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Kinetic and Thermodynamic Study of Transesterification for Biodiesel production from Sunflower Oil

*Fatima Almahdi, Aisha Al-Abbasi, Almahdy Almaki

Chemistry Department, Faculty of Science, Sebha University, Libya

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ABSTRACT

The study of chemical kinetics is essential in predicting reaction rates and mechanisms of chemical processes. In order to assess the kinetics and thermodynamic characteristics of transesterification, sunflower oil was transesterified with methanol in the presence of a BaO catalyst to produce fatty acid methyl esters, FAME, (biodiesel). kinetic and thermodynamic studies have been conducted in the presence of optimal reaction conditions that were determined in our previous study. Thus, reactions were carried out in 20:1 (molar ratio of oil to methanol) with 4.7 % weight of the catalyst used at temperatures of 60, 65, and 70 °C and for reaction times of 60, 120, 180, and 240 min. It has been determined that the pseudo-first-order reaction is followed during the transesterification of sunflower oil. The study of biodiesel derived from sunflower oil underwent thermodynamic investigation at three distinct temperatures, specifically 60, 65, and 70 °C. The non-spontaneous nature of the endothermic transesterification process was demonstrated by the positive values of the enthalpy ($\Delta H = +66.602$ kJ mol^{-1}) and Gibbs free energies. Furthermore, it is shown that the reaction is moving towards regulation by the negative entropy ($\Delta S = -99.975$ J K^{-1} mol^{-1}).

الدراسة الحركية و اترموديناميكية لعملية الأسترة التحويلية لإنتاج وقود الديزل الحيوي من زيت دوار الشمس

*فاطمة المهدي و عائشة العباسي و المهدي المكي

قسم الكيمياء، كلية العلوم، جامعة سبها، ليبيا

الكلمات المفتاحية:
محفز *BaO*
زيت دوار الشمس
وقود الديزل الحيوي
الأسترة التحويلية
الدرجة الأولى الكاذبة

الملخص

تعتبر دراسة الحركية الكيميائية ضرورية لاستنتاج معدلات التفاعل وآليات العمليات الكيميائية. من أجل تقييم الخواص الحركية والديناميكية الحرارية لعملية الأسترة التبادلية، تم إجراء أسترة زيت عباد الشمس مع الميثانول في وجود محفز BaO لإنتاج استرات ميثيل الأحماض الدهنية، FAME، (الديزل الحيوي). تمت دراسة الحركية والثرموديناميكية للتفاعل في ظل ظروف التفاعل المثالية التي تم تحديدها في دراستنا السابقة. ولهذا، تم إجراء التفاعلات بنسبة 20:1 (النسبة المولية للزيت إلى الميثانول) مع 4.7% من وزن محفز اكسيد الباريوم وذلك عند درجة حرارة 60، 65، و70 درجة مئوية ولزمن تفاعل 60، 120، 180، و240 دقيقة. لقد تم تحديد أن تفاعل الدرجة الأولى الكاذبة يتم اتباعه أثناء عملية تحويل زيت عباد الشمس. خضعت دراسة وقود الديزل الحيوي المنتج من زيت دوار الشمس إلى دراسة ديناميكية حرارية عند ثلاث درجات حرارة مختلفة، وتحديداً 60، 65، و70 درجة مئوية. تم إثبات الطبيعة غير التلقائية لعملية الأسترة تحويل الماصة للحرارة من خلال القيم الإيجابية للمحتوى الحراري ($\Delta H = +66.602$ kJ mol^{-1})) وطاقات جيبس الحرة. علاوة على ذلك، فقد تبين أن التفاعل يتجه نحو التنظيم بواسطة الإنتروبيا السلبية ($\Delta S = -99.975$ J K^{-1} mol^{-1}).

1. Introduction

The process known as "transesterification" occurs when an ester reacts with alcohol to exchange its alkyl group with another alcohol (see **Scheme** (1)) [1]. Methanol is the most used alcohol because of its low cost and easiness of access [2-4]. The Transesterification of plant oils produces fatty acid methyl esters (biodiesel) and glycerol [5]. Fatty acid methyl esters (FAMEs) are a green resource of biofuels that are produced by the transesterification of a variety of oils and fats [6-9].

