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Biodiesel Production using Synthesized HY Zeolite Catalyst

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Abstract

Biodiesel was produced using oleic acid esterification and transesterification of the sunflower oil methods. Many different factors affecting production procedures were studied such as reaction temperature, the molar ratio of ethanol to oil, reaction time and concentration of HY catalyst.

Different techniques such as TGA, FTIR and Mass spectroscopy were used to syntheses biodiesel. Results showed that 78% of oleic acid maximum conversion was obtained at a temperature of 70°C with molar ratio 12:1 ethanol: oil with 5 wt.% catalysts at 90 min reaction time, while for sunflower oil conversion of 98% at 200oC with 5 weight ratio of ethanol: oil at a time of 3 h was successfully obtained.

Keywords: Biodiesel, Esterification, Transesterification, Oleic Acid, HY zeolite..

تحضير الوقود الحيوي باستخدام عامل مساعد غير متجانس نوع HY

الخلاصة:

تم تحضير العامل المساعد الزيولايت من خلال اعملنا السابقة بطريقة السول-جل تحت الظروف الحرارية، وكانت المساحة السطحية له تبلغ 612.83 م²/غم والذي كان فعالاً في تفاعل الاسترة لحمض الاوليك لانتاج الديزل الحيوي وبنسبة مقاربة للعامل المساعد التجاري بسبب الحامضية الجيدة للزيولايت المحضر المكبرت.

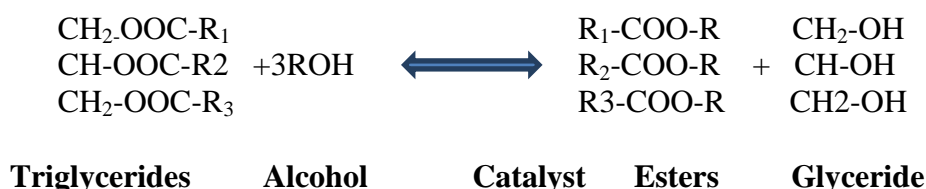
تم تحضير الوقود الحيوي باستخدام طرق مختلفة الطريقة الاولى تفاعل استرة حامض الاوليك والطريقة الثانية تفاعل الترانس لزيت عباد الشمس.

تم دراسة العوامل المؤثرة على عملية الانتاج مثل درجة حرارة التفاعل، النسبة المولية للكحول الى الزيت، زمن التفاعل ونسبة العامل المساعد المستخدم. كذلك تم تشخيص الوقود المنتج باستخدام التحلل الحراري TGA وباستخدام التحليل الكراموتوغراف GC-mass. كانت اعلى نسبة تحول متحققة لحمض الاوليك

بحدود 78% تم الحصول عليها عند درجة حرارة 70 درجة مئوية، 12 نسبة مولية من الكحول الى الزيت، 5% من العامل المساعد عند درجة حرارة 90 درجة مئوية. بينما كانت نسبة تحول زيت عباد الشمس بحدود 98% عند درجة حرارة 200 درجة مئوية، 5% نسبة الكحول الى الزيت خلال 3 ساعات.

1. Introduction:

Biodiesel is the fuel that attracted much attention and support as more renewable and potential cleaner fuel for diesel engines, producing less air pollution compared with conventional petroleum diesel. Biodiesel can be produced from numerous biological materials, including vegetable oils and waste fats [1]. Transesterification process is the most common way of producing biodiesel where a pure triglyceride is converted into fatty methyl or ethyl ester and glycerol [2].



Heterogeneous catalysts have been used due to their ease of separation from reaction stream, corrosion reduction and reusability. The objective of the research is firstly to investigate the activity of the synthesized HY catalyst for esterification of oleic acid to produce biodiesel under different reaction conditions (reaction time, temperature, catalytic ratio & alcohol/oil ratio). Secondly, transesterification of treated sunflower oil to produce biodiesel under various reaction conditions (reaction temperature and time). Zeolites have been used as catalysts to convert high free fatty acid oils to FAME. A good conversion of oil into biodiesel was observed at the time between 10 minutes and 50 minutes in the basic and acidic form of zeolites, such as NaY zeolites, while the negative influence of water resulted in low conversion [3]. Zeolite type Y was prepared from Iraqi kaolin with a final Si / Al ratio of 3.1 and used in oleic acid esterification as a catalyst. A variety of parameters such as molar ratio, temperature and mass load catalyst have been tested. It was observed that 70 ° C, loading 5wt% and 6:1 ethanol to oleic acid ratio fixed as the best reaction conditions. The conversion by zeolite catalyst was 85% after 60 min. Although the highest value was 76% for the commercial sample of HY zeolite.

