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Kinetics and Activation Complex Thermodynamic Study of the Acidity Removal of Oleic Acid via Esterification Reaction on Commercial 13X Zeolite

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Abstract

The study involved the removal of acidity from free fatty acid via the esterification reaction of oleic acid with ethanol. The reaction was done in a batch reactor using commercial 13X zeolite as a catalyst. The effects of temperatures (40 to 70 °C) and reaction time (up to 120 minutes) were studied using 6:1 mole ratio of pure ethanol to oleic acid and 5 wt. % of the catalyst. The results showed that acid removed increased with increasing temperature and reaction time. Also, the acidity removal rises sharply during the first reaction period and then changes slightly afterward. The highest acidity removal value was 67 % recorded at 110 minutes and 70 °C. An apparent homogeneous reversible reaction kinetic model has been proposed and solved with the experimentally obtained kinetics data to evaluate reaction rate constants versus temperature, pre-exponential factors, and activation energy values for the forward and the backward esterification reactions. The activation energies were 34.863 kJ/mol for the forward reaction and 29.731 kJ/mol for the backward reaction. The thermodynamics of the activation step of the forward and reverse reactions was studied based on the hypothesis of forming a complex material that decomposes into a product. The activation steps were studied using Eyring bimolecular collision theory approach, and both ΔH* and ΔS* were determined for forward and backward esterification reactions. The enthalpies of activation were 32.141 kJ/mol and 27.080 kJ/mol for the forward reaction and the backward reaction, and the entropies of activation were - 193.7 and -212.7 J/mol. K for the forward reaction and the backward reaction, respectively.

Keywords: Esterification, Biodiesel, Kinetics, Arrhenius, Eyring, Activation step.

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1- Introduction

Energy derived from fossil energy sources (coal, oil, and gas) or nuclear supplies is mainly responsible for the greenhouse effect, acid rain, and other negative impacts on health and the environment [1,2]. The continuation of the recent trend in energy demand and unsustainable ways of using it due to population increase and expectations of increased demand for it in the foreseeable future will mean the continuation of environmental problems and their harmful health effects on life [3].

Sustainable and renewable energies provided a vital opportunity to cover part of the energy requirements with little or no negative impacts on the environment and health [3,4].

Renewable energy produces from converting natural resources or materials that are recultivated or reproduced into acceptable forms of energy and are considered essential solutions in reducing the depletion of fossil resources with negative impacts. The most critical technical solutions are solar radiation, wind, falling water, gravitational forces, geothermal heat, and biomass [5].

Biofuel is one of the by-products of using and converting biomass and is one of the crucial solutions for energy alternatives.

Biodiesel is a product that attracts international attention. It is the alkyl ester of a long-chain fatty acid derived from a renewable lipid feedstock, such as vegetable oils or animal fats [6,7].

The biodegradable and non-toxic biodiesel offers an excellent alternative to fossil fuels or as an essential addition [8,9] that contributes to reducing fuel consumption and harmful emissions and its lubricating properties, which contribute to preserving the environment [10].

Biodiesel is produced by oils and fats that react with short-chain alcohol (methanol or ethanol) through a transesterification reaction, producing alkyl esters with glycerol using a base catalyst. Also, biodiesel is made from the esterification reaction, which produces alkyl citrate and water using an acid catalyst [11].

In esterification reactions, homogeneous acid catalysts (such as sulfuric acid, methane-sulfonic acid, phosphoric acid, trichloroacetic, and hydrochloric acids) are used [12,13]. Also, the heterogeneous catalysts are used in the esterification reactions, which do not cause corrosion problems in equipment and reduce the cost of separating the products later [13].

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Zeolites are valuable catalysts used in many processes, including biodiesel production by the esterification reaction. The importance of zeolite is due to its distinctive properties, including its high and tunable acidity, relatively high surface area, high thermal stability, and the size of microporous pores, which allow a smooth transfer of the reactant and product compounds through it [11–13]. Various types of zeolites have been as catalysts in the study of the esterification reaction such as; NaY zeolite [9,14], HY zeolite [15,17], ZSM-5 [18], FAU-type zeolite [19], modified ZSM-5, and 13X zeolite and its modified version [12,20].

This work aims to examine the kinetics of the esterification of oleic acid with ethanol by using commercial 13X zeolite (C13XZ). The study used the elimination of acidity as an indication for the conversion of oleic acid, followed by an analysis of the kinetics of the esterification reaction, which found reaction rate constants at various temperatures and with varying activation energies. Finally, a thorough investigation discovered the enthalpy and entropy of the esterification reaction of the activation step.

