

KINETICS OF ESTERIFICATION OF OLEIC AND LINOLEIC FREE FATTY ACIDS

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ABSTRACT

The kinetics of the esterification of oleic and linoleic acids using a batch reactor are described in this study. Effect of relevant factors on ester conversion, such as reaction temperature, dose of sulphuric acid as a catalyst, and methanol/FFAs (oleic and linoleic acid) mole ratios are studied. The results showed that the maximum conversion of oleic and linoleic were 88% at 40:1 methanol/FFA molar ratio at 68°C, catalyst 2 wt. % of FFA and reaction time 30 min. A pseudo-homogeneous kinetic model was proposed for the esterification. The influence of Temperature on the rate constants is presented by Arrhenius equation, and the activation energies were found to be 43.42 and 45.51 kJ/mol for linoleic and oleic acid, respectively.

Keywords: Esterification; Oleic acid; Linoleic acid; Methanol; Kinetics.

1. INTRODUCTION

Sustainable energy has attracted more awareness recently. The increasing demand of energy makes the implementation of sustainable fuels. Biodiesel has been recognized as substitute for diesel fuel produced from petroleum^[1]. Biodiesel is produced mostly from vegetable non – edible oils by trans esterification process. Some of these vegetable oils have a higher quantity of FFAs that causes undesired by-product of soap formation. Consequently an acid-catalysed esterification process can effectively pre-treat the FFAs prior to the biodiesel production since mineral acids can overcome the problem of soap formation^[2]. The necessity to remove FFA and the interest in studying the kinetics of the reaction of the two unsaturated fatty acids (oleic and linoleic) led to study and examine the effect of operational variables on the kinetics of esterification of the two fatty acids acid using sulphuric acid as a catalyst. The objective of this paper was to study the kinetics of acid esterification of the two

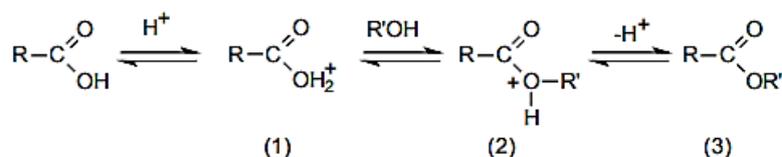
unsaturated FFA, using sulfuric acid as a catalyst.

2. ACID-CATALYSED ESTERIFICATION

1. General Mechanism

The carboxylic acids are esterified by reacting with alcohols in presence of an acidic catalyst as shown in scheme 1. The first step is protonation of the acid to produce an oxonium ion, which causes an exchange reaction with an alcohol to give the intermediate compound, and by losing this proton the ester is formed. The esterification reaction is reversible, therefore large excess of the alcohol is used to shift the reaction towards the formation of the ester. Donato et al^[3] stated that the presence of water causes the formation of the intermediate that is not favoured and esterification thus will not proceed fully.

The preferred conditions for the esterification of carboxylic acids are using large excess of the alcohol, and absence of water by using the adequate amount of acid as catalyst^[4].



Scheme 1. Acid-Catalysed Esterification of Fatty Acids.

2. Kinetics of Esterification Reaction

The kinetic results obtained from laboratory usually play a very important role in modelling and scale up designs for new biodiesel production units^[5]. The information obtained by differential technique of analysis has been used to find the kinetic model for FFA esterification. The conversion of FFA (x) according to the time at certain temperature was determined, and then finding the rate coefficients (k) as well as the orders of the reactions. According to Arrhenius law, the activation energy of the reaction can be determined from a plot of (ln k) vs. (1/T).

Thiruvengadaravi et al.^[6] optimized the pre-treatment process by studying the kinetic and thermodynamic of the esterification process. Cardoso et al.^[7] evaluated the use of SnCl₂·2H₂O as catalyst for the ethanolysis of oleic acid (pure and added to soybean oil) and investigated key parameters of reaction. Yadav, P. K. et al.^[8], optimized the conditions for production of palm fatty acid methyl esters. Berrios et al.^[9] examined the influence of operational variables on the kinetics using fatty acids in sunflower oil and methanol. Sendzikien et al.^[10] determined the optimal conditions of oleic acid esterification by methanol using acid catalyst and calculated the kinetic parameters of this process.

