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Kinetics of transesterifying multifeedstock oil into biodiesel

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Abstract

The synthesis of biodiesel is typically performed using homogeneous catalysts and high-temperature transesterification methods. This research aims to investigate the kinetics of transesterification reactions in biodiesel synthesis using a blend of six different types of oils: coconut oil, palm oil, soybean oil, canola oil, sunflower oil, and waste cooking oil. An equal volume of each oil is used to combine the multifeedstock oil, totaling 300 ml. After pretreatment, the multifeedstock oil is heated to 30, 40, 50, and 60°C, combined with a methoxide solution, and blended for a variable number of time intervals of 10, 20, 30, 40, 50, and 60 minutes. After a 24-hour stay, the biodiesel is cleaned and separated from the centrifuge's water content. The biggest conversion, which was attained at 60°C with a reaction time of 60 minutes, was reported in the study's results. Utilizing a base catalyst in accordance with the second-order kinetics of the biodiesel transesterification reaction of multifeedstock oil.

Keywords:
Biodiesel, multifeedstock, transesterification, kinetics.

1 Introduction

The biodiesel sector is expanding as an attractive option for lowering reliance on fossil fuels and decreasing greenhouse gas emissions [1]. A lot of researchers have investigated the production of biodiesel using various raw materials, such as palm oil [2], nut oil [1], soy oil [3], canola oil [4], sunflower oil [5], and corn oil [6]. In an effort to improve the sustainability and efficiency of production, research has been conducted to investigate the use of multifeedstock, which is a mixture of various types of vegetable oils as raw materials for the production of biodiesels [7].

Kinetic studies are essential for understanding reaction rates, assessing the impact of process variables, and constructing models that accurately predict reaction behavior [8]. Some researchers have studied the kinetic studies of the production process of biodiesel from various raw materials, among others from palm oil [2], olive oil [9], soy oil [3], canola oil [4], and sunflower oil [5]. However, although previous research has been done in this field, research on biodiesel kinetics of multifeedstock is still limited.

A profound understanding of the kinetics of biodiesel production from multifeedstock has important implications for the development of more efficient production processes, proper raw material selection, and accurate modeling [9]. Therefore, further research in this field is needed to fill existing knowledge gaps and make a significant contribution to a sustainable biodiesel industry.

Research into the biodiesel kinetics of multifeedstocks is becoming increasingly important in the context of global efforts to reduce dependence on fossil fuels and promote the use of renewable energy sources [10].

This work primarily focuses on the kinetics of transesterification processes, an essential stage in the production of biodiesel [11]. Multifeedstock transesterization reactions involve high complexity due to differences in chemical composition and the physical properties of each raw material used [10]. Therefore, an in-depth understanding of the kineticity of multifeedstocks is important to optimize the production process of biodiesels.

Although there has been previous research on biodiesel kinetics, specific research considering multifeedstock is still limited in scientific literature [12].

The multifeedstock biodiesel production process has a high degree of flexibility for a wide variety of feeds. We anticipate a high level of stability in the resulting biodiesel product, independent of the oil type. This process ensures the continuous production of biodiesel products, eliminating the need to wait for the availability of one of the feeds. In other words, the multi-feedstock process provides a high level of process flexibility.

Previous studies have looked at how biodiesel is made from a single feedstock. They found that process variables like temperature, the amount of alcohol to oil, and the type of catalyst have a big effect on how fast the transesterification reaction happens. Bokhari *et al.* [4] discussed the kinetics of biodiesel production from canola oil. Bermudez *et al.* [2] discuss the kinetics of biodiesel production from palm oil. Haryanto *et al.* [13] discuss the kinetics of biodiesel production from used cooking oil. Zhu *et al.* [3] discuss the kinetics of biodiesel production from soybean oil.

Until now, there has been no published research that discovers and discusses the kinetics of transesterification in producing biodiesel from multifeedstock.