2- Experimental Work

The esterification reaction was carried out in a hemispherical flask of 500 mL with a 3-neck flask. The central neck was close-fitting with a water-cooled condenser. A thermometer fixed in the second neck measured the reaction mixture temperature, while the third neck was closed with a movable stopper. An electromagnetic hot plate (MR Hei-standared / Germany) was used to stir and heat the reaction mixture, as in Fig. **1**.

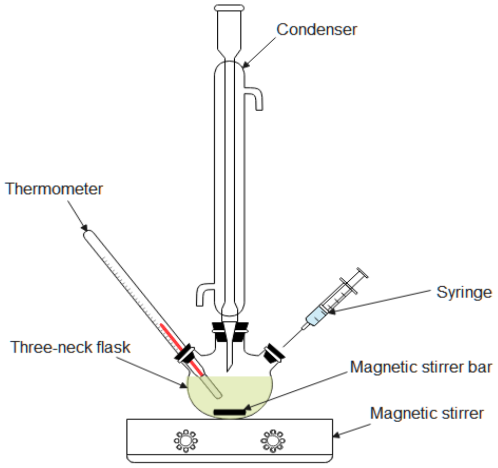

Fig. 1. schematic diagram of the batch reactor

The reactor was loaded with 150 mL (0.475 mol) of oleic acid and the required volume of pure ethanol (166.4 mL) to have the initial molar ratio of ethanol to oleic acid 6/1.

The agitation was kept at 300 rpm, which is necessary to increase the contact surface between ethanol and oil because ethanol and oil are immiscible.

The reaction mixture was heated to the preferred temperature (40 to 70 °C). After that, the 5 wt.% of C13XZ catalyst based on the oleic acid weight was added, and the reaction time recorded. The authors measured the properties of the used catalyst in the esterification reaction and summarized in Table **1**.

Table 1. C13XZ catalyst properties

Property	Si/Al	BET surface area, m^2/g	Pore volume, cm^3/g	Na content, %
Value	4.3	551.16	0.24	6.81

A sample of 2 mL was taken via a syringe at different intervals, and to get good phase separation, the sample was centrifuged for 10 min at 3000 rpm. Then upper layer (organic phase) was titrated with 0.1 N KOH and by using phenolphthalein as an indicator to obtain the acid value (AV) in Eq. (1).

$$AV = \frac{ml\ of\ KOH \times N \times 56.1}{Weight\ of\ sample} \tag{1}$$

The acidity removal fraction (E) was calculated using Eq. (2).

$$E = \frac{\left(AV_o - AV\right)}{AV_o} \tag{2}$$

Where: AV_0 is the initial acid value (acid number value for oleic acid: 197.35 mL KOH/g), and AV is the acid value at time (t) in minutes.

3- Results and Discussion

3.1. Kinetics Study

The results of the esterification of oleic acid, which was studied in the temperature range between 40 and 70 °C for about two hours, and presented in Fig. **2**, show that the fraction of acidity removal increases dramatically during the first 20 minutes.

The reason for this sharp increase is due to the absence of water molecules in the pores of the catalyst, which results from the reaction, allowing a rapid reaction of oleic acid on the clean and large number of active sites, and the decrease in acidity in the first period of the reaction [14, 21]. After that, the values of the acidity removal rise slightly to the end of the reaction time (less than 2 h). The increase in the esterification temperature positively affected the acidity removal of oleic acid. The highest recorded value of acidity removal was 67% at 70 ºC and 110 min. The increase in acidity removal with temperature belongs to the rise in the collision's frequency of reactant molecules causing growth in the probability of collision of molecules that carry the required activation energy to complete the esterification reaction [22].

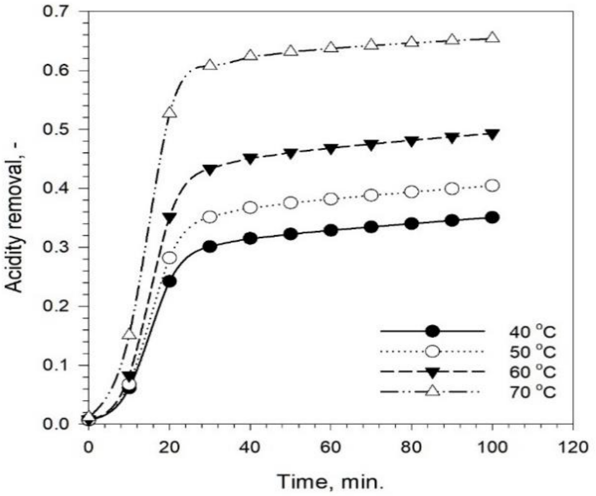

Fig. 2. Oleic acid acidity removal versus time at different esterification reaction temperatures using 6/1 pure ethanol/oleic acid initial molar ratio and 5 wt. % C13XZ