They found that a low zeolite content of Si / Al was the most appropriate for use in the esterification process. [4]

2. Experimental work

2.1 Materials

Table (1) Materials list of materials supplier and purity

Chemicals	Formula	Molecular weight g/gmol	Purity %	Supplier
Sunflower oil	C ₁₆ H ₃₂ O ₂ C ₁₈ H ₃₂ O ₂ C ₁₈ H ₃₄ O ₂ C ₁₈ H ₃₆ O ₂	876.16	-	Local market
Ethanol	C ₂ H ₅ OH	46.07	99.8	Scharlau
Oleic Acid	C ₁₈ H ₃₄ O ₂	282.47	99	Sigma
Phenolphthalein	C ₂₀ H ₁₄ O ₃	318.32	99	Sigma

2.2 Catalyst properties:

2.2.1 Synthesized HY zeolite prepared according to our previous work [5] having the properties listed in Table (2).

Table (2) properties of the prepared HY zeolite

property	value
Al ₂ O ₃ wt%	57.96
SiO ₂ wt%	19.01
Al ₂ O ₃ /SiO ₂ Molar ratio	5.2
BET surface area m ² /g	612.83

2.2.2 Esterification reaction of Oleic acid

The esterification reaction of Oleic acid and ethanol was performed in 500 ml batch reactor under total reflux condition. It was supplied with a heating magnetic stirrer. The required catalyst amount was subjected to drying at 120°C for a period of 2h. while 50 ml or about (44.75 g) of the oleic acid with different ethanol to oil weight ratios including (3, 6, 9 and 12) at a reaction temperature of 70°C at an interval time

of 15 min. 5 ml- samples were withdrawn from the reaction vessel- which was centrifuged for 10 min at 3000 rpm to separate the HY catalyst from the liquid mixture. Acid value (AV) was evaluated for the floating layer when titrated with 0.1N potassium hydroxide with the addition of Phenolphthalein indicator to be calculated according to equation (1):

$$AV = \frac{\text{ml of KOH} \times N \times 56.1}{\text{weight of sample}} \quad \dots (1)$$

The conversion of oleic acid can be calculated from each amount of catalyst using the acid value as shown in equation (2):

$$\text{Conversion \%} = \frac{AV_{to} - AV_t}{AV_{to}} \times 100 \quad \dots (2)$$

Where, (AV_{to}) is the acid value of the reaction product at a time (0) and (AV_t) represents the acid value of the reaction product at a time (t) [4] and [1].

2.2.3 Trans-esterification of Sunflower oil

2.2.3.1 Pre-treatment of sunflower oil

One of the important steps in transesterification reaction was to decrease the acid value to be lower than 2 mg of potassium hydroxide per each gram. Therefore, the sunflower oil was pre-treated to be suitable for the reaction. A glass reactor was loaded with 200 g of the oil and preheated to 70°C, and different ethanol to oil ratio was used (20, 25, 30, 35) as well as 1 wt.% of sulfuric acid was added in the reactor and the reaction continued for 30 min. Then the mixture was transferred to a separating funnel to separate treated oil from alcohol. The top layer was alcohol acid and part of Fatty Acid Ester (FFA) and the bottom layer was the treated oil [6] [2].

2.2.3.2 trans-esterification reaction

Reactions of the trans-esterification were implemented using a controlled temperature 500 ml glass reactor supplied with a stirring and condensation system. 250 g of pre-treated oil was loaded to the reactor and heated to the temperature of 70 to 200°C after that the heated ethanol and catalyst were added. After ethanolysis reaction finished; the product was left for some time in a separating funnel for

glycerol separation then the upper layer of ethyl esters was washed with warm water and heated in a rotary evaporator to remove the excess amount of ethanol.

The final amount of ethyl ester was separated and then dried using a rotary evaporation unit and weighed and the final conversion was calculated using equation (3). [6] [2].

$$\text{conversion \%} = \frac{\text{weight of Ethyl ester}}{\text{weight of original oil}} \times 100 \quad \dots(3)$$

3. Results and discussions

3.1 The Esterification Reactions

Oleic acid esterification with alcohol was carried out using a prepared HY zeolite as a catalyst. This type of reactions is classified to be a reversible reaction, thus an additional amount of ethanol was required for enhancing the reaction conversion. The esterification reaction is regulated by some factors including reaction temperature, reaction time, ethanol/ oleic acid ratio, and catalyst loading.