3. MATERIALS AND METHODS

a- Materials

1. Oleic acid was obtained from local market with composition of 74% by wt. (from GC-FID analysis). The specific gravity of the oleic acid was 0.895.
2. Linoleic acid was purchased from Sigma Aldrich with composition of

62% by wt. containing 30% by wt. oleic acid (from GC-FID analysis).

3. Methyl alcohol was obtained from local markets with specific gravity of 0.7692 (88 to 90 wt. %).
4. Sulfuric acid was obtained from local markets, the concentration of this acid was 98% (Sp.Gr. is 1.84).

b- Methods

The laboratory experimental set-up (shown in Fig. 1), consisting of a three-necked flask, was used for executing the esterification reaction. In this flask, one neck was fitted with a reflux condenser, the second neck was blocked with a rubber cork at the time of experiment, where it was opened to draw samples of the reaction mixture were at frequent intervals of time to be quenched in ice for the kinetic study. Reaction temperature was monitored by a thermometer. For controlling stirring and temperature of the reaction, a hot plate with magnetic stirrer and water bath was used. The reaction was carried out in the temperature range 23-68°C, while the catalyst concentration was varied from (0.8-8) wt. % of FFA. The molar ratio of methanol to FFA was varied from 2 to 80 and for linoleic acid was varied from 8 to 80. The reaction mixture samples were titrated against 0.1N NaOH aqueous solution using phenolphthalein as an indicator. The normality of FFA was calculated by (Eq.1):

$$V_{\text{FFA}} \times N_{\text{FFA}} = V_{\text{NaOH}} \times N_{\text{NaOH}} \quad \text{Eq.1}$$

Where V is the volume and N is the normality.

Normality of residual oleic acid was calculated by (Eq.2):

$$V_{\text{Sample}} \times N_{\text{Sample}} = V_{\text{NaOH}} \times N_{\text{NaOH}} \quad \text{Eq.2}$$

Free fatty acid conversion(X) was calculated by (Eq.3):

$$X = \frac{N_{\text{FFA}} - N_{\text{Sample}}}{N_{\text{FFA}}} \quad \text{Eq.3}$$

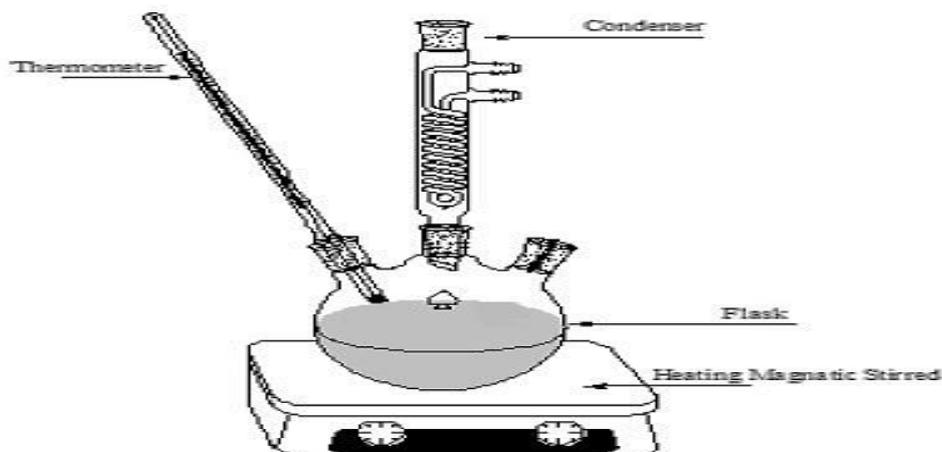


Fig.1. Experimental Setup for the Esterification Reaction

4. RESULTS AND DISCUSSION

4.1 Effect of Reaction Time on The Esterification Reaction

The impact of time on esterification of FFA with methanol is investigated by varying reaction time while other parameters had not been changed. The temperature was 68°C, the speed of agitation was 400 rpm, molar ratio of methanol to FFA alcohol was

40:1 and amount of catalyst was 2wt. % of FFA. Fig. 2 shows that oleic and linoleic acid conversions increased rapidly in the first 10 min. After 30 min, the conversion was rising very slowly and then become nearly constant till 90 min. This means that the reaction is at nearly equilibrium conditions. The production of methyl ester reached the maximum value after about 30 minutes.