The aim of this study is to investigate the kinetic model for transesterification of biodiesel from multifeedstock by considering the process as a 2nd-order reversible reaction.

2 Methods

The study used a multifeedstock mixture of canola oil, sunflower oil, corn oil, palm oil, soybean oil, and fried oil waste. All materials are obtained from mini markets and freezing residues in the Cepu Region, Blora, and Central Java. Additional ingredients used to support the study are NaOH catalysts, methanol (99.9%, Merck), phenolphthalein indicators, and aqadest. The set of equipment used can be seen in Fig. 1.

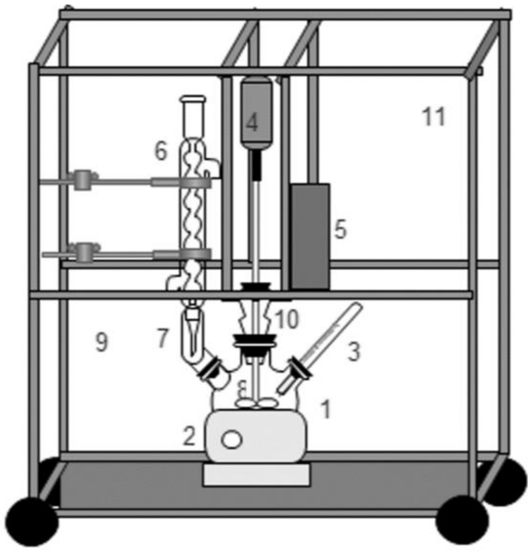


Fig. 1. Transesterification reaction tool kit: (1) three-neck pumpkin, (2) heating mantle, (3) thermometer, (4) propulsion motor, (5) motor controller, (6) condenser, (7) adapter, (8) mixer, (9) statifes and clamps, (10) adaptor, (11) portable frame.

Canola oil, sunflower oil, corn oil, palm oil, soybean oil, and fried oil residues are mixed as multifeedstock raw materials. Raw material analysis covers type mass, viscosity, and Free Fatty Acid (FFA) levels by weighing 10 grams of multifeedstock oil and nitrating using a 1 N NaOH solution. Then, make a methoxide solution by adding a NaOH catalyst to a 6 mol methanol solution. The mixture is then mixed in a beaker glass for about 5 minutes until dissolved.

The next is the transesterification reaction process performed with fixed parameters (methanol mol ratio: oil = 6:1), catalyst concentration (1% wt), and non-fixed parameters (reaction temperature: 30, 40, 50, and 60°C). Sampling is done every 10 minutes at each temperature parameter of the reaction. The separation of FAME and glycerol is done by stirring the solution for 24 hours.

The biodiesel obtained from the transesterification reaction is purified by washing with aquadest to a neutral pH. Then, the resulting biodiesel is inserted into the centrifuge for 10 minutes so that the biodiesel is separated from the water. The water content in the biodiesel is separated by a drying process at a temperature of 60ºC so that water can evaporate.

The conversion of biodiesel can be calculated using the Eq. 1.

$$\text{Conversion} = \frac{\text{mol FAME reaction}}{\text{mol first FAME}} \times 100\% \qquad (1)$$

Biodiesel results from transesterification reactions at various temperature and time variables that are analyzed using gravimetric methods to calculate the kinetic data of the reaction.

3 Results and Discussion

This study employed the characteristics of multifeedstock oil. The multifeedstock exhibits a high viscosity value of 61.75 cSt, indicating its thickness. However, it has a fairly low content of free fatty acids (FFA) (0.83%), so the production process of biodiesel can be carried out directly through a transesterification reaction.

Table 1 shows the result of biodiesel produced using a combination of temperature and reaction time. The produced biodiesel has a type mass between 0.86 and 0.87 grams/ml (according to SNI) and a viscosity of 3.79 and 5.53 cSt. (according to SNI). The results show that the higher the temperature, the higher the yield of biodiesel.