The kinetic of the esterification reaction was studied in terms of acidity removal value (*E*). The stoichiometric equation of the esterification reaction could be clarified in Eq. (3).

$$C_{17}H_{33}COOH + C_2H_5OH \rightleftharpoons C_{17}H_{33}COOC_2H_5 + H_2O \tag{3}$$

Eq. (3) can be expressed symbolically as Eq. (4).

$$A + B \underset{k2}{\overset{k1}{\rightleftharpoons}} C + D \tag{4}$$

A pseudo-homogeneous reversible with a single-step esterification reaction was assumed. Also, the first order for all the reactants and products was assumed, and the noncatalyzed reaction rates were neglected. The pseudo-homogeneous reversible reaction rate can be represented as Eq. (5).

$$-r_A = -\frac{dA}{dt} = k_1 [A][B] - k_2 [C][D] \tag{5}$$

Where: [A] is the concentration of oleic acid (initially, 1.5 mol/L); [B] is the concentration of the ethanol, [C] and [D] were the concentrations of produced biodiesel and water, respectively. In terms of acidity removal (E), Eq. (5) can be written as Eq. (6).

$$-r_A = A_o \frac{dE}{dt} = k_1 A_o^2 \left[1 - E\right] \left[\left(\frac{B_o}{A_o}\right) - E\right] - k_2 A_o^2 \left[E\right]^2 \tag{6}$$

The solving of Eq. (6) was carried out using the differential method approach with the least squares' method, and it was started by substituting the initial molar ratio of ethanol to oleic acid (B_o/A_o = 6/1) and utilizing the obtained kinetics data.

The reaction rate constants for forward and backward reactions (k_1 and k_2) and the correlation coefficients (R^2) at different temperatures were calculated and summarized in Table **2**.

Table 2. Constant values of the esterification reaction kinetic model for the forward and the backward reaction and values of the correlation coefficient

Temp. ºC	k_1, L/mol. min	k_2, L/mol. min	R^2, -
40	0.00097	0.00075	0.9521
50	0.00165	0.00161	0.9499
60	0.00219	0.00191	0.9474
70	0.00279	0.00257	0.9412

The results indicated that the reaction constants increase with temperature and that the values of the forward reaction constants were consistently higher than the values of the back reaction, which indicates the continuity of acid removal in this range of temperatures. The highest value of k was 0.00279 L/mol. min. at 70 ºC for the forward reaction and 0.00257 L/mol. min. for the backward reaction at the same temperature.

Arrhenius law (Eq. 7) [23] was plotted (Figure 3) and used to evaluate the effect of temperature on the rates of chemical reactions. Activation energies for the forward and the backward reactions and frequency factors values have been calculated and summarized in Table **3**.

$$\ln(k_i) = \ln(A_i) - \frac{E_{Ai}}{RT} \tag{7}$$

Where: k_i is the reaction rate constant for the forward and the backward reactions, A_i is the pre-exponential factor for the forward and the backward reactions, E_{Ai} is the reaction activation energy for the forward and the backward reactions, R is the general gas constant, and T is the absolute reaction temperature (in Kelvins).

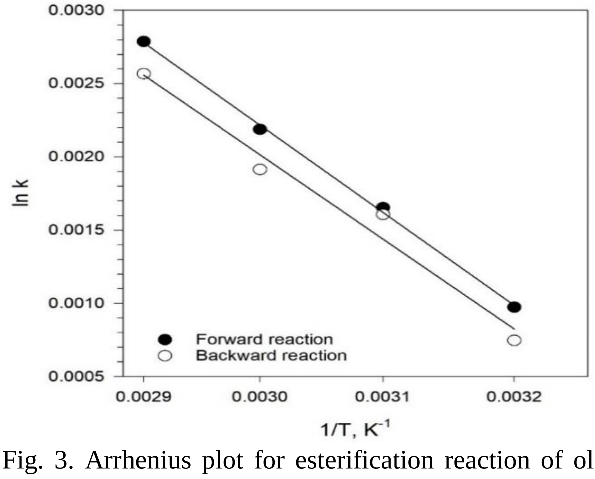

Fig. 3. Arrhenius plot for esterification reaction of oleic acid with ethanol using C13XZ

Table 3. Activation energies (E_{Ai}) and frequency factors (A_0) for forward and backward reaction

Reaction	E_{Ai}, kJ/mol	A_0, L/mol. min	R^2, -
Forward (1)	34.863	564.08	0.9157
Backward (2)	29.731	140.69	0.9664

The calculated activation energies were close to the results of the previous research [12], which adopted the analysis of a heterogeneous model of the esterification process of oleic acid over modified and prepared 13X zeolite.