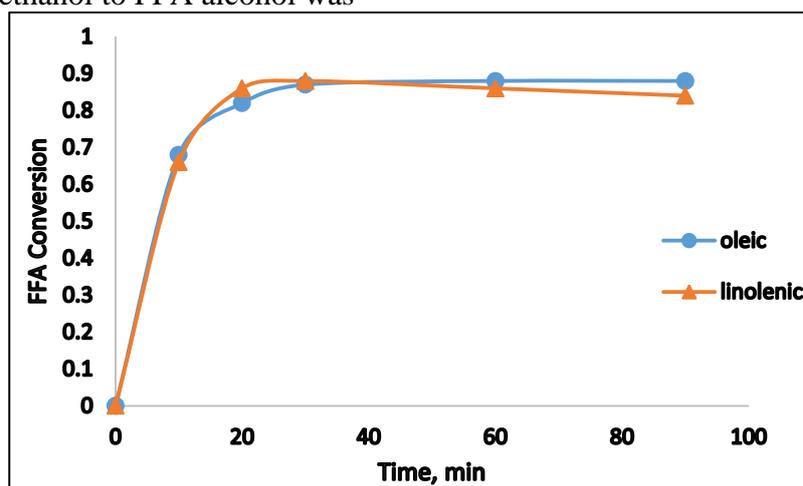


Fig.2. Effect of Reaction Time on FFA Conversion at a Molar Ratio Methanol: FFA (40:1), H₂SO₄ 2 Wt. % of FFA, Temperature of Reaction 68°C, and Mixing Speed 400 rpm.

4.2 Effect of Catalyst Amount on The Esterification Reaction

The amount of catalyst in this reaction was varied as 0.8, 2, 4, 6, and 8 wt. % of FFA at a temperature of 86°C and molar ratio of methanol: FFA of 40:1. Fig. 3 shows that the rate of conversion of linoleic acid was the lowest on using 0.8% H₂SO₄. Increasing the % H₂SO₄ from 2 to 8 wt. % of FFA led to an increase of initial conversion rate. It was found that more use of catalyst would add to the operating cost and has no effect on esterification reaction^[11, 12].

However, in case of oleic acid, (Fig. 4) shows that all percentages of H₂SO₄ used gave almost the same initial rate of conversions.

Moreover the final conversion increased from 62% to 88% on decreasing the % H₂SO₄ used. The optimal acid amount was 2 wt. % of FFA. Similar result had also been observed by other studies, where the conversion was reduced with further addition of sulfuric acid after the maximum conversion was achieved. This latter may be due to that the excess quantity of sulfuric acid consumes more NaOH during neutralization, which was accounted as FFA^[13, 14].

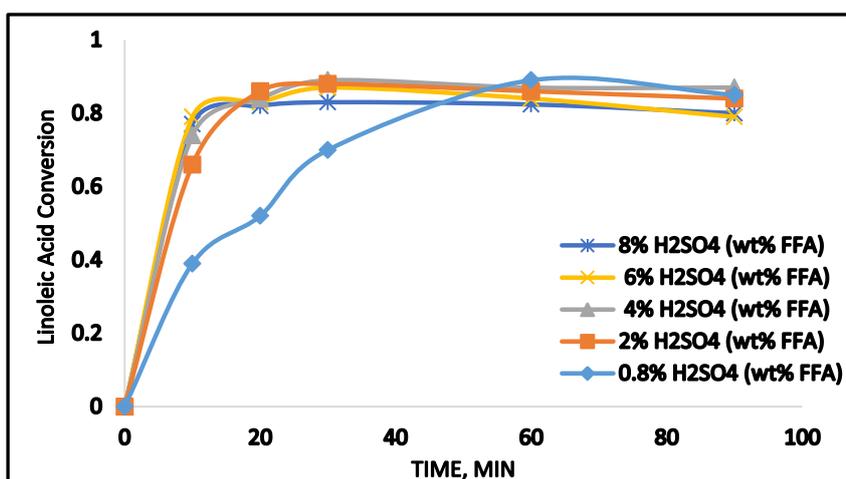


Fig.3. Effect of Catalyst Amount on Linoleic Acid Conversion at a Molar Ratio of Methanol: Linoleic Acid (40:1), Temperature of Reaction 68°C, and Mixing Speed 400 rpm.