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*Corresponding author:
E-mail addresses: Soseysosey28@gmail.com, (A. Al-Abbasi) ais.alabbasi@sebhau.edu.ly, (A. Almaki) mah.almaky@sebhau.edu.ly

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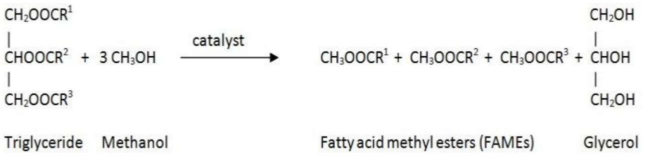

Fig. 1: Triglyceride transesterification reaction

Generally, this reaction is catalyzed by a base or an acid catalyst. There are several different types of heterogeneous catalysts (acids, bases, and enzymes), each with unique properties that can be used in oil transesterification [10, 11]. Alkali earth catalyst materials present many advantages, namely, cheaper, environment-friendly long catalyst life, high activity, have low solubility in methanol, have relatively high basic strength, and require only moderate reaction conditions [12-15]. Among them, barium oxide was employed as a heterogeneous catalyst, for the transesterification reaction [2, 4, 13, 16, 17]. Many researchers have studied the variables affecting the vegetable oil transesterification reaction, However, there have been few attempts to study the kinetics of this reaction [18, 19]. As a continuing our research group [20-27], we investigate the transesterification of sunflower oil using 4.7 % w of BaO as the catalyst and methanol: sunflower molar ratio of 20:1. The study is focused on the kinetic and thermodynamic of the Transesterification reaction, calculating the rate constants and the thermodynamic parameters.

2. Experimental Section and Materials

2.1 Materials

All chemicals were employed directly without additional purification. EDTA (>99 %), barium chloride (>96 %), citric acid (>99.5 %), ammonia (34 %), and Sunflower (SFO) oil was obtained from local shops located in Sabha city. Barium oxide (prepared and characterized in our previous paper [4] as follows: Barium chloride, EDTA, and citric acid were mixed in deionized water in a 1:1:1.5 M ratio; the pH of the reaction media was controlled at 6 using an NH3 solution. The resulting mixture was dried at 60 ◦C overnight, yielding a dense black gel. The gel was then calcined at 600 ◦C for 6 h until it turned into a white powder.

2.2 Transesterification of sunflower oil with methanol

The transesterification of 10 g SFO oil was carried out in a 50 ml round-bottomed flask fitted with a condenser and magnetic stirring system [4, 28]. 4.7% of barium oxide was added to methanol (The oil-to-methanol ratio was 1:20). For 1, 2, 3, and 4 hours, the reaction mixture was left. Thereafter, the solution was separated by a funnel to isolate the biodiesel layer from the aqueous layer, which was then washed three times with distilled water before drying. A detailed procedure has been provided elsewhere [4, 11]. The biodiesel yield can be calculated by the following equation:

$$\textit{Biodiesel yield}\ (\%) = \frac{\textit{Weight of biodiesel}}{\textit{weight of SFO oil}} \times 100 \tag{1}$$

3. Results and Discussion

The effect of reaction parameters, such as temperature (°C), and time (min) were studied to calculate the kinetic and thermodynamic parameters. Table 1 and Figure 1 present the results of considering each of the abovementioned parameters.

Table 1: Values for the biodiesel yield (%) at different reaction parameters

Temp. (^{O}C)	Time (min)	Yield %
60	60	55.8
60	120	58.12
60	180	62.5
60	240	56.26
65	60	57.8
65	120	63.24
65	180	68.81
65	240	71.36
70	60	61.3
70	120	66.8
70	180	72.53
70	240	78.38

The Table 1 displays that the biodiesel yield was influenced by time. Additionally, increasing the transesterification time improves the biodiesel income [4].

