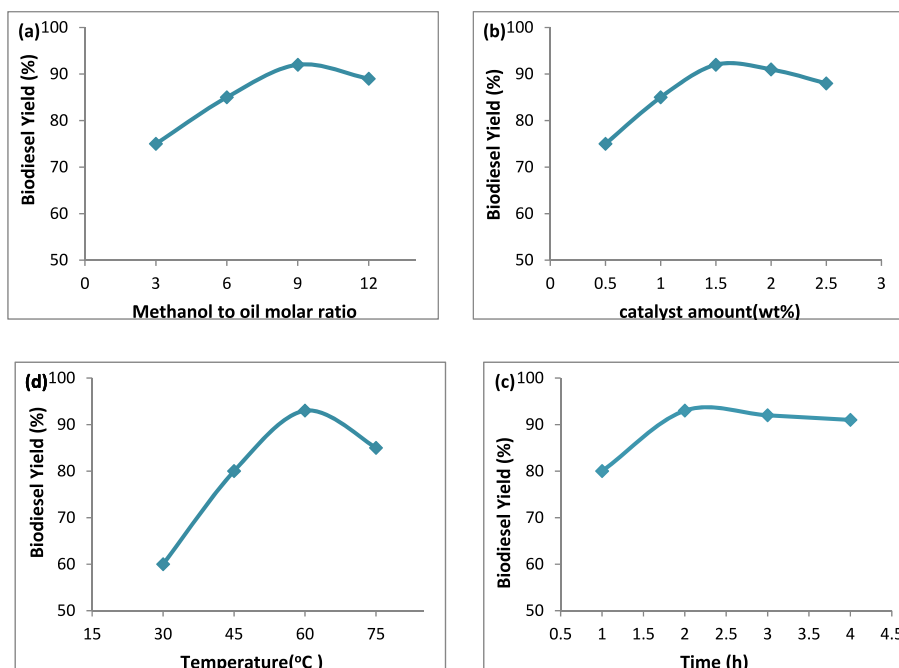


Fig. 9. Effect of methanol/oil molar ratio (a), catalyst amount (b), reaction time (c), and temperature (d) on the biodiesel yield.

### 3.2.3. FTIR spectrum

The pattern of Cat.TS-7 IR spectrum is related to availability of active function and bonds. Several bonds observed as shown in Fig. 6, which assigned to various functional groups. As a strong and broad in the region 3000–3750  $\text{cm}^{-1}$  which indicated the presence of free hydrogen bonded in O–H groups, and the band about 1640  $\text{cm}^{-1}$  related to asymmetric stretching of O–H groups, and the IR broad band at  $\sim 506 \text{ cm}^{-1}$  and  $\sim 768 \text{ cm}^{-1}$  assigned to the O–Al–O and O–Fe–O, respectively [29–31].

### 3.2.4. Basic site characterization

Calcined Cat.TS-7 is vacuumed at 200  $^{\circ}\text{C}$  for 6 h and exposed to methanol vapor for 24 h, then the quality of basic centers were determined by FTIR method, and quantity of basic sites was determined by CO<sub>2</sub>-TPD method.

As shown in Fig. 7, the bands at 2893 and 2925  $\text{cm}^{-1}$  indicate to methanol adsorption an Brønsted base centers and the band at 1450  $\text{cm}^{-1}$  related to the coordination band between methanol and metallic atom in Cat.Ts-7 [32].

The temperature programmed desorption of CO<sub>2</sub> from Cat.Ts-7 was performed in the range 20–600  $^{\circ}\text{C}$ . As shown in fig(8) we divided the spectrum into three parts: The range between 20 and 150  $^{\circ}\text{C}$  by loss mass about 0.807 m mol/g which indicated the weak basic centers, the range between 150 and 300  $^{\circ}\text{C}$  by loss mass about 0.056 m mol/g which indicated the moderate basic centers and the range between 300 and 500  $^{\circ}\text{C}$  by loss mass 0.282 m mol/g which indicated the strong basic centers [33,34]. As we can see from previous results the solid base Cat.Ts-7 has strong surface basic properties.