The reason for this convergence of the activation energies of the esterification process of oleic acid may be due to the similarity of the physicochemical properties of the commercial catalyst (used in this research) with those properties that the researchers [12] reached after the preparation and modification process, especially the ratio of silica to alumina.

The obtained activation energies were within the same magnitude as the activation energies (28.6 to 42.6 kJ/mol) found using different zeolites [14, 17].

3.2. Thermodynamic Study

The thermodynamics of the esterification process was studied using Eyring bimolecular collision (Eq. 8) [24], and activated complex of relatively high energy was generated with a certain change in enthalpy (ΔH*) and the change entropy (ΔS*). The same approach was used for the forward and backward reactions.

$$k_i = \frac{k_B T}{h} \exp\left(\frac{\Delta H^*}{RT}\right) \exp\left(\frac{\Delta S^*}{R}\right) \qquad (8)$$

Where: k_B is Boltzmann's constant (1.381×10^{-23} J/K), h is Planck's constant (6.626×10^{-34} J.s), R is the gas constant, and T is the absolute temperature in Kelvin (K).

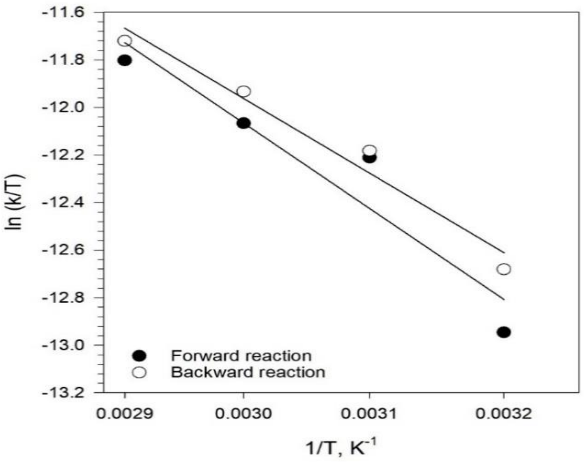

Fig. 4. Eyring plot for forward and backward esterification reactions of oleic acid with ethanol using C13XZ

The plot of ln (ki/T) versus 1/T for the values of reaction rate constants for forward and backward reactions (Fig. **4**), produced a straight-line (for each reaction) with a negative slope equal to ΔH*/RT and intercept equal to ΔS*/R + ln kB/h. The obtained values of the ΔH* and ΔS* were listed in Table **4**.

Table 4. Obtained $\boldsymbol{\Delta H^*}$ and $\boldsymbol{\Delta S^*}$ for forward and backward esterification reactions

Reaction	ΔH*, kJ/mol	ΔS*, J/mol. K	R^2, -
Forward	32.141	-193.7	0.9017
Backward	28.080	-212.7	0.9658

The positive values of $\boldsymbol{\Delta H^*}$ showed that both the forward and the backward esterification reactions were endothermic. The higher value of $\boldsymbol{\Delta H^*}$ of the forward reaction indicated that the heat was a critical parameter for the esterification reaction. The change in $\boldsymbol{\Delta S^*}$ had a negative quantity for both esterification reactions because the reactant molecules combine to form a single activated complex, leading to decreasing in molecules of the system and reducing in entropy [24].

4- Conclusions

In this study, the acidity of free fatty acids can be effectively removed by the esterification reaction of oleic with ethanol utilizing C13XZ. The removal of acidity was rapid in the first reaction period because the catalyst was clean, and its active sites were not filled with produced water that breakdown the forward reaction. The removal of acidity of oleic acid was increased with increasing temperature along the time of reaction because of the increase in the collision's frequency of reactant molecules. A 67% was the maximum value of the acidity removal recorded at 70 ºC and 110 min with a 6/1 mole ratio of ethanol/oleic acid and 5% wt. C13XZ. The kinetic parameters of the suggested model were obtained involving reaction rate constants, pre-exponential factors, and activation energies for the forward and the backward esterification reactions.