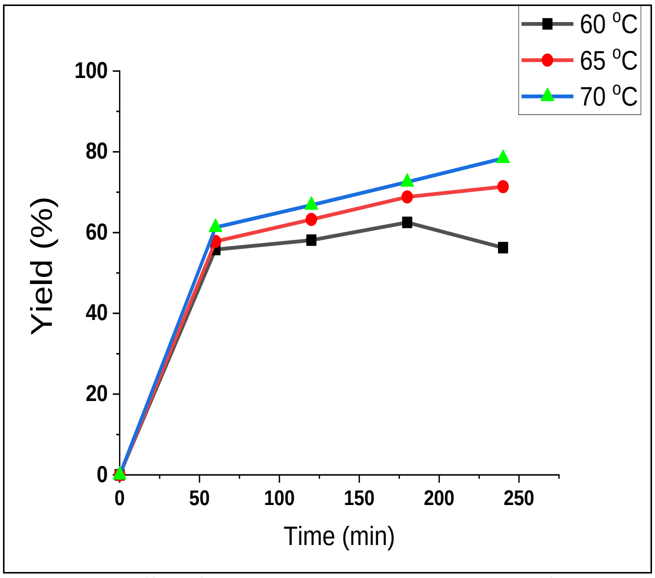

Fig. 2: Effect of time, and temperature on the transesterification

The influence of temperature on the output of biodiesel from sunflower oil was also examined. Figure 2 displays the influence of the temperature on the biodiesel transformation efficiency [4]. At the methanol/oil ratio was 20:1, the highest conversion efficiencies of 78.38 and 78.1 were achieved at 70 °C after 240 min and at 70 °C after 180 min, respectively.

The feasibility of employing barium zirconate as a catalyst to produce biodiesel from methanol and Karanja oil was examined by Sahani et al. [29]. They discovered that a biodiesel conversion of 98.79% was attained at 1.0 w% catalyst loading, 1:27 oil: methanol, and 65 °C for three hours. Ba-doped CaO is made from waste Turbonilla striatula shells and is utilized as a catalyst in the transesterification of leftover cooking oil. A 6:1 methanol to oil molar ratio, 3 hours, 1.0 w% of catalyst, and a reaction temperature of 65 °C were found to be the optimal parameters for a reaction [30]. To generate biodiesel from maize oil, sol-gel synthesized SiO2 doped with BaO is employed as a catalyst. eight hours, a 6% catalyst running at 60 °C, and a 16:1 methanol to oil molar ratio. There was an 82.1% yield of FAME produced. Olutoye et al. [31] investigated the transesterification of spent cooking oil (WCO) in the presence of barium-modified montmorillonite K10 (BMK10).

3.1 Transesterification kinetic

3.1.1. Kinetic model

The following kinetics model was structured as the following [11, 32]:

$$\text{Reaction rate} = -\frac{d[SFO]}{dt} = k[SFO] \tag{2}$$

Integrating Equation (2) results in:

$$[SFO]_t/[SFO]_0 = \exp(-\mathrm{kt}) \tag{3}$$

The oil concentration at t = 0 is $[SFO]_0$ and at different t is $[SFO]_t$, where $[SFO]_0 > [SFO]_t$ Noting that at any time the conversion of oil into biodiesel is X, we will have:

$$X = 1 - ([SFO]_t/[SFO]_0) = \exp(-\mathrm{kt}) \tag{4}$$

by substituting into Equation (3) and dividing all terms by $[SFO]_0$ we have:

$$1 - \mathrm{X} = \exp(-\mathrm{kt}) \tag{5}$$

In this case, oil conversion to biodiesel (X) is equal to biodiesel yield calculated by using Equation (1). Therefore, Equation (5) can be presented as:

$$1 - \mathrm{X} = \exp(-\mathrm{kt}) \tag{6}$$

$$\ln(1 - \mathrm{X}) = -\mathrm{K}\ \mathrm{t} \tag{7}$$

Plotting of Equation (7) with t and the value of natural logarithm (1 – X) as ordinate can be used to determine the values of the reaction rate constant (k, mole/minute) at various temperatures as in Figure 3. For the transesterification reaction of sunflower oil, the rate constants for the transesterification reaction were 0.0014, 0.0025 and 0.0029 determined at 60, 65, and 70 °C, respectively, Table 2.

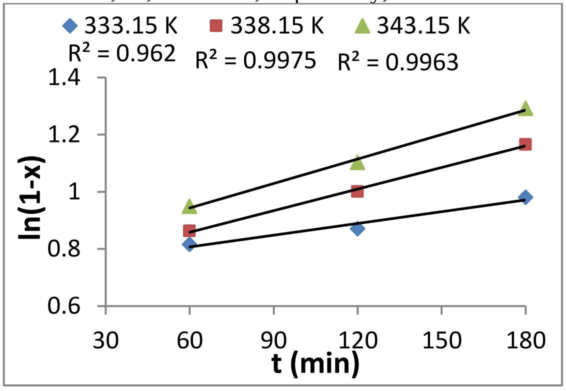

Fig. 3: Determination of the kinetic rate constants according to the pseudo-first-order kinetic model

The values of the correlation coefficient, R^2 of the straight lines in Figure 3 can be fitted to the pseudo-first-order equation. The slope of each straight line represents the reaction rate constant at the corresponding temperature in min^{-1}, and that is the reaction rate K increases with increasing temperature. The low k-value in the kinetics study is linked to a lower level of unsaturated FFA in the sunflower oil.