3.1.1 Reaction Temperature Effect on the oleic acid conversion

One of the reaction kinetics key factors is the reaction temperature because the rate of reaction is a temperature-dependent function under Arrhenius's law. Therefore, oleic acid esterification with ethanol takes place in the liquid phase and the targeted reaction was carried out below the boiling point of ethanol. The temperatures 60 and 70°C were investigated at different molar ratios for ethanol to oleic acid of (3/1, 6/1, 9/1 and 12/1).

It is obvious from Figures (4.1) & (4.2), the conversion increased from 64 % to 74 % as the reaction increased from 60 to 70°C. This effect was predicted as the temperature enables the molecular activity to be increased under the theory of collision (i.e. the need for more molecular energy could overcome the energy barrier of reaction and reacts very well).

There is also a reason for the increased viscosity of the reactant decrease when the temperature increases which means that the molecular diffusion is increased through the internal pores of the catalyst. This leads to a quick reaction for the first 90 minutes at temperature 60 and 70°C within the vital sites of the catalyst. The conversion of oleic acid was subsequently decreased due to the deactivation of the zeolite HY catalyst which could be resulted from the clustering of water molecules within the catalyst's pore based on the hydrophilic nature of zeolite, thus raising the reverse reaction which led to a decrease in conversion.

Figures (1) & (2) also show the reaction of oleic acid conversion as expected the fractional conversion increases as the reaction time rises with-molar ratio. It was found that the best maximum conversion of 77 % is obtained at a 12/1 molar ratio at 70°C, which means that reaction reaches equilibrium. All results are compatible with previous results reported in [7-10].

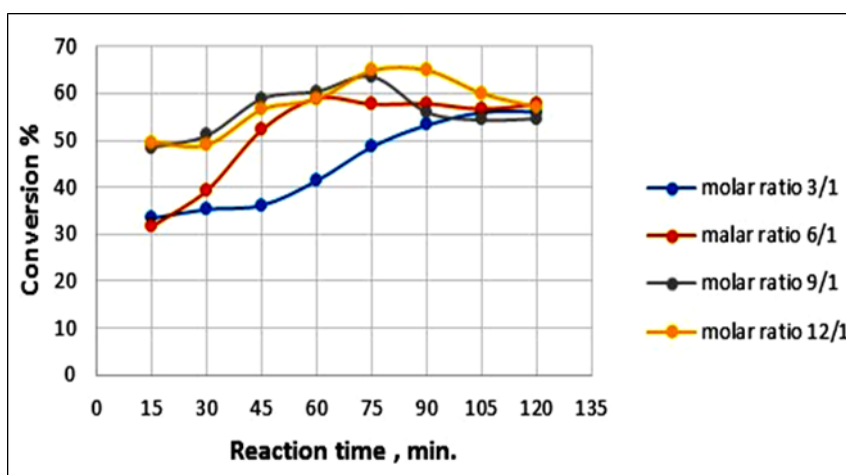


Fig. (1) Oleic acid conversion as a function of molar ratio Ethanol / Oil at 60°C.

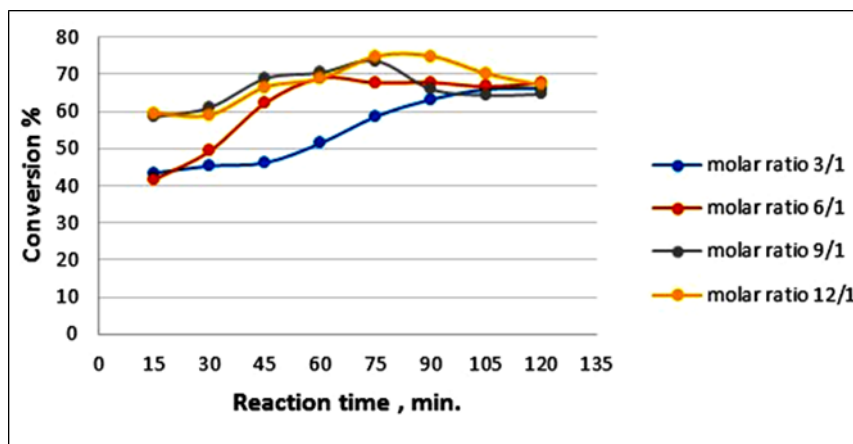


Fig. (2) Oleic acid conversion as a function of molar ratio Ethanol / Oil at 70°C.

3.1.2 Impact of catalyst quantity on oleic acid conversion

In the esterification reaction of oleic acid with ethanol, the reality of weight per cent of catalyst to oil was used to test the behavior of prepared HY catalyst. Reactions were performed at a constant temperature of 70°C and with a fixed ratio of 12/1 ethanol to oil. The effect of different weight per cent of the catalyst effect is shown in Figure (3). The best results at 5 wt. % of the catalyst.

