



Kinetic Study on Ultrasound Assisted Biodiesel Production from Waste Cooking Oil

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Abstract. The objective of this research was to study a kinetic model of biodiesel production from waste cooking oil assisted by ultrasound power. The model considered the biodiesel production process as a 2nd order reversible reaction, while its kinetic parameters were estimated using MATLAB, based on data extracted from Hingu, *et al.* [1]. The data represented experiments under low-frequency ultrasonic wave (20 kHz) and variations of temperature, power, catalyst concentration, and alcohol-oil molar ratio. Statistical analysis showed that the proposed model fits well to the experimental data with a determination coefficient (R^2) higher than 0.9.

Keywords: *kinetic model; validation; ultrasound; transesterification.*

1 Introduction

Biodiesel is a liquid fuel that contains mono-alkyl esters of long-chain fatty acids. Biodiesel is mostly derived from vegetable oil or animal fat and it can be used as a substitute for the current diesel from fossil fuel [2]. Biodiesel can be produced through transesterification of triglycerides (TG) with alcohol and a base catalyst. Biodiesel can also be derived directly from free fatty acids (FFA) through esterification using an acid catalyst [3].

Process intensifications of biodiesel production have been investigated by previous researchers, such as homogenous catalyst transesterification and esterification [4], heterogeneous base-catalyst [5], enzymatic transesterification [6], non-catalyst supercritical transesterification [7], microwave-assisted transesterification [8], and ultrasound-assisted esterification [1,9-11]. Although these intensifications could improve yield and efficiency, several drawbacks were discovered. Base-catalyst transesterification has disadvantages in catalyst separation that lead to large energy consumption. Moreover, for oil with high free fatty acids, base-catalyst esterification has a tendency of saponification. On the other hand, acid-catalyst esterification can produce biodiesel but under a low reaction rate as compared to base-catalyst esterification [3]. The production

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of biodiesel using an enzymatic reaction brings along higher costs and a longer processing time [6]. The use of non-catalytic supercritical transesterification has disadvantages in technical operation that may increase the cost of production [6]. Intensification to reduce processing time has also been attempted, using microwaves and ultrasound as power utilities [8-11]. It turned out that the yield of biodiesel produced by microwave-assisted transesterification was lower than by ultrasound-assisted production [10-11]. However, compared to the conventional method, the ultrasound-assisted esterification showed a better and more efficient process, including shortening the reaction time. The production of biodiesel using ultrasound achieved 92% conversion within 30 minutes, while the conventional method achieved 91% conversion within 1 hour [10]. In order to design a biodiesel reactor with ultrasound as power source, a kinetic model of biodiesel production assisted by ultrasound is required. From a literature search, the number of studies on the prediction of kinetic models for ultrasound-assisted esterification is very limited. The objective of this study was to investigate a kinetic model for ultrasound-assisted transesterification of waste cooking oil by considering the process as a 2nd order reversible reaction.

2 Kinetic Modeling

The reaction that occurs in biodiesel production is (trans)esterification. Transesterification is a reaction between triglyceride (TG) and alcohol that produces alkyl esters (fatty acid methyl esters – FAME) with glycerol as by-product. The molar ratio of triglyceride to alcohol is commonly 1:3 but most of the reactions use a higher ratio to ensure that all TG will be converted to biodiesel. The transesterification reaction is represented in Figure 1.

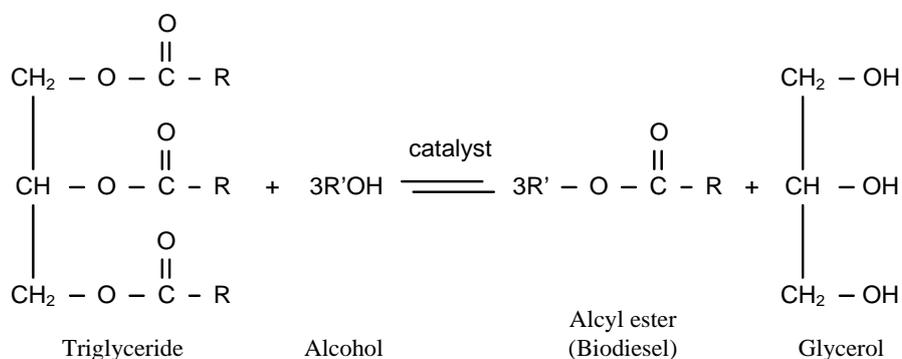
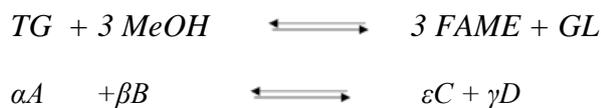