Similarly, the longer the reaction time, the greater the biodiesel yield [14]. The triglyceride-methanol ratio also influences the biodiesel results. The researchers discovered that the ratio of triglyceride concentration to methanol is 1:6 [15], resulting in optimal biodiesel conversion.

The study examines the effects of reaction temperature (ºC) and time (minutes) on triglyceride conversion (Xa). The level of methyl esters increased significantly at a reaction temperature of 60ºC. The content of biodiesel produced would be higher than if higher temperatures and longer transesterification reaction times were used. A temperature of 60ºC and a time of 60 minutes are the optimal conditions for a transesterification reaction. Fig. 2 illustrates how reaction temperature (C) affects triglyceride conversion (Xa).

Table 1. Biodiesel output data

Temp. (°C)	Time (minutes)	Results (%)	Temp. (°C)	Time (minutes)	Results (%)
30	10	0	40	10	58
	20	57.8		20	59
	30	59		30	61.9
	40	61.9		40	62
	50	63.5		50	65.8
	60	65.2		60	67.5
50	10	61.5	60	10	62.1
	20	63		20	64.1
	30	63.9		30	64.7
	40	64.5		40	65.5
	50	67		50	67.7
	60	69		60	70.2

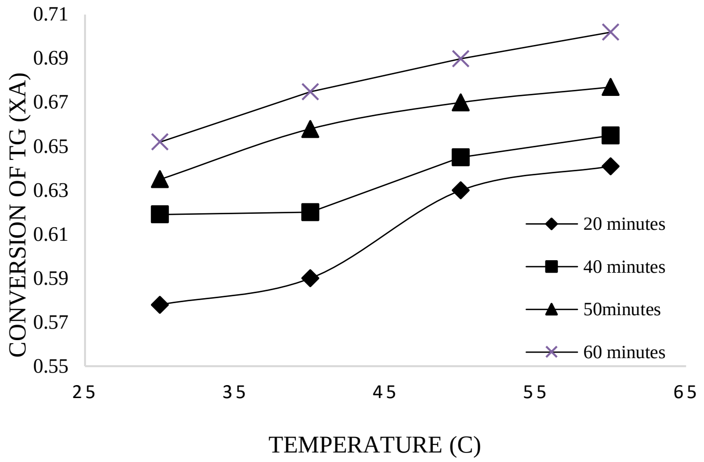
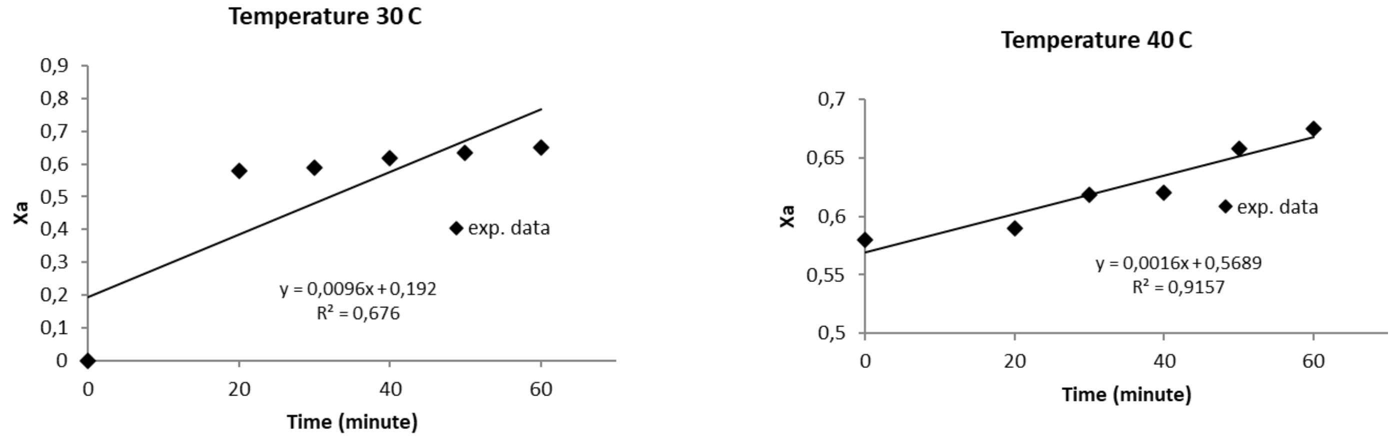