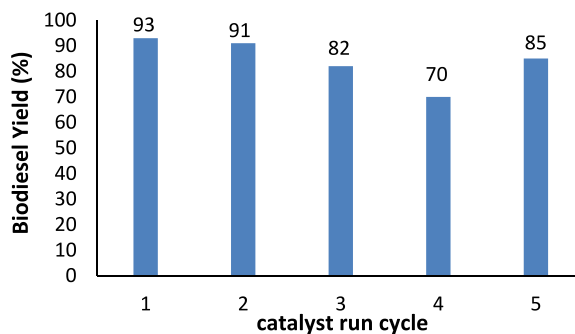


Fig. 10. Effect of catalyst run cycle on FAME yield.

### 3.3. Optimization of reaction conditions

The effect of changing the reaction parameters as: molar ratio of methanol/oil, amount of catalyst, reaction time, and reaction temperature on the transesterification of waste oil were investigated see (Fig. 9).

#### 3.3.1. Effect of methanol/oil molar ratio

The influence of using various molar ratios (1:6, 1:9, 1:12) was studied at a reaction temperature of 60 °C. The amount of the catalyst was 3% of the weight of the oil and the reaction time was 3 h. As seen from Fig (9a), the transesterification reaction was not complete on using the molar ratio less than (1:9). However, it can be noticed the highest biodiesel yield (91%) was observed on increasing the molar ratio from (1:6) to (1:9). This could be explained that the amount of methanol added was sufficient to convert the oil and was not excessive to exceed the dissolution of glycerin resulting from the transesterification process of the oil which was the problem found using the molar ratio (1:12). It seems on increasing the methanol more than the proper ratio (1:9), the yield of biodiesel decreases. It is evident that one of the reaction limitation, is the increase of glycerin solubility, which makes glycerine separation from the reaction solution difficult.; Furthermore, the presence of glycerin in the reaction solution shifts the reaction towards the reactants, therefore biodiesel yield decreases [35].

#### 3.3.2. Effect of catalyst amount

The amount of catalyst percentages to the weight of the oil was changed (0.5, 1, 1.5, 2, 2.5). All the experiments were performed at a temperature of 60 °C, molar ratio (1:9) and reaction time of 3 h. As presented in Fig (9b), the reaction yield increases with the increase in the amount of catalyst to reach a maximum at 1.5%. Further increase of the catalyst leads to a decrease in the reaction yield. This is due to the fact that the excess amount of the catalyst increases the viscosity of the system and so appropriate homogenous mixture is not reached, where the diffusion coefficient plays a major role on the yield [36,37]. On the other hand, on using ratios less than 1.5%, a decrease in the yield is observed, due to the lack of sufficient amount of active centers on the catalyst to complete the reaction. As a result, the amount of catalyst (1.5%) was chosen to be the optimum percentage to obtain the highest yield of biodiesel 92%.

#### 3.3.3. Effect of reaction time

The effect of the reaction time on the yield was studied at the time intervals (1 h, 2 h, 3 h), at a temperature of 60 °C, molar ratio (1:9) and the amount of catalyst (1.5% of the oil weight). The reaction rate increased to reach a maximum at a reaction time of 2 h. Yield of biodiesel reached 92% (see Fig (9c)). This shows the time required to perform complete transesterification reaction. It can be stated that 1 h was not sufficient to give the best yields of biodiesel. Additionally, increasing the reaction time more than 2 h revealed a decrease in the yield, due to the possibility of decomposing the resulting biodiesel with increasing the reaction time thus displacement of the reaction in the reverse direction, which has an effect on the reaction yield [37].