Figure 1 Reaction of triglyceride and alcohol to form biodiesel (alkyl ester).

This reaction mostly occurs in a reversible process. To determine the kinetic model, the following reactions were considered:



The kinetic model was formulated with the following assumptions:

1. The reaction is not elementary but only a 2nd order reversible reaction.
2. The initial concentrations of methyl esters (biodiesel) and glycerol are zero and therefore triglyceride is merely considered a limiting reactant.

The reversible reaction then can be formulated as:

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A^\alpha C_B^\beta - k_2 C_C^\varepsilon C_D^\gamma \quad (1)$$

Since the reaction is assumed to be a non elementary reaction ($\alpha = 1$, $\beta = 1$, $\varepsilon = 1$ and $\gamma = 1$), the kinetic model in Eq. (1) was then modified to:

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A C_B - k_2 C_C C_D \quad (2)$$

According to the stoichiometry, $C_A = C_{A0}(1 - X_A)$; $C_B = C_{B0} - C_{A0} X_A$; $C_C = C_{C0} + C_{A0} X_A$; $C_D = C_{D0} + C_{A0} X_A$; where $M = C_{B0}/C_{A0}$; $C_C = C_{C0} + C_{A0} X_A$; $C_D = C_{D0} + C_{A0} X_A$; where $C_{C0} = C_{D0} = 0$, then $C_C = C_{A0} X_A$; $C_D = C_{A0} X_A$, where k_1 and k_2 are rate reaction constants ($\text{litr.mol}^{-1}.\text{min}^{-1}$).

Table 1 1st Order Kinetics of Irreversible Transesterification.

Researcher	Raw Material	Temperature	k (min. ⁻¹)
Endang, et al. [12]	Waste cooking	50°C	k=0.0305
Fahri [13]	Rice bran	60°C	k=0.00223
Sahirman, et al. [14]	Nyamplung	45°C	k=0.0663
Berrios, et al. [15]	Sun flower	60°C	k ₁ =0.02 and k ₂ =0.005
Vujicic, et al. [16]	Sun flower	60°C	k=0.00267
Joelianingsih, et al. [17]	Palm oil	250°C	k=0.0034
Zhang, et al. [18]	Palm oil	70°C	k=0.00099
Vyas [19]	Castor oil	50°C	k=0.091
Tania, et al. [20]	CPO	55°C	k=0.000278

The values of k_1 and k_2 have been evaluated for different vegetable oils and process conditions. Table 1 shows previous works on biodiesel production from various vegetable oils and different temperature variables. Most of the researchers assumed that the transesterification was a 1st order irreversible transesterification reaction. The value of k_1 is in the range of 0.0002-0.091

1/min at a temperature of 45-70°C. Joelianingsih, *et al.* [17] performed a supercritical experiment with high temperature.

According to another assumption, transesterification occurs in a 2nd order reaction (Table 2). Renita [21] proposed a kinetic model of the 2nd order and irreversible reaction, while Murni [22] and Lopez [23] proposed a kinetic model of the 2nd order and reversible reaction. Furthermore, Darnoko and Cheryan [24] and Pojanalai and Sookkumnerd [25] proposed a kinetic model of the 2nd order under three stages of mechanism reactions and irreversible reaction. Nouredini and Zhu [26] proposed a kinetic model of the 2nd order under a three-step reaction mechanism and a reversible reaction.

Table 2 2nd Order Kinetic Models of Transesterification.