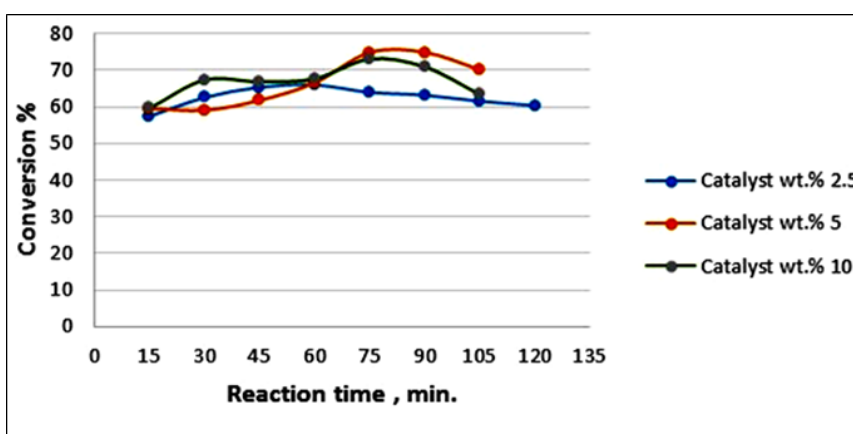


Fig. (3) Oleic acid conversion as a function of catalyst ratios

As seen in Figure (3) the esterification reaction was directly proportional to the quantity of catalyst loaded, and this issue was expected because the rise in catalyst quantity implies a rise in other active sites where the esterification reaction occurred. There is a slight increase in conversion between 5wt.% and 10wt.% and this not

remarkable because at a higher amount the catalyst although of the available high surface area of the catalyst but this cause more accumulation of water on internal catalyst pores resulting from the hydrophilic properties. These observations were in strong alignment with other researches that stated that an increase in the volume of catalyst above 5 wt. % did not affect the acid value being decreased [11], [12].

3.1.3 Molar ratio of Ethanol / Oil influence on the conversion of oleic Acid

The oleic acid esterification reaction with ethanol is a reversible reaction with an ethanol/oil molar stoichiometry ratio of 1:1. For improved processing, an additional quantity of ethanol is usually required. Unreacted ethanol has to be recovered and a significant amount of energy is required, so the optimum combination of energy-saving and effective reaction efficiency should be calculated as effectively as possible. Four ethanol/oil molar ratios were used 3:1, 6:1, 9:1 and 12:1, with a specified 5wt. % catalyst and a steady 70oC reaction temperature. A substantial rise in oleic acid production can be observed, as seen in Figures (4) & (5). It can be concluded that as the molar ratio rises there was a major change in oleic acid production. This excess alcohol moved the equilibrium reaction to the direction of product formation.

Another clarification is the viscosity of the reaction medium, the viscosity of the mixture decrease if the ratio increases since the viscosity of ethanol is being lower than oleic, then at high ratio (low viscosity) the effect of reactant diffusion to catalyst particles was reduced leading to increase in the reaction productivity. It can be observed in different studies and previous work, which the abroad range of the alcohol/oil ratio up to 30/1, also at a higher ratio. But it must be taken into account that at a high ratio there will be higher water and this undesirable since it reduced the final product [3, 13, 14, 15].

3.1.4 Comparison between prepared and commercial HY Zeolite Catalyst

Comparison between prepared and commercial HY catalyst was investigated at 5 wt.% of catalyst and 12/1 Ethanol /oil molar ratio and the conversion was about 77 for synthesized catalyst while for the commercial catalyst is about 80 % as shown in Fig.4. There was a slight increase in conversion between commercial and prepared

catalyst due to large pore volume and higher surface area and this delayed the deactivation of the catalyst [16].