#### 3.3.4. Effect of reaction temperature

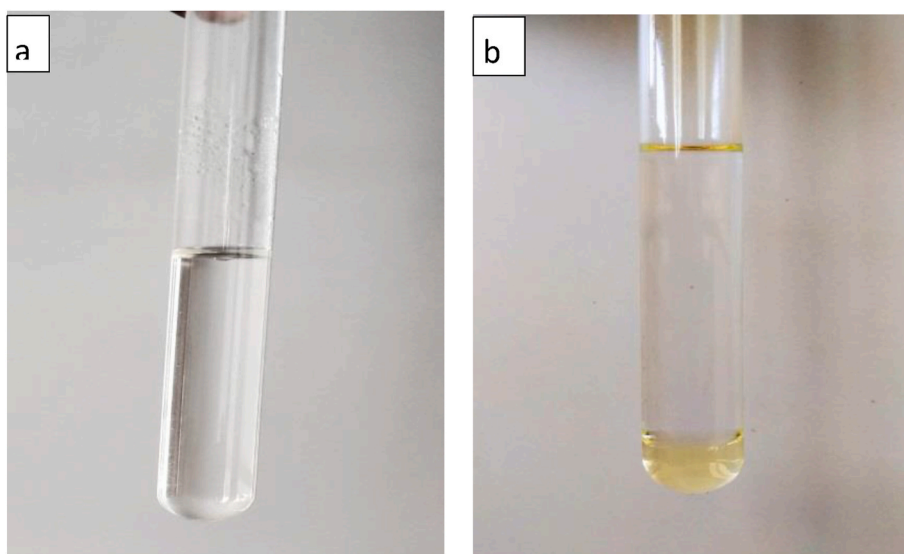
The effect of temperature on biodiesel yield was studied. The reaction temperature varied (30, 45, 60, 75 °C) at molar ratio (1:9), catalyst quantity (1.5% of oil weight) and reaction time of 2 h. The reaction rate increases with increasing temperature up to 60 °C due to the increase in the rate of transesterification reaction as the viscosity of the oil decreases and better mixing between the reactions (see Fig. 9d) [38]. However above 60 °C the yield of biodiesel decreases as the temperature is exceeding the boiling point of methanol (64.7 °C), and consequently the evaporation of part of the methanol, which in turn led to a decrease in the yield and this is consistent with previous studies [37]. Therefore, transesterification reaction temperature was performed at 60 °C as the best temperature to achieve the highest yield of 91% biodiesel.

### 3.4. Reusability of the catalyst

The reuse of the catalyst is an indication of the stability of the catalyst and it is of great importance in reducing the cost of biodiesel production. The reusability tests of the catalyst was done by using 1.5% amount of catalyst (Cat.TS-7) for five consecutive cycles at the

**Table 1**  
Physical and chemical properties of prepared biodiesel.

Physicochemical properties	Experimental values	Europe EN 14,214	ASTM D 6751
Density at 15.5 °C (g/cm <sup>3</sup> )	0.87	0.86-0.90	0.875-0.90
Kinematic viscosity at 40 °C (mm <sup>2</sup> /s)	4.8	3.5–5	1.9-6
Specific gravity at 15.5 °C	0.8708	–	–
API gravity	29.2	–	29.2
Aniline point (°C)	87.5	–	–
Diesel index	55.33	–	–
Cetane number	49.84	51mini	47mini
Acid value (mg KOH/g oil)	0.45	<0.5	<0.8
Flash point (°C)	180	101mini	130mini.
Pour point (°C)	–1	–	–15 to +10
Water and sediment (%)	0.01	500 mg/kg	<0.05



**Fig. 11.** (a) Biodiesel sample with methanol, (b) Oil sample with methanol.

optimal reaction conditions (molar ratio (1:9), 60 °C, 2 h), where the catalyst is recovered after the reaction by centrifuge and filtering it. After then the catalyst is dried at 100 °C for 24 h before being reused. As presented in Fig. 10 there was no significant loss in the activity the first three successive cycles, then a significant decrease in the yield of biodiesel (70%) during the fourth cycle may be due to blockage of some active sites by dense intermediates products and a small amount of catalyst is lost during reuse. Consequently, the catalyst was reactivated after the fourth cycle by calcination at 750 °C for 2 h and then reused in a fifth cycle at the same reaction conditions. A significant improvement in the reaction yield were observed as a yield was obtained. It can be concluded from the previous results that the catalyst can be reused for at least for 3 cycles without deactivation and it is possible to regenerate the catalyst without loss in activity.

### 3.5. Characterization of the produced biodiesel

#### 3.5.1. Physical and chemical properties of prepared biodiesel

The biodiesel produced under optimum reaction conditions was characterized by means of EN 14,214 and ASTM D 6751 standard specifications. The obtained results are listed in Table 1 and it fits these standard specifications [39,40].