Researcher	Raw Material	Temperature (°C)	Reaction	k (mol.min) ⁻¹
Renita [21]	Palm oil	80	Irreversible	k=0.00984
Murni, <i>et al.</i> [24]	Waste cooking oil	30	Reversible 1 step	k ₁ =0.000349; k ₂ =0.000189
Lopez [23]	Castorseed oil	26	Reversible 1 step	k ₁ =0.047; k ₂ =0.814
Darnoko and Cheryan [24]	Palm oil	50	Irreversible 3 steps	k ₁ =0.018; k ₂ =0.036 ; k ₃ =0.112
Pojanalai and Sookkumnerd [25]	Palm oil	45	Irreversible 3 steps	k ₁ =0.0982; k ₂ =0.1282; k ₃ =0.0572
Nouredini and Zhu [26]	Soybean oil	50	Reversible 3 steps	k ₁ =0.05; k ₂ =0.11 k ₃ =0.215; k ₄ =1.228 k ₅ =0.242; k ₆ =0.007
Avramovic [27]	Sun Flower oil	40	Irreversible 1 step	k ₁ =0.04

Our work evaluates kinetic parameters of biodiesel production assisted by ultrasound power. For this purpose, Eq. (2) was converted into conversion terms and re-arranged as:

$$-\frac{X_A}{dt} = k_1 C_{A0}^2 (1 - X_A)(M - X_A) - k_2 C_{A0}^2 X_A^2 \quad (3)$$

When the equilibrium is reached, Eq. 3 must be equal to zero ($-r_A$) = 0. Thus Eq. (2) is transformed into Eq. (4).

$$k_1 C_{Ae} C_{Be} = k_2 C_{Ce} C_{De} \quad (4)$$

where $C_{Ae} = C_{A0}(1 - X_{Ae})$; $C_{Be} = C_{A0}(M - X_{Ae})$; $C_{Ce} = C_{A0} X_{Ae}$; $C_{De} = C_{A0} X_{Ae}$.

The equilibrium constant is then obtained as:

$$\frac{k_1}{k_2} = K_\varepsilon = \frac{X_{A\varepsilon}^2}{(1 - X_{A\varepsilon})(M - X_{A\varepsilon})} \quad (5)$$

If Eq. (5) is substituted into Eq. (3), then the biodiesel conversion can be obtained as:

$$-\frac{X_A}{dt} = k_1 C_{A0} \left[\frac{X_{A\varepsilon}^2 (1 - X_A)(M - X_A) - X_A^2 (1 - X_{A\varepsilon})(M - X_{A\varepsilon})}{X_{A\varepsilon}^2} \right] \quad (6)$$

Eq. (7) will be evaluated for its parameters based on data obtained from Hingu, *et al.* [1] who worked on ultrasound-assisted esterification. The effect of power or frequency supplied by ultrasound to the rate constant will be correlated via the Arrhenius equation based on the following equation:

$$k = A e^{E_a/RT} \quad (7)$$

where E_a is the activation energy as a function of ultrasound power (P). The effect of ultrasound power may follow quadratic, exponential and logarithmic equations (Eqs. (8)-(11)). The equation with the highest determination coefficient (R^2) will be selected as the best fit.

$$E_a = a.P^b + c \quad (8)$$

$$E_a = a.P^b x e^c \quad (9)$$

$$E_a = a.P^2 + bP + c \quad (10)$$

$$E_a = a.\log(P) + b \quad (11)$$

where a,c was estimated and b = variation between 0.9 and 1.4.

3 Model Simulation and Parameter Estimation

3.1 Parameter Estimation

Model simulation and parameter estimation in this study were conducted based on data obtained from Hingu, *et al.* [1]. They performed biodiesel production experiments using ultrasound in a low-frequency bioreactor (20 kHz). The effect of different operation parameters, such as alcohol-oil molar ratio, catalyst concentration, temperature, and ultrasound power, were investigated. The experimental setup used for synthesis of biodiesel is shown in Figure 2.

