

## Kinetic study for biodiesel production from dairy waste via catalytic microwave heating

MUHAMMAD Ayoub<sup>1,a\*</sup>, SITI AMINAH Mohd Johari<sup>1,b</sup>,  
MUHAMMAD RASHID Shamsuddin<sup>1,c</sup>, BAWADI Abdullah<sup>2,d</sup>, SARAH Farukkh<sup>3,e</sup>,  
SALMAN RAZA Naqvi<sup>4,f</sup>, MUHAMMED Danish<sup>5,g</sup>

<sup>1</sup> Universiti Teknologi PETRONAS, HiCoE, Centre for Biofuel and Biochemical Research (CBBR), Institute of Sustainable Living (ISB), 32610 Seri Iskandar, Perak, Malaysia

<sup>2</sup> Biomass Processing Laboratory, Centre for Biofuel and Biochemical Research, Chemical Engineering Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610 Perak, Malaysia

<sup>3</sup> Department of Petroleum Engineering, Universiti Teknologi PETRONAS, 32610, Seri Iskandar, Perak, Malaysia  
Department of Petroleum Engineering, Universiti Teknologi PETRONAS 32610, Seri Iskandar, Perak, Malaysia

<sup>4</sup>National University of Sciences & Technology, 54000, Pakistan

<sup>5</sup>Universiti Kuala Lumpur Malaysian Institute of Chemical and Bio-Engineering and Technology, Lot 1988, Taboh Naning, Alor Gajah 78000, Melaka, Malaysia

<sup>a</sup>muhammad.ayoub@utp.edu.my, <sup>b</sup>aminahjohari1402@gmail.com, <sup>c</sup>mrashids@utp.edu.my, <sup>d</sup>bawadi\_abdullah@utp.edu.my, <sup>e</sup>maqsood.ahmad@utp.edu.my, <sup>f</sup>salman.raza@scme.nust.edu.pk, <sup>g</sup>danish@usm.my

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**Abstract.** Biodiesel production from waste such as wastewater sludge, palm oil mill effluent and dairy waste provide more sustainable approach and greener energy. This paper analyzes the kinetic modelling for biodiesel production from dairy waste scum oil via microwave heating transesterification. The results from this study show that transesterification of dairy waste scum oil is a first order kinetic which defines that the biodiesel production is dependent on the concentration of one reactant linearly. The activation energy for the reaction was validated to be 18.12 J/mol and frequency factor was 3.163 s<sup>-1</sup>. It is validated that the activation energy of transesterification process in this study is lower than the past works have been done. The comparison of the value is as tabulated in the kinetic analysis section.

### Introduction

Nowadays, diesel engines are renowned for their high torque and thermal efficiency. However, due to the increased demand for the energy together with the rapid depletion of fossil fuels and the requirement to consider emission regulations have led researchers to develop alternative fuels from renewable resources without any engine modifications. In research from Ashnani et al. [1], the transport section produces almost a quarter of global energy-rated greenhouse gas emissions where the road transportation covers the largest portion (more than 70%), followed by marine (15%), and aviation (10%).

Biodiesel has been found as a compatible alternative due to its advantages which are renewability, lower greenhouse gas emissions, higher flash points, and biodegradable with low carbon footprint. Biodiesel is an alternative for conventional diesel which is formulated based on plants product, animal fats, and recycled restaurant or factory grease. The conversion of the sources to the biodiesel is commonly undergo transesterification process. Transesterification of

triglycerides such as vegetable oils, animal fats, or industrial fatty waste with alcohols (methanol, ethanol, propanol) in the presence of a homogeneous catalyst such as inorganic solid bases like sodium hydroxide (NaOH), potassium hydroxide (KOH) and sodium methoxide (CH<sub>3</sub>ONa) or organic acids such as sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and hydrochloric acid (HCl), have been the most widely used method to synthesize biodiesel for the past two decades.

The major drawback of using homogeneous catalyst is non-recyclability of catalyst and deactivation by high moisture and higher saponification [2]. As a result, a thorough investigation into the manufacture of biodiesel with a heterogeneous catalyst has been conducted to overcome the homogeneous process economic and environmental limitations. There are many advantages of a heterogeneous catalytic reaction include quick separation from the reaction mixture by mechanical filtration, the ability to reuse the catalyst for further transesterification, ease of regeneration with less corrosion, lower environmental hazard, and lower cost.