#### 3.5.2. Biodiesel confirmation by warn quist 3/27

Warn quist 3/27 it is the test that is useful to know the degree of conversion of triglycerides to biodiesel. This test is important and inexpensive compared to analyzes using gas chromatography. This test can be done during the experiment to find out the time needed for complete transformation, and it can be done after the reaction to compare it with other samples using different catalysts [41]. 3 mL of the produced biodiesel was dissolved in 27 mL of methanol and left undisturbed for 30 min to find the unconverted glycerides in the biodiesel after transesterification process. Since, FAME is soluble in polar solvent it will get completely dissolved in methanol Fig. (11a), the nonpolar unconverted oils remain as precipitate Fig.(11b) [42].





Fig. 12. FTIR for oil sample.

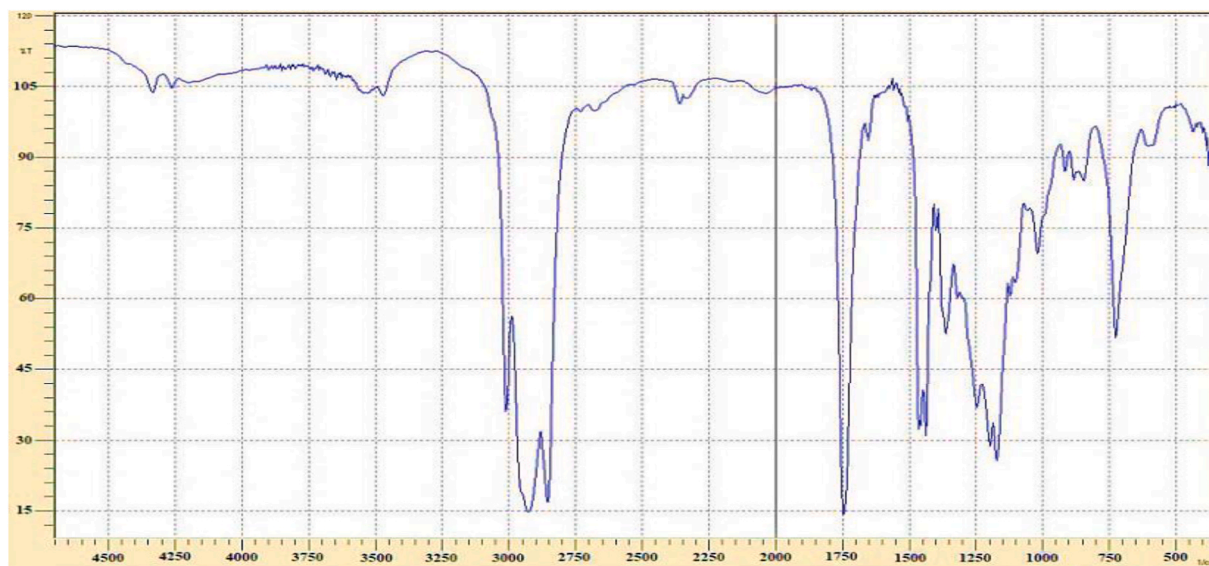


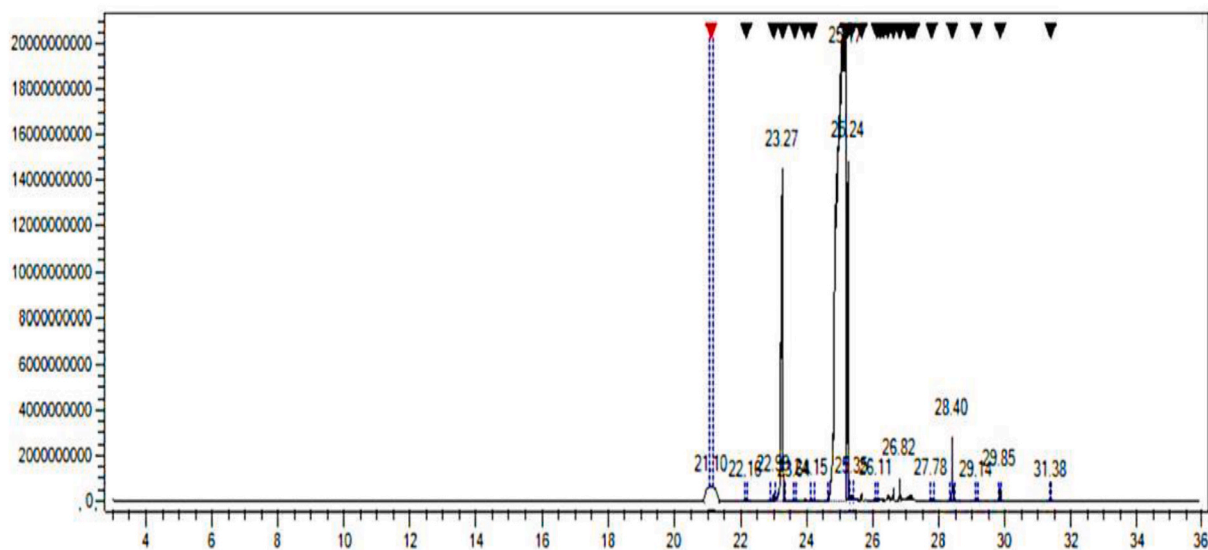
Fig. 13. FTIR for biodiesel sample.

**Table 2**  
FTIR wave numbers for different peaks of oil.

Group attributed	Wave number of oil (Cm <sup>-1</sup> )
CH <sub>2</sub> -rocking	721
Bending vibration of CH <sub>2</sub> group	1375
C=O ester stretch	1750
C-O stretching	1163
Bending vibration of the CH <sub>2</sub>	1456
CH <sub>2</sub> stretching	2925

**Table 3**  
FTIR wave numbers for different peaks of biodiesel.

Group attributed	Wave number of biodiesel ( $\text{Cm}^{-1}$ )
$\text{CH}_2$ -rocking	721
Split C-O stretching	1195
	1168
$\text{CH}_3$ -O stretching	1245
Bending vibration of $\text{CH}_2$ group	1363