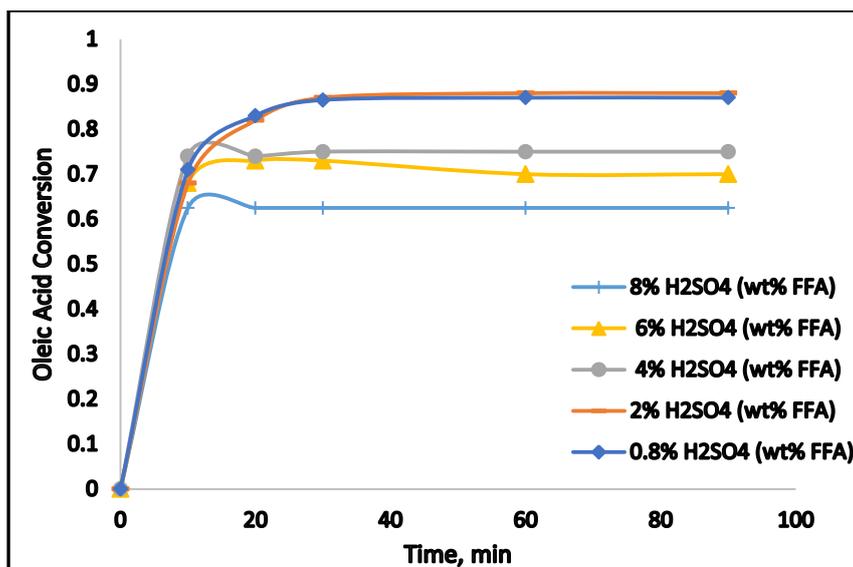


Fig.4. Effect of Catalyst Amount on Oleic Acid Conversion at a Molar Ratio of Methanol: Oleic Acid (40:1), Temperature of Reaction 68°C, and Mixing Speed 400 rpm.

4.3 Effect of Molar Ratio of Methanol to Free Fatty Acid on Esterification Reaction

The molar ratio of methanol to FFA is one of the most influencing factors on the esterification reaction. Excess methanol is required to drive the equilibrium towards forward reaction and to increase the rate of formation of esters^[15]. Fig. 5 shows the influence of methanol to oleic acid molar ratio in the range of (2:1) to (80:1) at a temperature of 68°C, and 2 wt. % H₂SO₄. It is clear that the initial rate of oleic acid conversion was the lowest at alcohol: FFA molar ratio of (2:1). Further increase in this molar ratio from (4:1) to (80:1) increased the initial rate of conversion. Yet in this range of molar ratio the difference in initial rate of conversion is negligible. On the other hand on considering the final conversion, it

is clear that increasing the molar ratio from (2:1) to (80:1) lead to an increase in the final conversion from 64% to 88%.

Similar results were obtained on using linoleic acid and alc.: FFA molar ratios from 8:1 to 80:1. Fig. 6 shows that the lowest initial rate of conversion was obtained at molar ratio of 8:1. Further increase in this molar ratio from (10: 1) to (40:1) increased the final conversion from 66% to 88%, additional methanol did not improve the conversion. At low molar ratios, the amount of residual alcohol is very low and hence water produced from the reaction would be separated as separate layer from the methyl ester formed and residual fatty acid^[16, 17]. This separated water may dilute the percentage sulfuric acid, thus decreasing the final conversion.