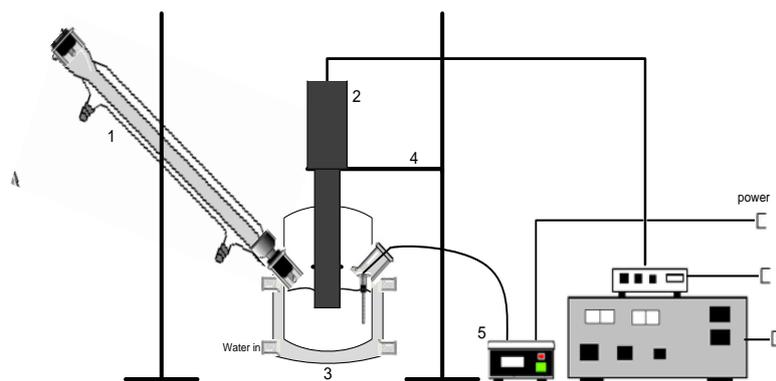


Figure 2 Schematic representation of experimental setup for synthesis of biodiesel (1. condenser, 2. transducer, 3. biodiesel reactor, 4. support stand, 5. temperature sensor, 6. ultrasonic generator) [1].

3.2 Statistical Analysis

The kinetic model and optimum parameters were evaluated using the following statistical tests: *coefficient of determination* (R^2), *sum of squares error* (SSE), and *root mean square error* ($RMSE$). The selected kinetic model of the transesterification reaction was the model with the lowest criteria value of SSE , $RMSE$, and the highest value of R^2 ($R^2 \sim 1$).

$$R^2 = 1 - \frac{SSE}{SST} \quad (12)$$

SST is the sum squared total that was calculated with this equation.

$$SST = \frac{1}{N} \sum_{j=1}^N (X_{A_{exp}} - \bar{X}_A) \quad (13)$$

$$SSE = \frac{1}{N} \sum_{j=1}^N (X_{A_{exp}} - \bar{X}_{A_{data}})^2 \quad (14)$$

$$RMSE = \left[\frac{1}{N} \sum_{j=1}^N (X_{A_{data}} - \bar{X}_{A_{exp}}) \right]^{\frac{1}{2}} \quad (15)$$

4 Results and Discussion

4.1 Ultrasound Effect in Kinetic Model

In order to evaluate the effect of ultrasound on biodiesel production, the Arrhenius equation was employed. Hence, the objective of the parameter estimation was to find values of the activation energy (E_a) and the collision frequency factor (A) that fit well to the experimental data.

Table 3 shows the results of parameter estimation for different activation model expressions. The frequency factor (A) was found to be constant (= 0.0011) and it was not influenced by the ultrasound power level. The optimal value of Ea was found by an expression of $aP^{0.9} + c$, which is indicated by its lowest value of SSE and RMSE.

Table 3 Effect of Ultrasound Power on Activation Energy.

$E_a = f(P)$	$\overline{R^2}$	\overline{SSE}	$E_a = f(P)$	$A \neq f(P)$	$\overline{R^2}$	\overline{SSE}
a.P.exp (b)	0.9782	0.0097	$a.P^{0.9} + c$	0.0011	0.9787	0.0096
$a.P^{0.9}.exp$ (b)	0.9008	0.0476	$a.P^{1.0} + c$	0.0011	0.9785	0.0097
$a.P^{1.5}.exp$ (b)	0.9008	0.0476	$a.P^{1.1} + c$	0.0011	0.9783	0.0097
$a.P^2 + b.P + c$	0.9008	0.0476	$a.P^{1.2} + c$	0.0011	0.9784	0.0097
$a.P^{1.5} + b.P + c$	0.9009	0.0476	$a.P^{1.3} + c$	0.0011	0.9784	0.0097
a. log (P)+ b	0.9009	0.0476	$a.P^{1.4} + c$	0.0011	0.9786	0.0096