$\text{CO-O-CH}_3$	1436
Methyl ester group	
$\text{CH}_2$ -In-plane bend	1463
C=O ester stretch	1750
$\text{CH}_2$ -stretching	2933



**Fig. 14.** GC-MS chromatograms of the prepared biodiesel sample.

**Table 4**  
The composition of fatty acid methyl ester (FAME) in biodiesel from waste cooking oil.

No	Compound	Molecular Formula	Molecular Weight	Retention Time (minutes)	Area %
1	Tridecanoic acid, methyl ester	$\text{C}_{14}\text{H}_{28}\text{O}_2$	228.37	21.10	0.1
2	Hexadecenoic acid, methyl ester, (Z)-7	$\text{C}_{17}\text{H}_{32}\text{O}_2$	268.44	22.99	0.1
3	Hexadecanoic acid, methyl ester	$\text{C}_{17}\text{H}_{34}\text{O}_2$	270.45	23.27	12.1
4	9-Octadecenoic acid (Z)-, methyl ester	$\text{C}_{19}\text{H}_{36}\text{O}_2$	296.49	25.17	78.1
5	Methyl stearate	$\text{C}_{19}\text{H}_{38}\text{O}_2$	298.50	25.24	7.4
6	9,12-Octadecadienoic acid, methyl ester, (E,E)-	$\text{C}_{19}\text{H}_{34}\text{O}_2$	294.47	25.35	0.1
7	11,14-Eicosadienoic acid, methyl ester	$\text{C}_{21}\text{H}_{38}\text{O}_2$	322.53	25.65	0.1
8	Z,Z,Z-4,6,9-Nonadecatriene	$\text{C}_{19}\text{H}_{38}$	266.51	26.22	0.1
9	9,12,15-Octadecatrienoic acid, methyl ester, (Z,ZZ)-	$\text{C}_{19}\text{H}_{32}\text{O}_2$	292.46	26.45	0.2
10	9-Octadecenoic acid (Z)-, methyl ester	$\text{C}_{19}\text{H}_{36}\text{O}_2$	296.49	26.62	0.2
11	Pentadecanoic acid, 14-methyl-, methyl ester	$\text{C}_{17}\text{H}_{34}\text{O}_2$	270.45	26.82	0.3
12	Decanoic acid, methyl ester	$\text{C}_{11}\text{H}_{22}\text{O}_2$	186.29	29.14	0.2