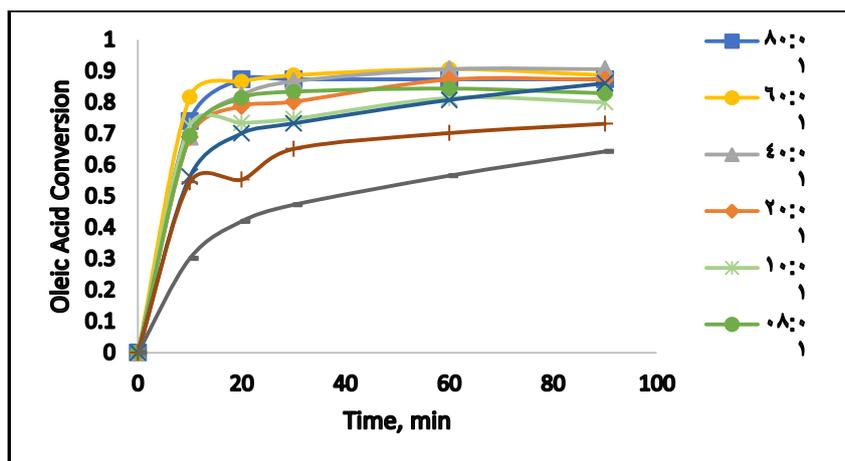


Fig.5. Effect of Molar Ratio on Oleic Acid Conversion at a Reaction Temperature of 68°C, H₂SO₄ 2wt. % of FFA, and Mixing Speed 400 rpm.

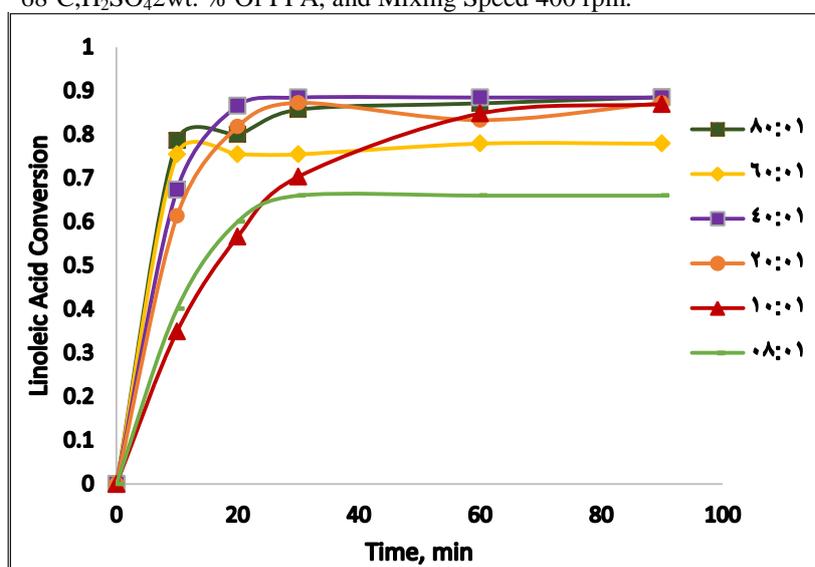


Fig.6. Effect of Molar Ratio on Linoleic Acid Conversion at a Reaction Temperature of 68°C, H₂SO₄ 2wt. % of FFA, and Mixing Speed 400 rpm.

4.4 Effect of Temperature on Esterification Reaction

Temperature is one of the most important variables affecting the conversion of FFA in esterification reaction (Figs. 7,8). The reactions were carried out at temperatures (22°C), 30, 40, 50, and 68°C respectively, at fixed conditions of methanol to FFA molar ratio 40:1, catalyst 2 wt. %, and reaction

time of 90 min. The conversion of FFA increased on increasing temperature due to the increase of molecular activity, which means that more molecules will have more energy^[18], thus, the possibility of molecules to react increases. As expected, increasing the temperature from 22°C to 68°C increased rate constant for the both tested free fatty acids (Table 2).