Dairy waste scum is produced by dairy industries that handle raw and chilled milk as well as milk products such as butter, yoghurt, and ice-cream [3]. Transformation of dairy waste scum into biodiesel can be done via pyrolysis, dilution or blending, micro-emulsion and transesterification techniques. Among these four methods mentioned above, transesterification is the most common and convenient technology in production of biodiesel [4]. The transesterification reaction occurs between the lipid and an alcohol to form esters and a glycerol by product. Commercially, biodiesel production occurred frequently via alkali-catalysed (e.g., sodium hydroxide, potassium hydroxide) transesterification with excess methanol, which results in formation of fatty acid methyl ester (FAME) and glycerol [5]. Moreover, Marx [6] also added that base catalyzed transesterification is the most preferred method for biodiesel production due to high conversion obtained with shorter reaction time at relatively low cost.

In any study, kinetics modelling is important to determine the activation energy ( $E_a$ ) and frequency factor ( $A$ ) of the process. Activation energy acts as a barrier that the reactant in a chemical reaction has to overcome to form a product. The higher the activation energy, the more energy that a process consumed to achieve the desired product. Thus, it is preferable to have a reaction process with lower activation energy in order to save the energy consumed to form a desired product. Normally, the activation energy can be reduced by using catalyst by altering the reaction's transition state. After that, the reaction follows a different path/mechanism than the uncatalyzed reaction. The net energy difference between the reactant and the product is unaffected by the catalyst. On the other hand, the frequency factor represents the frequency of collisions between reactant molecules at a standard concentration. In this paper, the focus was on kinetic modelling of biodiesel production as there has been limited knowledge regarding kinetic modelling for dairy waste scum oil feedstock.

## **Experimental**

### *Materials and reagents*

Methanol (99.9%, Merck 106009), potassium hydroxide, sulfuric acid and isopropyl alcohol. Eggshell from kitchen waste for CaO catalyst generation.

### *Preparation of catalyst*

The discarded eggshells were obtained from a burger stall at university campus. First and foremost, the waste eggshells were cleaned up by using tap water to remove the unwanted contaminants or impurities. Then, the membrane of the eggshells was removed thoroughly. Consequently, the eggshells were left in the drying oven for 24 hours at 100°C to be dried. After 24 hours, the dried eggshells were collected from the oven and crushed into powder by using blender. The powder formed of eggshells were placed in cubicles and calcined for 3.5 hours in a furnace at 900°C to maximize the biodiesel yield. After calcination process completed, a cold solid is obtained and stored in a desiccator for 24 hours.

### Extraction of dairy waste scum oil.

The dairy waste scum was collected at a milk factory waste effluent. The raw dairy waste scum needs to undergo extraction process to obtain the scum oil. Firstly, the collected waste scum was put in a 100 ml beaker and heated to 100°C on the hot plate for 30 minutes to evaporate the moisture in the mixture. Then, the liquid scum was allowed to settle for a few minutes until sediments and solid contaminants float to the top surface. By using fine steel coarse mesh, the undesired solid waste and suspended particles were removed. The liquid scum was centrifuged for a few times in a centrifuge machine for several minutes with 5000 rpm. The steps are repeated for a few times until a pure anhydrous scum oil is achieved.

### *Pre-treatment and Acid Esterification*

For the synthesis of biodiesel, esterified scum oil was trans esterified using a calcium oxide catalyst via microwave irradiation method to heat 100 mL of esterified samples. Normally, the free fatty acid (FFA) contents in the extracted scum oil are more than 2%. Therefore, it must undergo pre-treatment and acid esterification process to determine the FFA content value. In case the FFA content is more than 2%, the acid esterification process must be taken. The scum oil was undergone acid esterification process for high FFA (>2%). A 100 mL of the sample's preheated oil is poured in a separate flask and placed on a mechanical stirrer set to 600 rpm. The reaction mixture is stirred for approximately 60 minutes at a temperature of 60°C with a known amount of 1% v/v H<sub>2</sub>SO<sub>4</sub> and 20 mL methanol. After cooling the reaction mixture, it was transferred to the separating funnel for phase separation. The top layer is a mixture of excess unreacted methanol and water was removed, while the bottom layer is an esterified oil sample that will be rinsed with distilled water to remove any residue and heated to evaporate any remaining water. The FFA level of esterified scum oil was determined for subsequent transesterification reactions.