Fig. 2. Effect of reaction temperature (C) on triglyceride conversion (X_a) at different reaction times (minutes).

The rate of transesterification of multifeedstock oil into biodiesel determines the reaction order. We use graphical methods to order experiments on three levels of reaction order: 0.1, and 2. The corresponding order is represented by a correlation value (R^2) that is close to one.

We determine a zero-order reaction by creating a graph of triglyceride (X_a) conversion versus time (t). Fig. 3 shows a graph with a straight line and a slope value. The slope on the graph yields the reaction speed setting value. We obtained a correlation coefficient value (R^2) within the range of 0.7407–0.9047 at order zero.

Plotting -ln (1-Xa) with t allows us to determine the first-order reaction. Fig. 4 yields a graph with a straight line. The slope yields the value of the reaction speed setting. The correlation coefficient (R^2) is in the range of 0.676–0.9243 on order one.



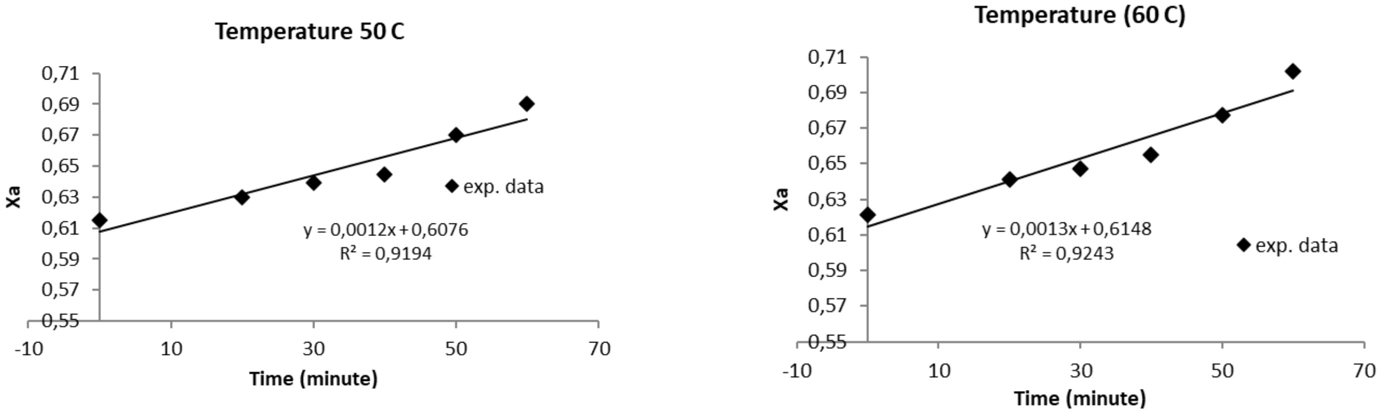


Fig. 3. Value of zero-order correlation coefficient.