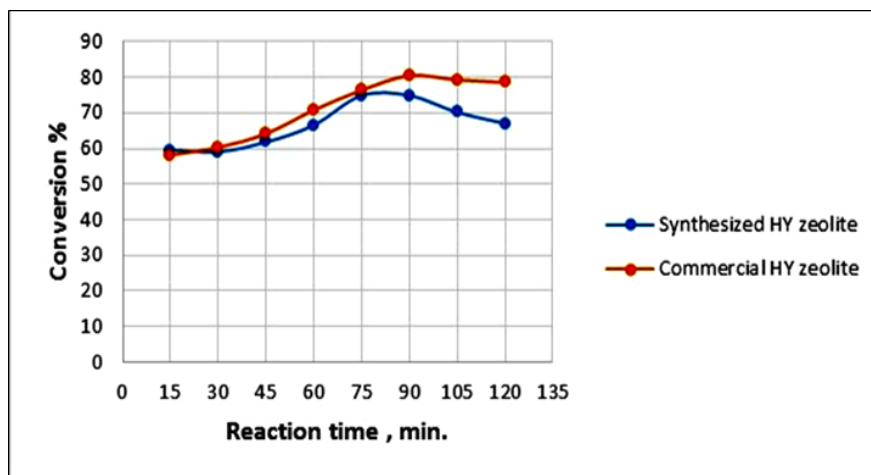


Fig. (4) Activity comparison between prepared and commercial HY zeolite at 70°C, 12/1 Ethanol / Oil molar ratio.

3.2 Transesterification Reaction

3.2.1 Production of Biodiesel

Trans-esterification reaction is carried out using HY synthesized catalyst at different reaction conditions. Best biodiesel yield was about 98 % obtained at 3h reaction time at 200o C, Ethanol /oil ratio = 5 and 5 wt. % HY catalyst as shown in Figures (5) and (6). These results are compatible with [4] because they achieved a yield of about 92 % by transesterification using 10wt.% KOH on NaY zeolite at 60°C 4 h and 15/1 ethanol/oil ratio.

As seen in literature the sunflower oil contains four fatty acids which are palmitic acid (C₁₆H₃₂O₂), linoleic acid (C₁₈H₃₂O₂), oleic acid (C₁₈H₃₄O₂), and stearic acid (C₁₈H₃₆O₂) so these fatty acids could convert to ester-type which is the biodiesel. The yield of biodiesel is calculated according to the following equation:

$$\text{Yield \%} = \frac{\text{weight of biodiesel}}{\text{weight of oil used}} \quad \dots (4)$$

The transesterification of oil occurs in presence of proton H⁺, and due to the transfer of proton to the oxygen atom which is double-bonded to the carbon atom, so a positive charge will be attached to the oxygen atom. Then the positive charge will

be localized on the carbon atom and in the second step, the positive charge will be attacked by an oxygen atom of a hydroxyl group in the alcohol giving a water molecule and ester is formed [17].

So, if there is no sufficient acidity in the catalyst, the reaction in step one and formation of the carbonium ion will be weak and the above mechanism will be disturbed. Sulfonated HY catalyst considered to have good strength acidity, besides its pore volume gives rise to the diffusion of large fatty acid to react inside it producing more biodiesel. [18]. the suggested mechanism is shown in scheme 1 [19].

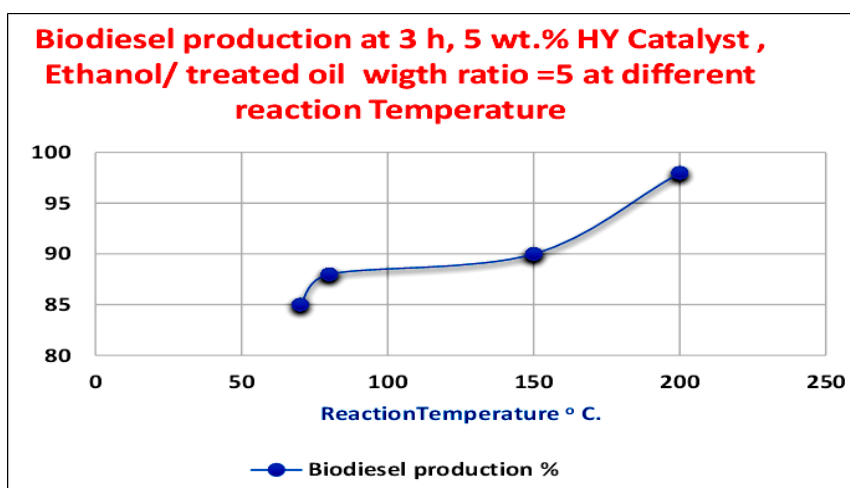


Fig. (5) Biodiesel Yield % at different reaction temperature.