4.2 Model Validation

Figure 3 shows the predictions of the kinetic model compared to the experimental data with respect to the influence of temperature on conversion. The model did not fit to the experimental data at a reaction time of 5 minutes and temperatures of 35 and 45°C. This may be due to temperature fluctuation occurring during the reaction. Nevertheless, the simulated distribution of

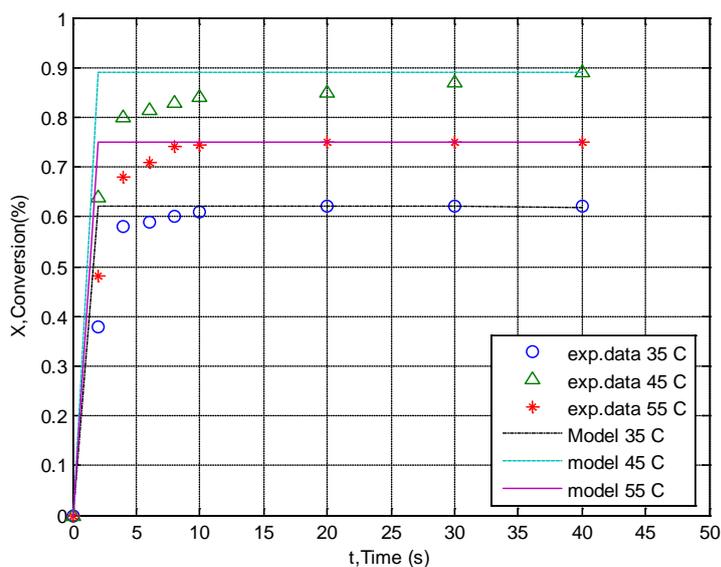


Figure 3 Influence of temperature on transesterification kinetic model.

predicted points generally provided good agreement with the experimental data points. The simulation result indicates that a low temperature leads to a lower extent of conversion and when the temperature increases the conversion increases up to certain limit. The increase of temperature from 35 to 45°C results in an increase of conversion from 64% to 89%. However, increasing the operation temperature can enhance the solubility of the methanol in the other phase and also enhance the cavitation effects, leading to a higher conversion.

4.3 Influence of Ultrasound Power

Figure 4 depicts the model simulation and experimental data from Hingu, *et al.* [1] with ultrasound power levels of 150, 200, and 250 Watt. It can be seen that the model fits well to the experimental data except for an operation time of 5-10 minutes. At a power of 150 Watt, 66% conversion was achieved, while increasing the power level up to 200 W increased the conversion up to 89%. However, a further increase in power to 250 Watt did not provide a significant increase of conversion. This can be due to the fact that at higher power levels, usually a cushioning effect is observed, which results in a decreased transfer of energy into the system and hence lower cavitation activity.

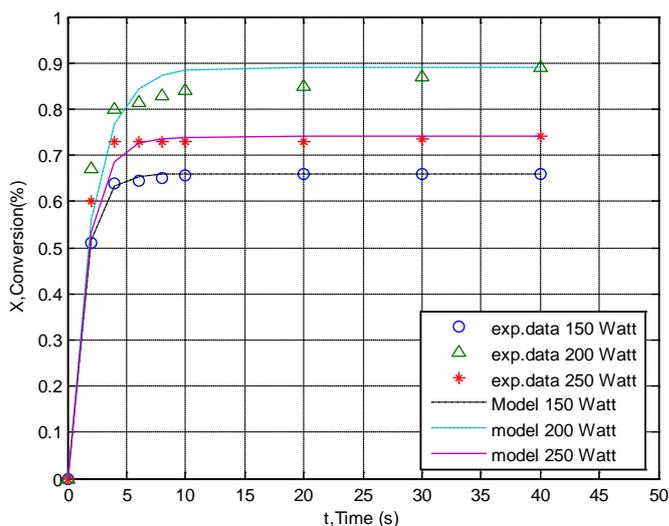


Figure 4 Influence of ultrasound power on transesterification kinetic model.