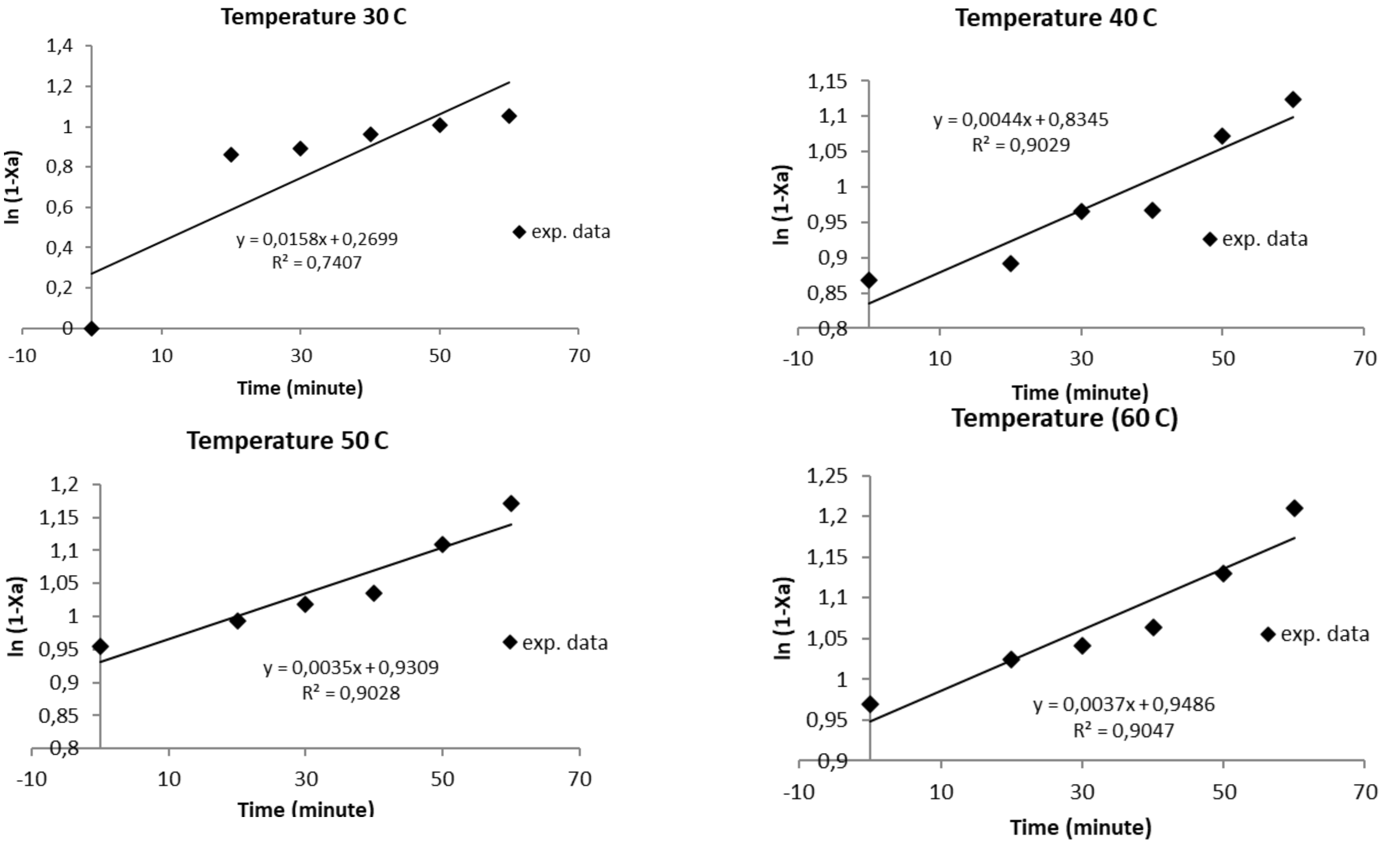
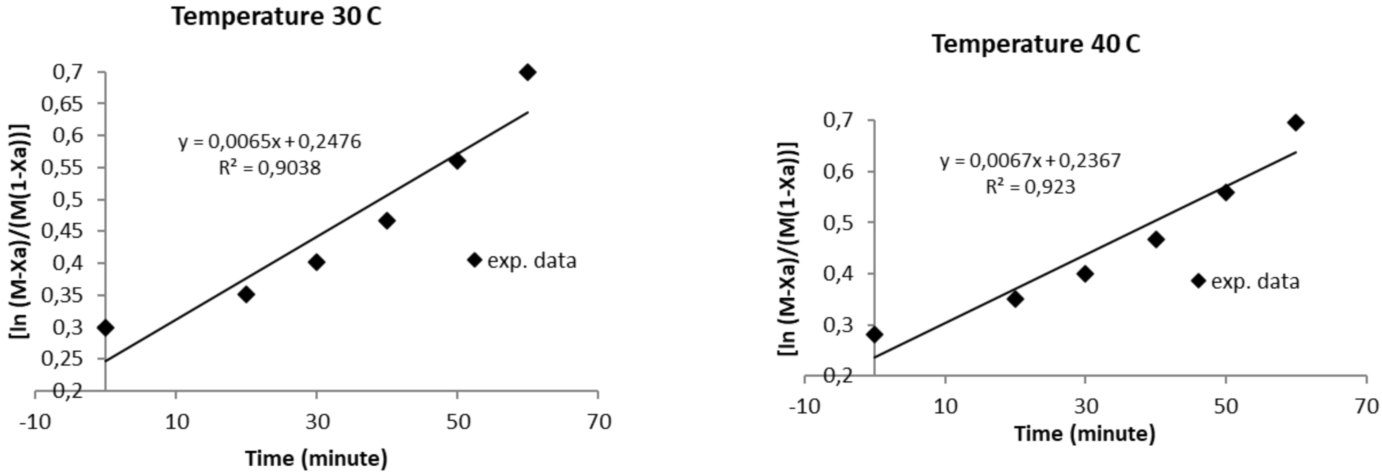