The activation energies obtained through fitting the kinetic model with the experimental results were 34.863 kJ/mol for the forward reaction and 29.731_kJ/mol for the backward reaction. The thermodynamic study of the activation step has been investigated using the Eyring bimolecular collision theory approach. The enthalpies of the activation step showed that the acidity removal process onto C13XZ was endothermic; the value was 32.141 kJ/mol for the forward reaction and 27.080 kJ/mol for the backward reaction. The entropies of activation were -193.7 and -212.7 J/mol. K for the forward reaction and the backward reaction, respectively.

Nomenclature

No.	Symbol	Meaning
1	[A]	The concentration of oleic acid (mol/L).
2	$[A_0]$	The initial concentration of oleic acid (mol/L).
3	Ai	The pre-exponential factor for the forward and the backward reactions (L/mol. min).
4	[B]	The concentration of the ethanol (mol/L).
5	$[B_0]$	The initial concentration of the ethanol (mol/L).
6	[C]	The concentration of produced biodiesel (mol/L).
7	[D]	The concentration of produced water (mol/L).
8	E	Acidity removal fraction (-).
9	E_{Ai}	The activation energy for the forward and the backward reactions (J/mol).
10	h	Planck's constant (6.626×10-34 J.s).
11	ΔH*	Change in enthalpy (J/mol).
12	k_i	The reaction rate constant for the forward and the backward reactions (L/mol. min).
13	k_B	Boltzmann's constant (1.381×10-23 J/K).
14	R	The general gas constant (8.314 J/mol. K).
15	R^2	Correlation coefficient (-).
16	ΔS*	The change in entropy (J/mol. K).
17	t	Time (min.).
18	T	The absolute reaction temperature (in Kelvins).

Abbreviations

No.	Symbol	Meaning
1	AV	Acid value.
2	AV_0	The initial acid value.
3	C13XZ	Commercial 13 X zeolite.

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دراسة حركية و ثرموديناميكية المعقد المنشط لازالة الحامضية من حامض الاوليك عبر تفاعل الاسترة باستخدام زيولايت تجاري نوع13X

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الخلاصة

تناولت هذة الدراسة ازالة الحموضة من الحوامض الدهنية بواسطة اجراء تفاعل الاسترة في مفاعل دفعي باستخدام عامل مساعد نوع زيولايت×13 تم تطبيقة على حامض الاوليك و الايثانول بنسبة (6:1) و بدرجات حرارة مختلفة (40–70) درجة سليزية و اضافة 5 % من العامل المساعد نسبةً الى وزن حامض الاوليك و كان زمن التفاعل بحدود 120 دقيقة. اظهرت النتائج ان كمية الحامضية المزالة ازدادت مع ارتفاع درجة الحرارة و ان الازالة كانت بمعدل عالي في بداية التفاعل ثم استقرت. تم تسجيل اعلى قيمة لازالة الحامضية بمقدار 67% بظروف 70 درجة مئوية و 110 دقيقة من زمن التفاعل. تم دراسة حركية التفاعل على انه تفاعل عكسي و ايجاد معادلة حركية التفاعل و ثوابت سرعة التفاعل و المعاملات الاسية للمعادلة، كما تم حساب طاقة التنشيط لكلا التفاعلين الامامي و العكسي بواسطة قانون ارينوس. كانت قيم طاقة التنشيط للتفاعل الامامي هي 34.863 كيلوجول\ مول و29.731 كيلوجول\مول للتفاعل العكسي .كذلك تناولت الدراسة دراسة خطوة التنشيط للتفاعلين الامامي و العكسي و حساب الخواص الثرموديناميكية (الانثالبي و الانتروبي) بتطبيق نظرية ارينك للتصادم الثنائي للجزيئة و بفرضية تكوين المعقد المنشط. اظهرت نتائج الخواص الثرموديناميكية ان التفاعل ماص للحرارة و كانت قيم انثالبي التنشيط 32.141 كيلوجول\مول للتفاعل الامامي و و27.080 كيلوجول\مول للتفاعل العكسي وقيم انتروبي التنشيط 193.7- و212.7- جول\مول كلفن للتفاعل الامامي و التفاعل العكسي على الترتيب.

الكلمات الدالة : تفاعل الاسترة، الوقود الحيوي، حركية التفاعل، معادلة ارينوس، معادلة ارينك، خطوة التنشيط.