### 3.5.3. FTIR spectra for oil and biodiesel

Oil and biodiesel were analyzed by FTIR as shown in Figs. 12 and 13, the results shown in Tables 2 and 3. The IR spectra of the oil and biodiesel samples are very similar to each other because the reaction simply consists of removing glycerin and substitution of a methyl group in the hydrocarbon chain. The only significant difference can be seen in the bands lying between  $1000$  and  $1500\text{ cm}^{-1}$ . Particularly, the bands at  $1163$  and  $1097\text{ cm}^{-1}$  in the oil sample which corresponds to the expansion vibration of the (C-O) group bound to ( $\text{CH}_2$ -) which shifts to  $1168\text{ cm}^{-1}$  in the biodiesel sample. However, new bands at  $1195$  and  $1436\text{ cm}^{-1}$  were observed in the biodiesel sample associated with the bending and oscillation vibrations of the ( $\text{CH}_3$ -O) group which are not present in the spectrum of

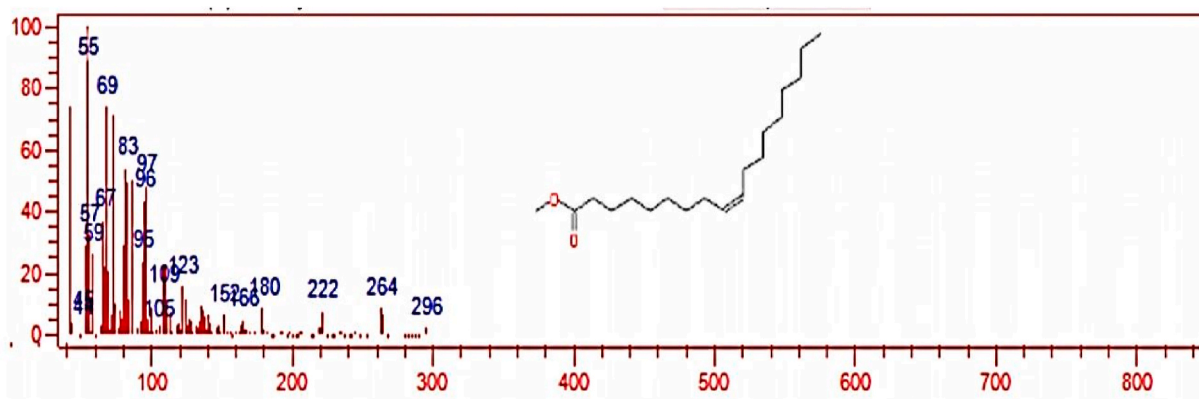


Fig. 15. Mass spectrum of 9-Octadecenoic acid (Z)-, methyl ester.

Table 5

Physical and chemical properties of biodiesel samples (B100, B5, B20) in comparison with (ASTM) and (EN).

Physicochemical properties	B <sub>100</sub>	B <sub>5</sub>	B <sub>20</sub>	Syrian Petro-diesel	Europe EN 14,214	ASTM D 6751
Density at 15.5 °C (g/cm <sup>3</sup> )	0.87	0.8405	0.8530	0.82-0.85	0.86-0.90	0.875-0.90
Kinematic viscosity at 40 °C (mm <sup>2</sup> /s)	4.8	2.9	3.2	2.0-4.5	3.5-5	1.9-6
Specific gravity at 15.5 °C	0.8708	0.8413	0.8539	0.858	–	–
API gravity	29.2	36.69	34.2	33.418	–	29.2
Aniline point (°C)	87.5	69.2	74.8	50min	–	–
Diesel index	55.33	57.44	56.99	46min	–	–
Cetane number	49.84	51.35	51.03	51min	51mini	47mini
Acid value (mg KOH/g oil)	0.45	0.05	0.1	0.08max	<0.5	<0.8
Flash point (°C)	180	63	74	55min	101mini	130mini.
Pour point (°C)	–1	–10	–4	–4 to –10	–	–15 to +10
Water and sediment (%)	0.01	Nil	Nil	0.05max/Nil	500 mg/kg	<0.05

Table 6

Comparison of catalytic activity of Cat.TS-7 catalyst with reported Ca-based solid alkali catalysts.