Fig. 4. Illustrates the order one correlation coefficient value.

Plotting ln (M-Xa) / (M(1-Xa)) against t yields the reaction of order two. Fig. 5 displays a straight line with a slope value of k. We obtained correlation values (R^2) in the order two range of 0.9038–0.9231.

In this study, at a temperature of 60°C and a time of 60 minutes, the correlation value (R^2) approaches 1, specifically at order two of 0.9243. However, if C_{B0} is significantly larger than C_{A0}, it will remain constant at all times. Thus, the reaction of the second order will be the order of the first order [16].

The activation energy can indicate how easy or difficult a reaction is, and theoretically, if the reaction has a smaller activation energy, it will tend to react faster and more easily than a reaction that has a larger activation energy and tends to respond harder and longer.



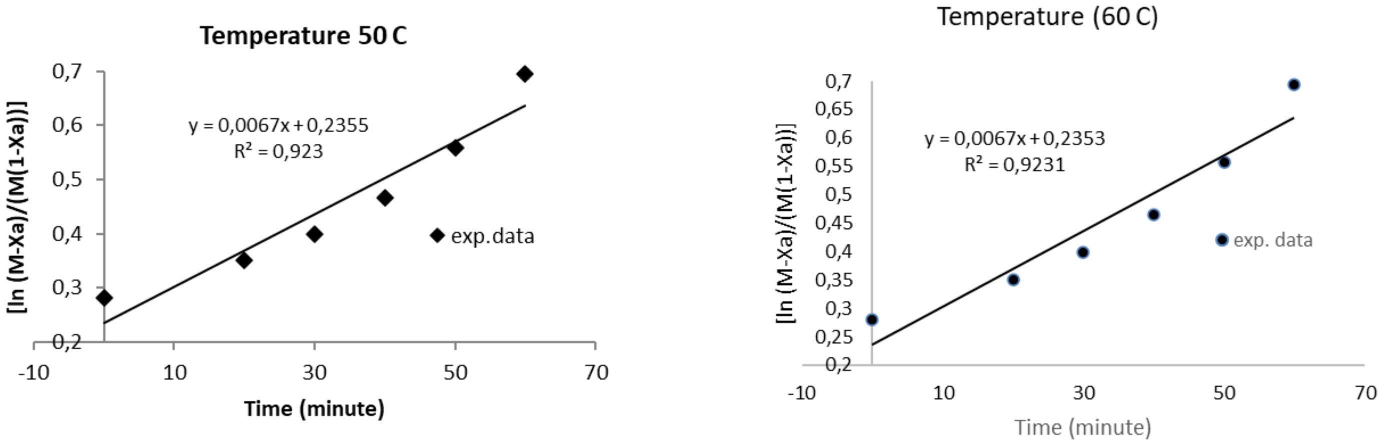


Fig. 5. Second-order correlation coefficient value.