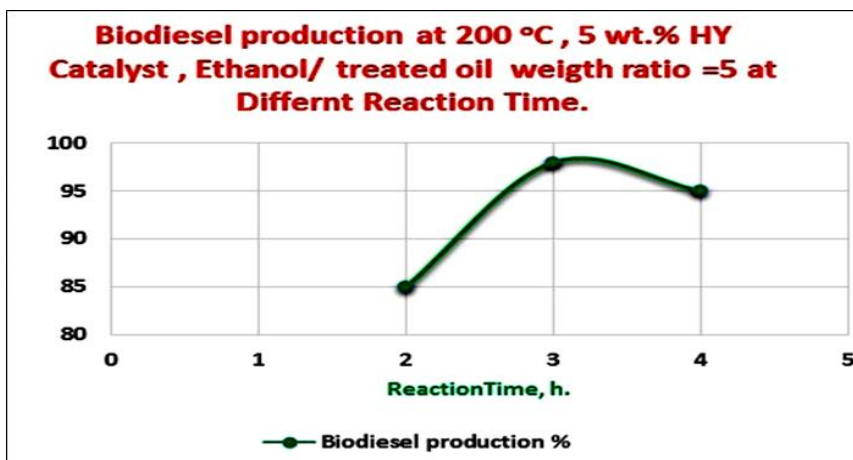
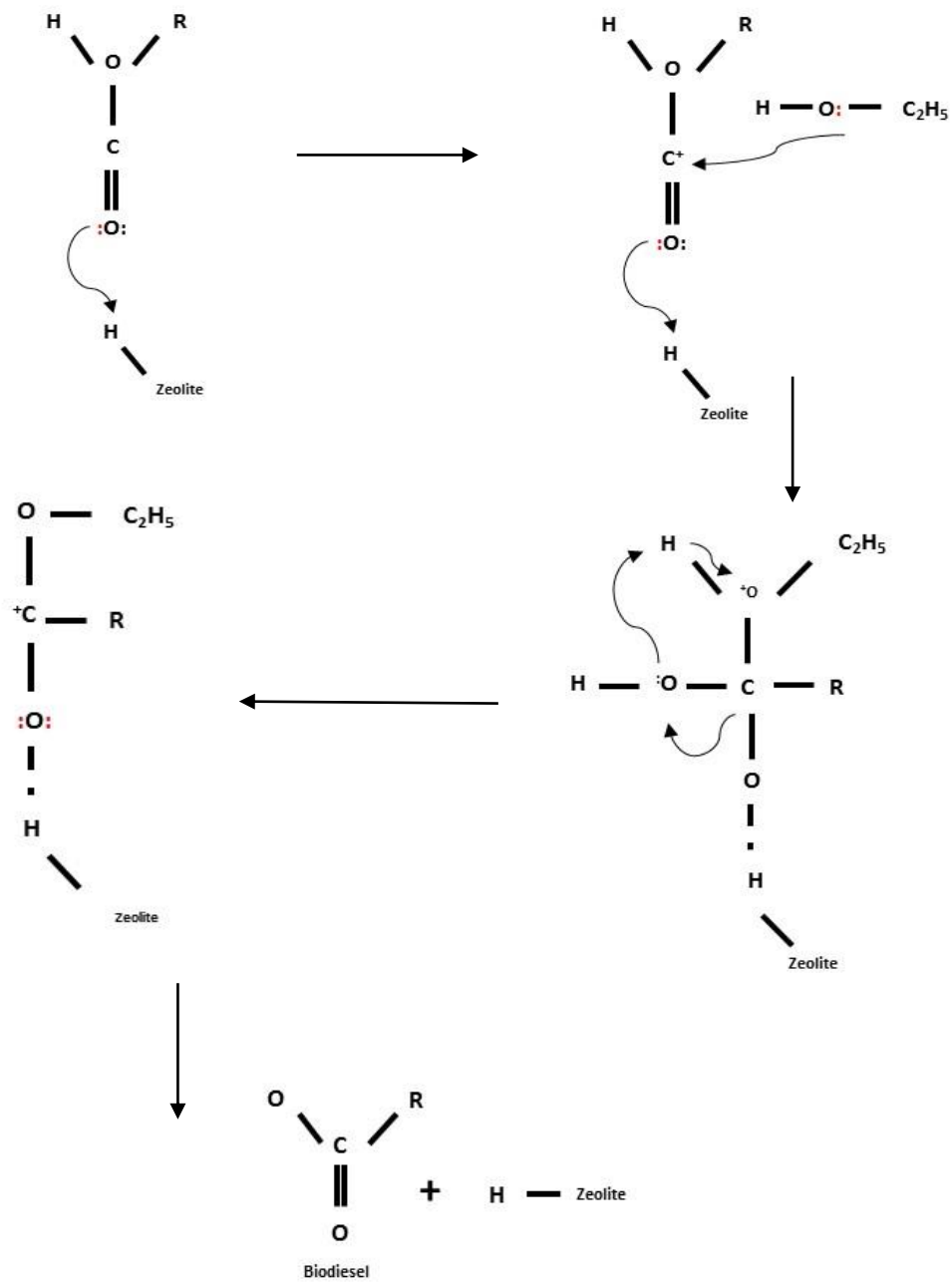


Fig. (6) Biodiesel Yield % at different reaction time.