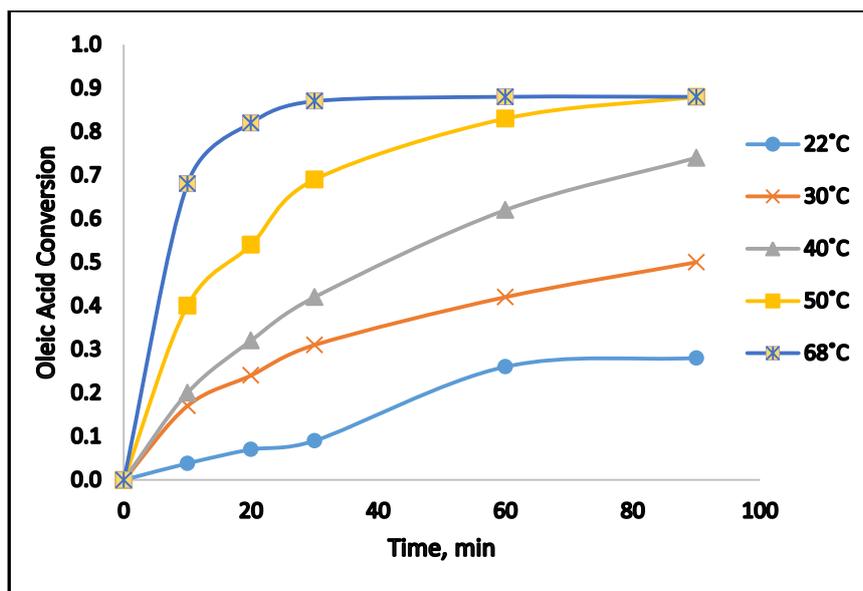


Fig. 7. Effect of Temperature on Oleic Acid Conversion at a Molar Ratio of Methanol: Oleic Acid (40:1), H₂SO₄ 2wt. % of FFA, and Mixing Speed 400 rpm.

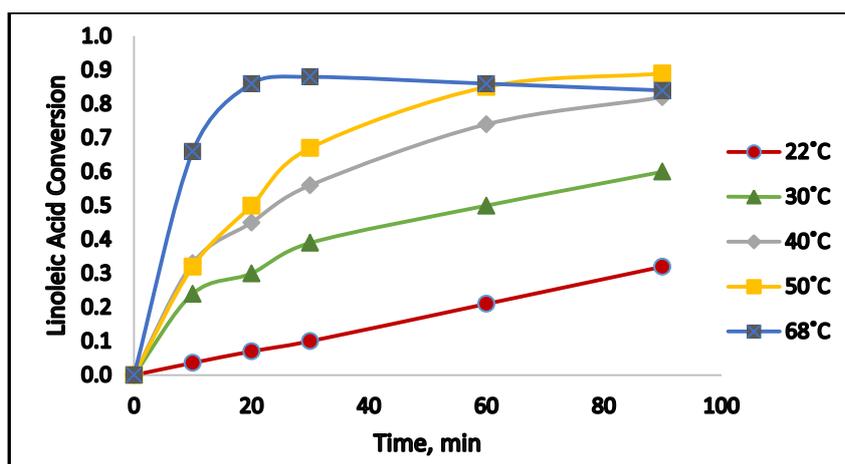


Fig.8. Effect of Temperature on Linoleic Acid Conversion at a Molar Ratio of Methanol: Linoleic Acid (40:1), H₂SO₄ 2wt. % of FFA, and Mixing Speed 400 rpm.

5. THE KINETIC STUDY OF OLEIC AND LINOLEIC FFAs

5.1 Determinations of Order and Initial Rate of the Reaction

It is well known that if one of the reactants is taken in large excess, that means concentration of any one reactant is very high, then the rate of reaction depends on concentration of the reactant at lower concentrations. In the present case the esterification of FFA with methanol was

carried in a large excess of alcohol (40:1 molar ratio), where the rate law is expected to follow pseudo first order dependence^[19]. Fig. 9 shows that, within the experimented conditions, an increase in the molar ratio causes the initial rate of conversion to increase according to (Eq. 4), which describes the variation of concentration of the substrate in relation to time:

$$r_A = k C_A^n \text{ Eq. 4}$$

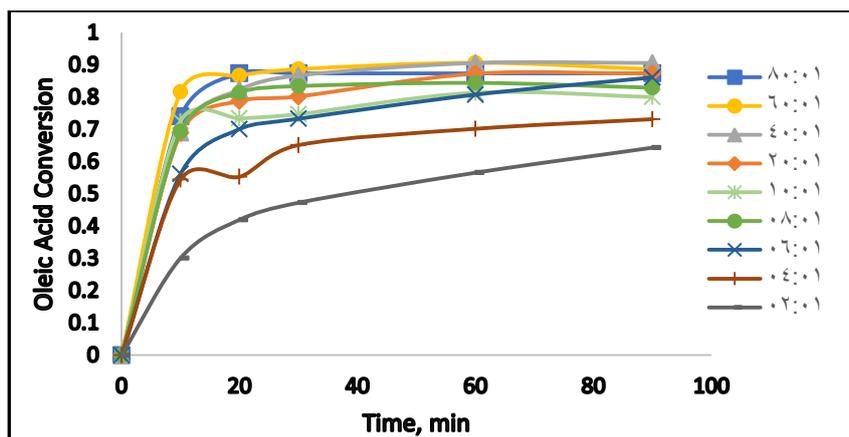


Fig.9. Determination of Initial Rate of Reaction at Different Molar Ratios of Oleic Acid, Temperature of Reaction 68°C, H₂SO₄ 2wt. % of FFA, and Mixing Speed 400 rpm.

Table1. Initial Rate at Different Molar Ratios

Molar Ratio of (methanol: FFA)	Initial Rate of Oleic Acid	Initial Rate of Linoleic Acid
2:1	0.035	-
4:1	0.05	-
6:1	0.06	-
8:1	0.07	0.038
10:1	0.08	0.04
20:1	0.11	0.07
40:1	0.11	0.08
60:1	0.125	0.1
80:1	0.18	0.11

Table 1 shows the different values of reaction rate constant as a function of molar ratio (Alc.: FFA) at 68°C. It is clear that for oleic acid, the reaction rate constant increased from 0.03 to 0.1 on increasing the molar ratio from (2:1) to (10:1). Further increase of molar ratio gave no increase in the value of (k).

For linoleic acid, it showed almost the same phenomena. Increasing the molar ratio from

(8:1) to (40:1) increased the value of k. Further increase of the molar ratio gave no increase in the value of k. A Plot of $\ln[r_A]$ versus $\ln[C_{A0}]$ gave a straight line for oleic acid with a slope equal to (n), the order of reaction. From this plot (Fig.10) it can be concluded that the esterification reactions of the two studied FFAs follow pseudo first order reaction.

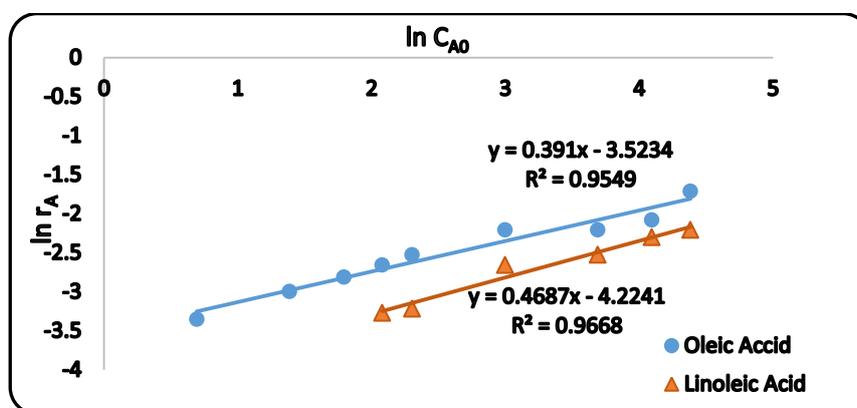


Fig.10. Determining Order of Reaction for the Two Fatty Acids.

Furthermore, the values of the overall rate constants shown in (Table (2)) were used to determine the activation energy (E_a)

following Arrhenius (Eq.5). It was found that with an increased (k) value, the reaction rate becomes faster and the conversion

obtained was increased^[20]. That phenomenon is appropriate with Arrhenius equation:

$$k = A e^{(-E_a/RT)} \text{ Eq.5}$$

Where k = rate constant (min^{-1}), E_a = activation energy (J/mol), T = absolute temperature (K), A = frequency factor

Table2. k Values at Different Temperatures.