Figure 4 also indicates that the proposed model of E_a is influenced by the ultrasound power level. The activation energy is the minimum kinetic energy that must be possessed by a particle to produce an effective collision for producing a chemical reaction. Ultrasound power can affect cavitation that damages the wall or membrane of the particle that reacted, so the activation

energy is lower. The lower activation energy will have the effect of facilitating particle interactions.

Table 4 Constant Values of Transesterification Reaction Rate for Temperature and Ultrasound Power.

Temp. (°C)	(ml ³ /mmol ³ .min.)		Ultrasound (Watt)	(ml ³ /mmol ³ .min)	
	k ₁	k ₂		k ₁	k ₂
35	0.0691	0.0271	150	0.0695	0.0303
45	0.0692	0.0301	200	0.0692	0.0301
55	0.0692	0.0333	250	0.0689	0.0300

Table 4 shows that calculation of the parameters for 35, 45, and 55 °C and 150, 200, and 250 Watt produces the same value for k₁, but a slightly different value for k₂. This indicates that the rate of triglyceride conversion to methyl esters (reaction to the right side) is the same at various temperatures but it has a different rate of methyl ester reduction (reaction to the left side). This also indicates that synthesis of biodiesel from waste cooking oil with a sonochemical reactor is a reversible reaction. This is in disagreement with Vyas, *et al.* [19] and Avramovic, *et al.* [27], who employed ultrasound but used a 1st and 2nd order irreversible kinetic model (Table 1).

4.4 Influence of Methanol to Oil Molar Ratio

Figure 5 shows the effect of molar ratio of reactant at 4:1, 5:1, 6:1, and 7:1. It was observed that the conversion of experimental ME at the 10th and 15th

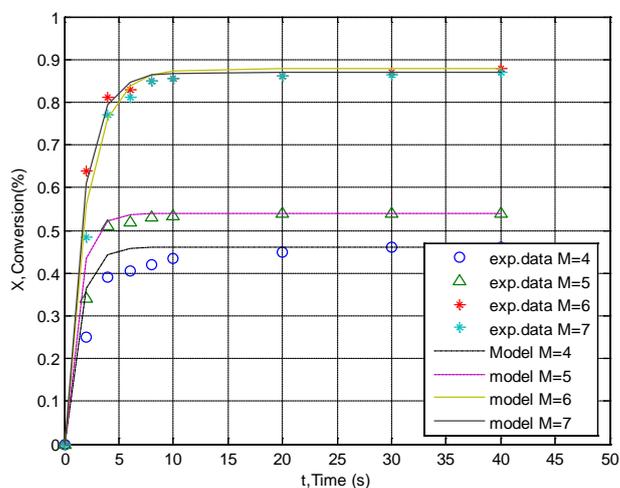


Figure 5 Influencing of reactant ratio on transesterification kinetic model.

minute for the 7:1 molar ratio did not match exactly with that of the model simulation. This may be due to the temperature fluctuation that took place during the reaction. It was also observed that with an increase in the molar ratio from 4:1 to 7:1, the extent of conversion increased from 46% to 89%. This result can be attributed to the higher cavitation intensity due to the presence of the higher quantity of methanol in the system. Staravache, *et al.* [19] have reported similar effects of using excess methanol leading to an enhanced number of cavitation events and hence enhanced conversion of vegetable oil by transesterification.

4.5 Influence of Catalyst Concentration

Figure 6 shows the effect of the catalyst concentration at 0.5%, 0.75%, 1%, and 1.25%. It can be seen that conversion of the experimental methyl ester at the 5th, 10th, and 15th minute at 1% catalyst concentration did not match exactly with the simulated curves. It can also be seen from the figure that an increase in the catalyst concentration from 0.5 wt% to 1 wt% resulted in an increase in conversion from 55% to 89%. Initially, an insufficient amount of KOH resulted in incomplete conversion of triglycerides into esters, as indicated from its lower ester content. However, above a catalyst concentration of 1%, a further increase in the concentration of catalyst to 1.25 wt% resulted in a decrease in conversion to 82%. The observed results can be attributed to side reactions like saponification simultaneously occurring with the transesterification, which reduces the conversion of triglycerides to esters.