Scheme. (1) Suggested mechanisms where R = Alkyl group

3.2.2 Characterization of Biodiesel:

The product specifications are very important since from which it can decide the validity of the produced biodiesel. The properties of prepared biodiesel are characterized using different techniques:

3.2.2.1 GC –Mass, Gas Chromatography Mass Spectroscopy:

GC-Mass spectroscopy was done on specimens of synthesized biodiesel, and the results of mass spectrum for produced was performed to investigate the ethyl ester group. The main characteristics peaks of fatty acid ester appeared by the retention time and the fragmentation pattern data.

The four peaks identified as 9-hexadecanoic acid methyl ester (C16:1), 9,12-Octadecadienic acid methyl ester (C18:2), 9-Octadecanoic acid methyl ester (C18:1) and Octadecanoic acid methyl ester (C18:0) [1], [5]. Table (3) identified the composition of FAMES presents at optimum prepared biodiesel and as shown from data, the glycerol characteristics peak is present at GC –MS analysis of prepared biodiesel at a retention time of (5 to 21 min).

These results confirm our selected condition and completeness of the trans-esterification process of triglycerides in the vegetable oil into biodiesel.

Table (3) Fatty acid ethyl ester [1].

<i>Peak</i>	<i>Retention Time</i>	<i>Fatty Acid Ethyl Ester</i>	<i>Common Name</i>
1	5.41	C16	Methyl palmitic
2	18.67	C18:0	Methyl stearate
3	20.87	C18:1	Methyl oelate
4	21.16	C18:2	Methyl linoalte

3.2.2.2 TGA – Thermal Gravimetric analysis:

TGA is an effective way to quantify the produced biodiesel due to the large temperature difference between the weight loss temperature of oil and biodiesel as shown in Figures (7) and (8). It is well known that the biodiesel starts to thermally decompose at approximately 150°C and continue its thermal decomposition until complete vaporization. However, the vegetable oil begins its thermal degradation at

approximately 300°C. Accordingly, the percentage of biodiesel conversion can be determined from weight loss as mentioned in the literature. Biodiesel vaporized completely around 330°C and the optimum weight loss percentage from 120 to 330°C as regards total weight loss was about 95%.

This compatible with transesterification results. These confirm successful biodiesel production. Also, confirm previous GC-MS analysis results.