Temperature	k oleic acid (min^{-1})	k linoleic acid (min^{-1})
22	0.004	0.004
30	0.019	0.027
40	0.023	0.04
50	0.04	0.04
68	0.07	0.07

It is clear from (Table 2) that k values of linoleic acid at temperatures more than 22°C are higher than those for oleic acid. This can be expected since there is only one double bonds in oleic acid, while linoleic acid has two double bond which leads to increase in

the molecular activity, thus, the reaction rate. At temperatures more than 40°C the difference in the k values is fading because the effect of temperature on the reaction rate is predominating over the effect of the number of double bonds.

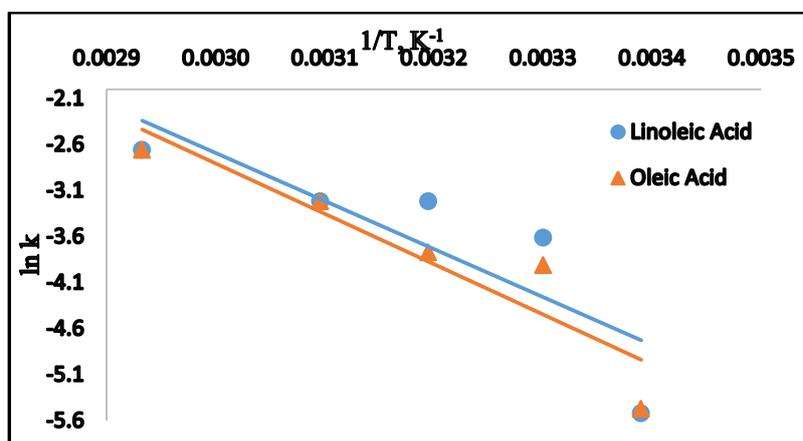


Fig.11. Arrhenius Plot for the Two Fatty Acids

Table3. The Activation Energy of FFAs.

FFA	Activation Energy (J/mol)
Linoleic acid	43416
Oleic acid	45506

It is clear from (Table 3) and (Fig. 11) that the obtained activation energy for linoleic acid is slightly less than that for oleic acid. This can be expected as a result of the two double bonds in linoleic acid compared to one double bond in oleic acid. Moreover from GC analysis of linoleic acid it was found that it has almost 30% by wt. of oleic acid.

6. CONCLUSION

In this study, suitable reaction conditions were investigated for esterification of oleic

and linoleic acids with methanol by using H_2SO_4 as a catalyst. Results showed that the reaction is pseudo first order reaction. Linoleic and oleic acids have the same initial rate at a molar ratio, methanol: FFAs of 40:1, temperature was 68°C and amount of H_2SO_4 was 2 wt. % of FFA. By increasing the temperature the rate constants of linoleic acid at temperature more than 22°C are slightly higher than those for oleic acid.

The activation energy of the linoleic and oleic acids are nearly equal (43.416 and

45.506 kJ/mol) respectively. Since both FFA were not pure and the molecular weight is high, the effect of having one more double bond in the molecule was slightly manifested.

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دراسة حركية التفاعل لاسترة الاحماض الدهنية الحرة

الملخص:

تهدف هذا البحث الي دراسة حركية تفاعل الاسترة لنوعين من المركبات الدهنية الغير مشبعة وهما حامض الاوليك واللينوليك وتحويله الي وقود حيوي .وفيه تمت دراسة بعض من المتغيرات المؤثرة علي هذا التفاعل من درجة الحرارة وكمية العامل المساعد المستخدم والنسبة المولية بين الكحول الميثيلي والحامض الدهني المستخدم . و قد أثبتت الدراسة ان التفاعل يتبع تفاعلات أقرب للدرجة الاولى و أن أقصى تحويل لحامض الأوليك واللينوليك هي 88% عندما كانت النسبة المولية بين الكحول الميثيلي والحامض الدهني هو 40:1 و درجة الحرارة 68 درجة مئوية ونسبة العامل المحفز هي 2% (نسبة وزنية) وكذلك وقت التفاعل هو 30 دقيقة وتم استعراض تأثيردرجة الحرارة على ثابت معدل التفاعل باستخدام معادلة أرهينيوس، واستنتاج قيمة دالة طاقة التنشيط ووجدت تساوي 43.42 و 45.51 كيلو جول لكل مول لكلا من حمض اللينوليك وحمض الأوليك، على التوالي.