3.2 Evaluation of the thermodynamic functions

Values of K at different temperatures of 60, 65, and 70 °C are used to determine the activation energy value (E_a) of the reaction using the Arrhenius equation:

$$k = A\exp\left(-\frac{E_a}{RT}\right) \qquad (8)$$

where A is the frequency factor for molecular collision, T is the absolute temperature (K), and R is the universal gas constant (8.314472 J/mol K). Plotting of 1/T vs. the value of the natural logarithm of rate constant (K), The straight line obtained with slope was used in calculating the activation energy for the reaction as shown in Table 2 and Figure 4.

The entropy ΔS* and enthalpy ΔH* were calculated from the transition state equation

$$K = \left(\frac{RT}{N_A h}\right) e^{\Delta S^*/R}\, e^{-\Delta H^*/RT} \qquad (9)$$

where N_A is Avogadro's number, and h is Planck's constant. From the slope of the obtained straight line (Figure 5), the heat content values were calculated, while the entropy was calculated from the value of the folded part of the y-axis. As for the free energy values from the equation (ΔG) = ΔH-TΔS, they were calculated at different temperature

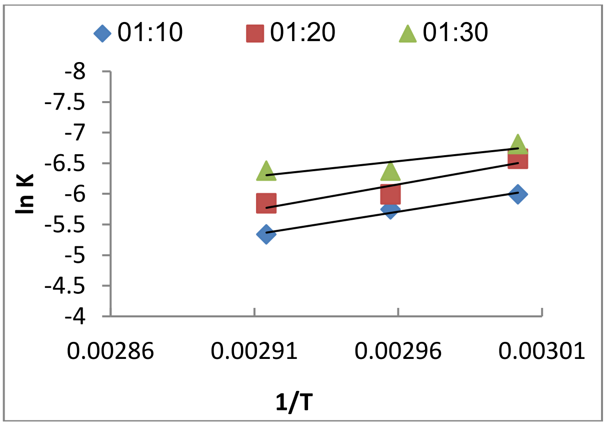

Fig. 4: Diagram of the Arrhenius equation for the energy activation calculation

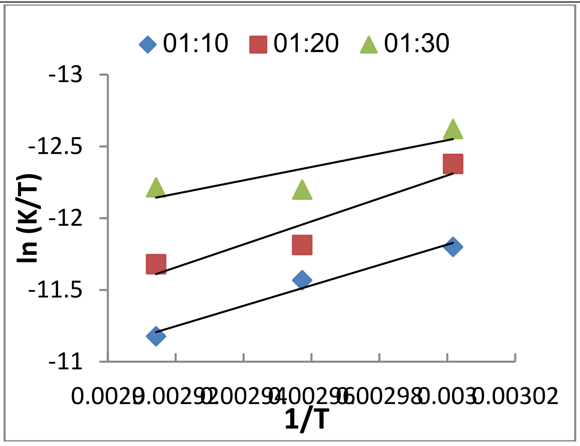

Fig. 5: Diagram of the transition state equation for enthalpy and entropy calculation

Table 2 Thermodynamic values for the transesterification reaction

T (K)	ΔE^* (KJ/mol)	ΔS^* (J/mol)	ΔH^* (KJ/mol)	ΔG^* (KJ/mol)
333.15	69.410	-99.975	+66.602	+33.373
338.15				+33.872
343.15				+34.370

From the thermodynamics study, the positive value for the activation energy and the enthalpy implies the transesterification reaction is endothermic, the large pre-exponential factor of (1.15×10^8 min^{-1}) points to a high probability of successful collisions. Furthermore, from Table 2 we note the entropy has a negative value, which indicates that the reaction is proceeding to regulation. At the same time, the positive Gibb's free energy suggests a non-spontaneous reaction, signifying that external energy is required for the reaction to progress.

4. Conclusion

The current paper focuses on chemical kinetics and thermodynamic, studies on synthesis of biodiesel from sunflower oil in transesterification reaction using BaO catalyst. The following conclusions can be taken from this study:

- The results obtained also show that an increase in time and temperature enhance the reaction rate.
- The kinetics of sunflower oil transesterification reaction are a pseudo-first-order.
- The estimated rate constants indicate an Arrhenius dependence on temperature.
- The transesterification reaction is endothermic and non-spontaneous
- the reaction is proceeding to regulation

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