Catalyst	Reaction conditions				FAME yield (%)	Refs.
	Temp. (° C)	Catalyst amount (wt.%)	Methanol/oil molar ratio (mol)	Time (h)		
Cat.TS-7	60	1.5	9	2	93	This study
Oyster shell	65	25	15	5	73.8	[45]
Angel wing shell	65	9	150	1	84.11	[46]
Chicken eggshell	65	9	15	8	80.2	[47]
Chicken bone	65	5	15	4	89.33	[48]

the oil. The bands in the range of 1435 – 1460 cm<sup>-1</sup> in the biodiesel spectrum are due to the asymmetric vibration of methane (CH<sub>3</sub>), indicating the conversion of the used oil to biodiesel as found by previous studies [43].

#### 3.5.4. GC-MS analysis of biodiesel (FAME)

The chemical composition of biodiesel prepared from waste cooking oils was determined using Gas chromatography-mass spectrometry by comparing the mass spectra produced for each vertex of the GC-MS chromatogram with the mass spectra available in the library (NIST) available in the device. After analyzing the biodiesel, 12 components were identified through the GC-MS chromatogram shown in Fig. 14, Table 4 shows the biodiesel components, which constitute 98% of the (FAME). The results shown in Table 4 indicate that the main components of biodiesel, according to their percentages, are as follows: 9-Octadecenoic acid (Z)-, methyl ester (78.1%) Fig. 15, Hexadecanoic acid, methyl ester (12.1%), Methyl stearate (7.4%)

#### 3.6. Studying the possibility of mixing prepared biodiesel with petroleum diesel

Two samples of biodiesel mixed with petroleum diesel at proportions (5%, 20%) were prepared and their physical and chemical properties were studied and compared to the American (ASTM) and European (EN) standards. The results shown in Table 5 indicated that the physical and chemical properties of pure biodiesel (B<sub>100</sub>) and the two samples of biodiesel mixed with Syrian diesel (B<sub>5</sub>, B<sub>20</sub>) were in conformity with the internationally proven specifications [39,44], and thus concludes that it is possible to mix biodiesel with

Syrian diesel fuel. The results also indicate that the mixing ratio B<sub>20</sub> is the best in terms of improving the values of density, kinematic viscosity, cetane number and flash point.

### 3.7. Comparison of Cat.TS-7 catalyst with other catalysts

Table 6 contains a comparison of the present catalyst with some Ca based catalysts. Although the biodiesel yield achieved with other catalysts in Table 6 was lower than the yield achieved in our current study, the reaction conditions were higher. When using Cat.TS-7 catalysts, a higher yield was obtained at lower temperatures, lower catalyst amount, and in a shorter time. This means lower production costs, which is the desired situation in biodiesel production.

## 4. Conclusion

Based on the research that was conducted, it can be concluded that the production of biodiesel from waste cooking oils using heterogeneous catalyst (Cat.TS-7) originated from natural zeolite can be implemented. The optimized Cat.TS-7 showed excellent results (93% yield) under the following reaction conditions; ratio of methanol to oil (1: 9) mol, the amount of catalyst (1.5% of the weight of the oil), reaction temperature of 60 °C, and reaction time of 2 h. High purity biodiesel was obtained. The produced biodiesel was characterized and compared with international standards, and the results were in accordance with the American (ASTM) and European (EN) standards. Reusability testing shows that the catalyst (Cat.TS-7) derived from natural zeolite is reusable up to 5 times, the results also showed that the best mixing ratio was B<sub>20</sub>.

### Author contribution statement

Mayas Abdo yousef Saad: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Baraa Siyo, Hussam Alrakkad: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

### Data availability statement

Data will be made available on request.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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