### *Transesterification*

For the synthesis of biodiesel, esterified scum oil was transesterified using a calcium oxide catalyst (calcined eggshells) where microwave irradiation method was used to heat 100 mL of the esterified samples. The methanol and oil were heated in a microwave oven with 6:1 molar ratio at 45°C, 50°C, 55°C, 60°C by using a magnetic stirrer and an infrared temperature sensor while the oven is able to maintain constant stirring and temperature control without the need for direct contact. 750 W was set up to irradiate the mixture. The microwave reactor was utilized in this process. The reaction time was taken in range of 10, 15, 20, 25 and 30 minutes. Once the reaction mixture has been allowed to settle for 5 minutes at room temperature, the top ester layer was poured into a new flask. Afterwards, a vacuum was used to remove the solid catalyst from the reaction, which was then transferred to the separating funnel and allowed to stand overnight to complete the phase separation process. Layers one, two, and three all contain FAME, while the bottom layer has traces of catalyst. Excess methanol and calcium oxide particles are removed from the filtered biodiesel by distillation and decalcification with citric acid.

### *Biodiesel purification*

In order to purify the biodiesel, the water washing process was utilized, and the biodiesel mixture was gently swirled to avoid foam formation. This process was done three times to guarantee that the biodiesel fraction was clear of most impurities. The washed biodiesel mixture was then maintained overnight in a separating funnel to separate into two phases: water impurities and biodiesel. To eliminate any leftover moisture, the washed biodiesel portion was heated to 100 °C for 1 hour. The yield of biodiesel was calculated by comparing the weight of biodiesel to the original weight of lipid. Subsequently, the biodiesel yield will be evaluated by calculating the amount of

biodiesel obtained after purification process compared to the amount of oil used in transesterification process in percentage. The formula to calculate the percentage of biodiesel yield is shown in Eq. 1.

$$\text{Biodiesel yield (\%)} = \frac{\text{weight of fatty acid methyl ester produced (g)}}{\text{weight of oil used (g)}} \times 100 \quad (1)$$

#### *Kinetic modelling evaluation for biodiesel production*

It is necessary to conduct batch trials to determine how well the transesterification process works at various reaction times and temperatures (318 K, 328 K, 338 K), where the lowest reaction temperature is limited to the mesophilic range (338 K) due to the slower glycerol production rates at lower temperatures. The highest reaction temperature is set at 338 K due to the range of 318 K, 328 K, and 338K (Pugazhendi,2020). In assumption, the transesterification process should follow first order kinetics as the function of biodiesel yield. The reaction temperature has the greatest influence on the time-dependent reaction rate constant. At various temperatures, the transesterification reaction's rate constant is computed. Biodiesel yield  $t$  and response time  $k$  are the rate constants in Eq. 2, which displays the differential form of a first-order rate equation.

$$\text{Reaction rate} = -\frac{d(Y)}{dt} \quad (2)$$

$$\text{Reaction Rate} = k(Y)$$

$$\frac{d(Y)}{dt} = k(Y) \quad (3)$$

Assuming the initial biodiesel yield as  $Y_0$  at time  $t=0$ , and the yield at time,  $t$  on integration, the Eq. 3 is expressed in Eq. 4.

$$k = \frac{\ln(Y_t) - \ln(Y_0)}{t} \quad (4)$$

It can be shown from Eq. 4 that the slope of the plot ( $\ln(d(Y)/dt)$  vs  $\ln(Y)$ ) supplied the reaction rate constant for the reaction.

Taking the natural logarithm and expressing the Arrhenius equation in Eq. 5 results in the formation of Eq. 6. The activation energy and frequency factor may be derived from the slope and intercept of  $\ln k$  against  $1/T$  in Eq. 6, which can be obtained here:

$$k = Ae^{\frac{-Ea}{RT}} \quad (5)$$

$$\ln k = \frac{-Ea}{RT} + \ln A \quad (6)$$

## **Results and discussion**

### *Kinetic modeling analysis*

In any study, kinetics modelling is important to determine the activation energy ( $E_a$ ) and frequency factor ( $A$ ) of the process. Activation energy acts as a barrier that the reactant in a chemical reaction has to overcome to form a product. The higher the activation energy, the more energy that a process consumed to achieve the desired product. Thus, it is preferable to have a reaction process with lower activation energy in order to save the energy consumed to form a desired product. Normally, the activation energy can be reduced by using catalyst by altering the reaction's transition state. After that, the reaction follows a different path/mechanism than the uncatalyzed reaction. The net

energy difference between the reactant and the product is unaffected by the catalyst. On the other hand, the frequency factor represents the frequency of collisions between reactant molecules at a standard concentration

The correlation between activation energy and frequency factor is shown in Arrhenius equation as formulated in Eq. 7.

$$k = Ae^{\frac{-E_a}{RT}} \quad (7)$$

By taking the natural logarithm on both sides, the Eq. 7 is expressed as Eq. 8

$$\ln k = \frac{-E_a}{RT} + \ln A \quad (8)$$

Where  $E_a$  is representing activation energy (J/mol) and  $A$  is indicating the frequency factor ( $\text{min}^{-1}$ ). The value of the  $R$ , universal gas constant is taken as  $8.314 \text{ J/mol.K}$  and  $T$  is the absolute temperature.