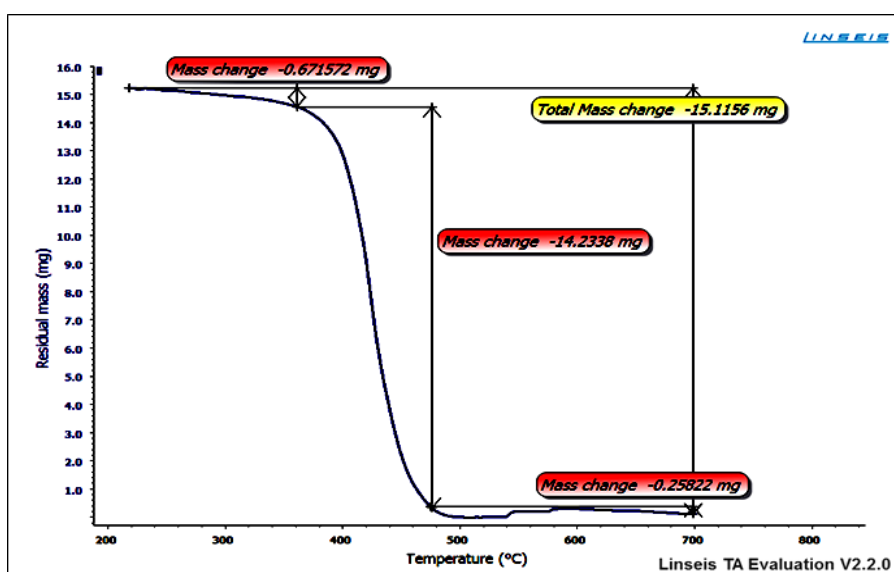


Fig. (7) TGA analysis for sun flower Oil

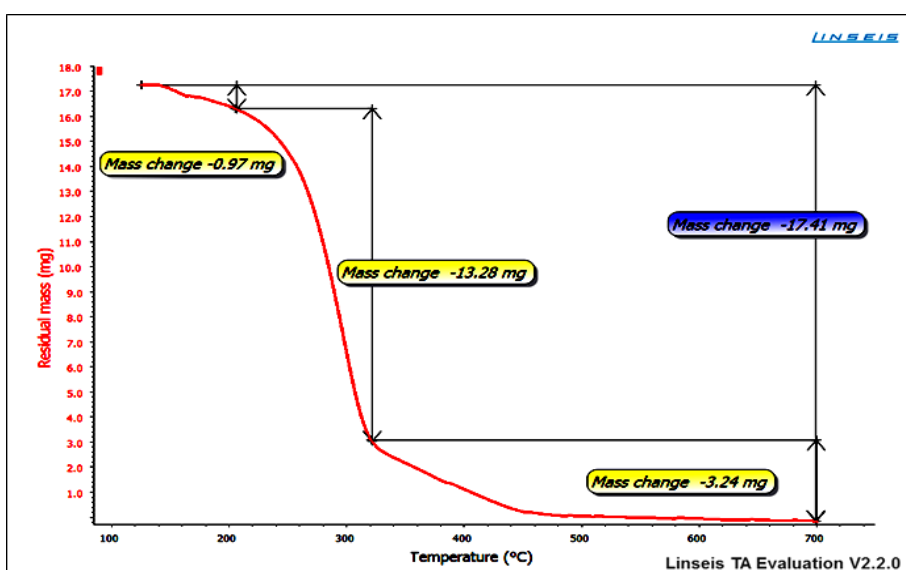


Fig. (8) TGA analysis for produced Biodiesel

3.2.2.3 FTIR Fourier Transform Infrared Spectroscopy

Fatty esters (FAME) are quantified using FTIR. The main functional groups present at produced biodiesel and vegetable oil. The most characteristic absorption peaks of the vegetable oil were indicated. The absorption peak appearing at 721 cm^{-1} is representative of $-\text{CH}_2$ rocking and the other one at 1745 cm^{-1} is representative of $\text{C}=\text{O}$ ester stretch. The produced biodiesel absorption peaks appearing at 1434 cm^{-1} which is the methyl ester group ($\text{CO}-\text{O}-\text{CH}_3$) and the characterization peak at 1195 cm^{-1} corresponding to $(\text{C}-\text{O})$ ester peak. The reduction of $\text{CH}_2-\text{O}-$ groups in oil and the appearance of $\text{CH}_3-\text{O}-$ vibrations in biodiesel were obvious. Also, the split of 1163 cm^{-1} in the oil sample into 1195 cm^{-1} and 1168 cm^{-1} in the biodiesel sample indicates the conversion of oil into biodiesel. The main difference between the two FTIR spectrums is related to the transformation of ester groups at the oil sample into methyl esters at the produced biodiesel.

3.2.2.4 Biodiesel properties:

Produced biodiesel has different properties that characterized it. These properties are listed below:

- **Flashpoint:** Flashpoint (closed cup) for a synthesized sample of biodiesel was measured and the result was 120°C , it is above the standard value of 93°C .
- **Density:** Specific gravity of produced biodiesel was measured and the result was 0.886 g/cm^3 .
- **Viscosity:** The measured kinematic viscosity was $5.3\text{ mm}^2/\text{s}$ at 40°C , which is in the range of standard mentioned above, between $1.4-6\text{ mm}^2/\text{s}$.
- **Pour point:** Measured pour point was -15°C .
- **Heating value:** The heating value was 34.64 KJ/Kg .

4. Conclusion

HY type zeolite had been successfully prepared in our previous work by the sol-gel method under hydrothermal conditions. Synthesized HY with BET surface area of $612.83 \text{ m}^2/\text{g}$ was an active catalyst for the esterification reaction of oleic acid producing biodiesel with conversion comparable to those of commercially HY catalyst, due to the good acidity of the prepared sulfonated HY catalyst.

Transesterification reaction of sunflower oil was carried out using synthesized HY zeolite. The optimum conversion was 98% at a reaction temperature of 200°C , Ethanol /oil ratio = 5 and 5 wt. % HY and 3 h reaction time, while the results proved the effectiveness of zeolite catalyst to obtain biofuels through the reaction of oleic acid esterification in the presence of ethanol, where highest conversion rate was obtained up to 78% under the reaction temperature of 70°C . The characterization of final produced ethyl ester (biodiesel) such as density, viscosity and heating value within the acceptable range of biodiesel. the flash point was higher constituted a safety guarantee for handling and storage.

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