The greater the constant value of the reaction rate, the faster it will take place. A faster response enables the collision of large quantities of particles in a relatively short time, lowering energy levels and achieving a balance faster.

We use the Arrhenius equation to determine the energy value of the transesterification reaction activation. We obtain plots between ln k and 1/T on the graph as slopes and intercepts. The graph's values include activation energy values, impact frequency values, and reaction speed settings equations (Table 2).

Table 2. Results of calculating activation energy values based on the Arrhenius equation

T	1/T	k	ln k
30	0.033333	0.0065	-5.03595
40	0.025	0.0066	-5.02069
50	0.02	0.0067	-5.00565
60	0.016667	0.0067	-5.00565

The calculation of the activation energy from the chart of relations of ln k to 1/T resulted in a slope of -1.9616 and an intercept of -4.9704. Then the activation energy (Ea) was 16.3597 J/mol, and the impact frequency was 0.00694. Thus, we obtained the equation for setting the rate of reaction as k = 0.00694 e(-1.9616/T).

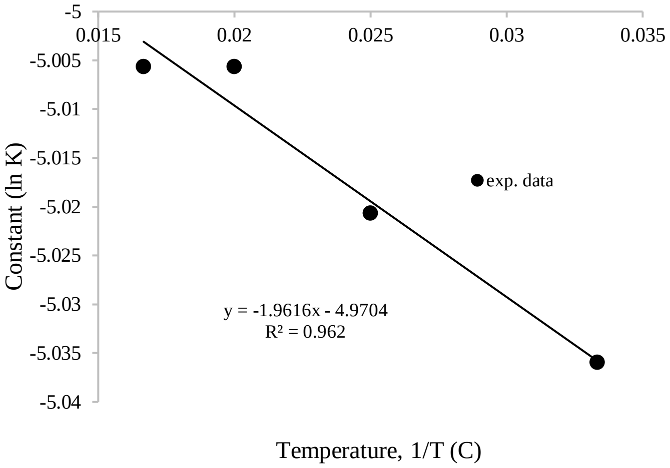


Fig. 6. The relationship between ln k and 1/T in the production of biodiesel through the transesterification reaction of multifeedstock oil.

Variability in the quality of individual oils in a multi-ingredient blend greatly affects reaction kinetics and biodiesel yield. Different parts of the oil, like the amount of fatty acid saturation, viscosity, and free fatty acid content, can change how fast the transesterification reaction happens and how well the catalyst works.

When using an alkaline catalyst, oils with a high free fatty acid content tend to slow down the reaction due to the saponification process. In addition, differences in chemical composition can alter the optimal temperature and time of the reaction and necessitate modifications in the method to achieve uniform and efficient biodiesel yields.

Research shows that differences in the chemical composition and physical properties of various oils can have a significant impact. Each type of oil has unique characteristics, such as the degree of fatty acid saturation, free fatty acid content, and viscosity. These factors affect the rate of the transesterification reaction and the effectiveness of the catalyst used in the process.

4 Conclusion

First, using longer transesterification reaction times and higher temperatures will result in higher conversions; second, the maximum conversion is 70.2% at 60°C and 60 minutes. We obtain the highest correlation value (R^2) at order two at 60°C and for 60 minutes at 0.9243, with an activation energy (E_a) of 16.3597 J/mol and a ratio of 1:6 between oil and methanol.

Acknowledgments

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