In the Eq. 8, it is noted that the linear correlation exists between  $\ln k$  and  $1/T$ . Therefore, the activation energy and frequency factor can be calculated from the slope of the and intercept of the correlation, respectively.

On top of that, the first-order kinetics equation has to be derived to obtain the reaction rate constant ( $k$ ) value. The reaction is assumed to be first order kinetics as research reported that in a process that molar ratio of methanol higher than triglyceride, the forward reaction is believed to be at pseudo first-order reaction. Thus, the rate law of equation is formulated as in Eq. 9.

$$\text{Rate} = -r = \frac{-d[TG]}{dt} = k[TG] \quad (9)$$

By integrating the Eq. 9, the rate law of equation becomes as follow:

$$\ln \frac{[TG]_o}{[TG]} = k_{TG} \cdot t \quad (10)$$

Where,

$$X_{ME} = 1 - \frac{[TG]}{[TG]_o} \quad (11)$$

Thus,

$$\ln (X_{ME} - 1) = -kt \quad (12)$$

Therefore, a linear correlation between  $\ln (X_{ME} - 1)$  and times will exhibit slope value that indicates the value of rate constant at particular temperature and reaction time. Fig. 1 shows the graph plotted to obtain the reaction rate constant of each temperature.

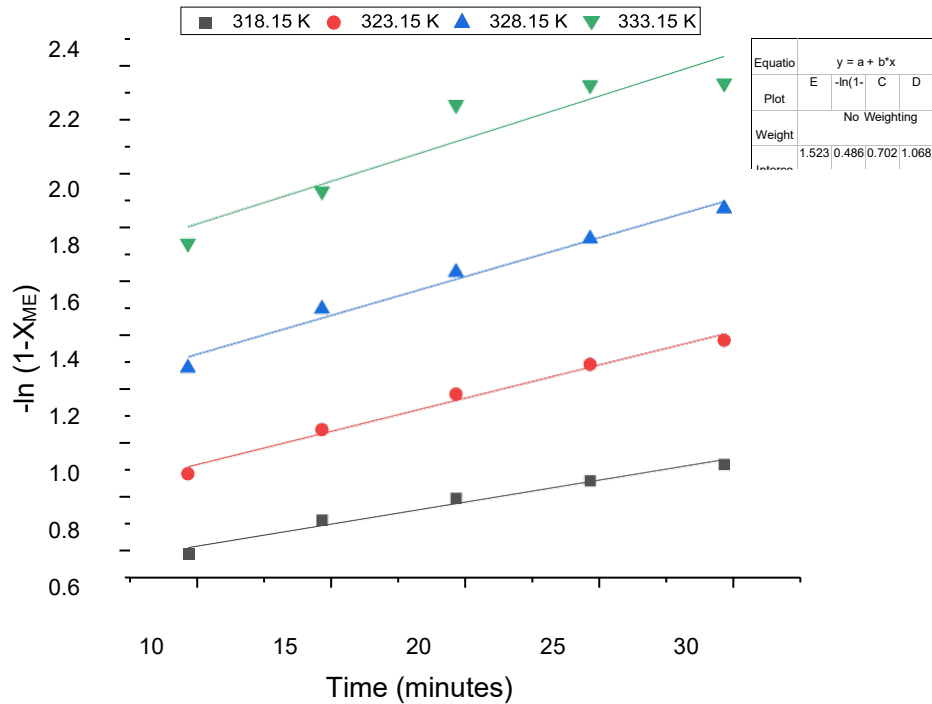


Figure 1: Graph  $-\ln(1-X_{ME})$  against time to find the rate constants,  $k$

From graph depicted in Fig. 1, the slope of each temperature is taken as the value of the rate constants,  $k$ . The value of the rate constants for each temperature is presented in Table 1.

Table 1: Value of Rate Constants,  $k$  at respective temperature

Temperature (K)	$k$ value	$\ln k$
318.15	0.01633	-4.11475
323.15	0.02467	-3.70217
328.15	0.02887	-3.54495
333.15	0.03164	-3.45333

Consequently, a graph  $\ln k$  against  $1/T$  is plotted as shown in Fig. 2 to obtain the value of the activation energy and frequency factor. The linear graph exhibits an equation which the slope is equal to -1.29. By substituting in the Eq. 11, the activation energy is defined at 10.73 J/mol.

$$\frac{-Ea}{R} = -2.18$$

$$Ea = 1.29(8.314 \frac{J}{mol}) \tag{11}$$

$$= 18.12 \frac{J}{mol}$$

On the other hand, the frequency factor of the reaction is determined at 3.163 which is the intercept of the graph.

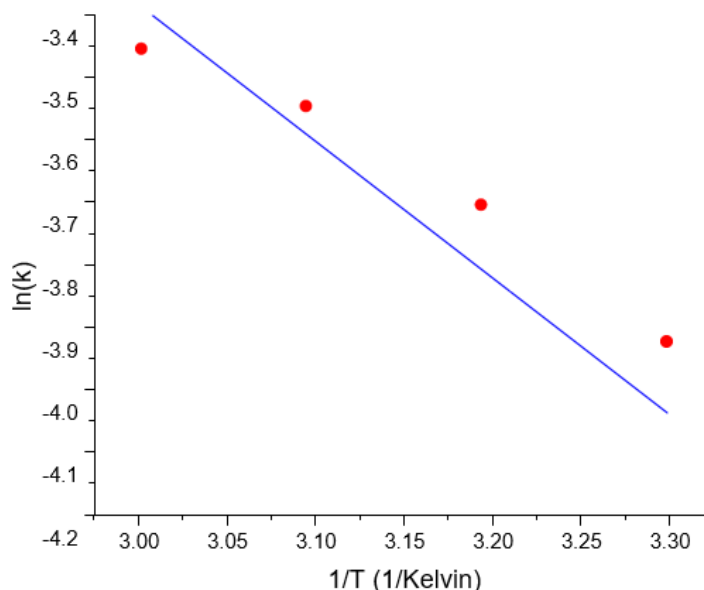


Figure 2: Graph of  $\ln k$  against  $1/T$  to obtain activation energy and frequency factor

Graph depicted in Fig. 2 shows the linear graph of  $\ln k$  against  $1/T$  to determine the slope which indicates the activation energy and also the intercept as frequency factor. From the calculation, the activation energy is obtained at 18.12 J/mol and 3.163 frequency factor. Therefore, in this study the minimum amount of energy that is required to activate atoms or molecules to a condition in which they can undergo chemical transformation is 18.12 J/mol of energy to form biodiesel. It is a good indication since previous studies with same feedstocks that using different type of catalyst has higher activation energy as described in literature. Table 2 in the data validation section shows the comparison data of activation energy between current study and previous study.

#### Data validation

The results of the kinetic studies showed that the use of derived calcined eggshells heterogeneous solid catalyst for the production of biodiesel from dairy waste scum oil under the influence of microwave heating has proved that it produces lower activation energy compared to other studies and the reactants achieved the equilibrium in a short interval by giving the maximum yield of biodiesel and conversion of triglycerides. The activation energy stated in the comparison Table 2 has shown that the use of dairy waste scum oil combined with calcined eggshells catalyst has minimized the activation energy of the transesterification process as compared to the other studies previously described in the literature which is the lowest activation energy is the most preferable reaction. The activation energy of the previous work is from the study by Yatish and Krishnamurthy.

*Table 2: The comparison of activation energy between present work and literatures.*

Feedstock	Catalyst	Activation Energy	References
Dairy ScumOil	Calcined Eggshells	18.12	Present Work
Dairy ScumOil	Nano CaTiO <sub>3</sub>	35.56	[7]
Dairy ScumOil	Snail Shell CaO	67.21	[2]

## Conclusions

The investigation of principle of kinetics reaction contributes well knowledge into biodiesel generation from dairy waste scum oil in presence of CaO from eggshell. The microwave assisted transesterification of dairy waste scum oil has produced lower activation energy compared to other studies which is significant to save energy especially when the production of biodiesel is in large scale industry which required to consume a lot of energy. The results also showed that microwave heating only need small amount of activation energy which fasten the biodiesel production with high yield. A lower activation energy process is preferable since it can produce the same production amount with low cost and energy.

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