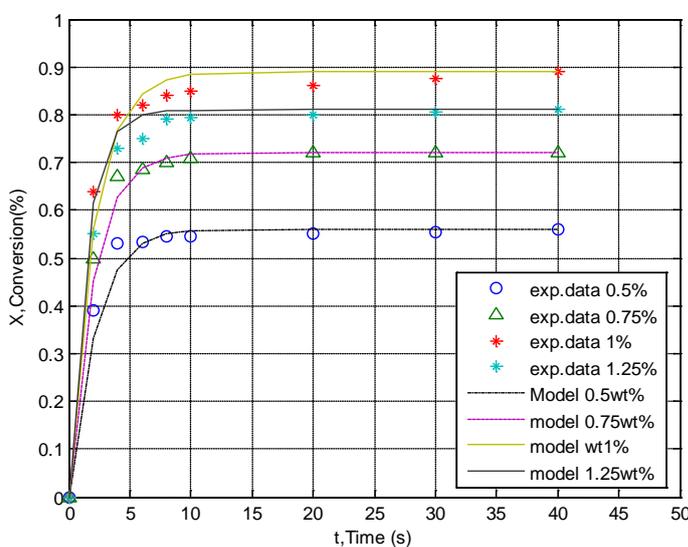


Figure 6 Influence of catalyst concentration on transesterification kinetic model.

Table 5 shows that the calculation of kinetic parameters for 4:1, 5:1, 6:1 and 7:1 molar ratio and 0.5%, 0.75%, 1%; and 1.25% catalyst concentration had the same value for k_1 but a different value for k_2 . This indicates that the rate of triglyceride reduction becoming methyl esters (production reaction) is the same at various temperatures but has a different rate of methyl ester reduction.

Table 5 Constant Values of Transesterification Reaction Rate for Molar Ratio and Catalyst Concentration.

Molar Ratio	$(\text{ml}^3/\text{mmol}^3.\text{min})$		Catalyst Concentration	$(\text{ml}^3/\text{mmol}^3.\text{min})$	
	k_1	k_2		k_1	k_2
4:1	0.0692	0.0301	0.5 wt%	0.0346	0.0151
5:1	0.0692	0.0301	0.75 wt%	0.0519	0.0226
6:1	0.0692	0.0301	1 wt%	0.0692	0.0301
7:1	0.0692	0.0301	1.25 wt%	0.0865	0.0377

4.6 Statistical Analysis

Table 6 shows the values of SSE, RMSE, and R^2 that were determined at various temperatures and ultrasound power levels. In general, the product distribution of the proposed model fits well to the experimental data; the values of SSE, RMSE were close to 0 and the value of R^2 was close to 1. Hence, based on the results shown in Table 6, the proposed model obtained best-fit values at a reaction temperature of 55°C, followed by 45°C and 35°C. As for ultrasound power, the proposed model obtained best-fit values at 150 W, followed by 250 W, and 200 W.

Table 6 Statistical Analysis of Kinetic Model on Temperature and Ultrasound Power Parameters.

Parameters	SSE	RMSE	R^2	Parameters	SSE	RMSE	R^2
35°C	0.0237	0.4904	0.9309	150 Watt	0.0015	0.2538	0.9960
45°C	0.0096	0.4131	0.9849	200 Watt	0.0139	0.4480	0.9780
55°C	0.0058	0.3183	0.9883	250 Watt	0.0039	0.3045	0.9917

Table 7 Statistical Analysis of Kinetic Model on Molar Ratio and Catalyst Concentration Parameters.

Parameters	SSE	RMSE	R^2	Parameters	SSE	RMSE	R^2
4:1	0.0009	0.1575	0.9948	0.5 wt%	0.0008	0.0834	0.9971
5:1	0.0023	0.2381	0.9910	0.75 wt%	0.0028	0.2990	0.9936
6:1	0.0158	0.5795	0.9755	1 wt%	0.0138	0.5327	0.9786
7:1	0.0369	0.5480	0.9458	1.25 wt%	0.0019	0.3014	0.9965

Table 7 shows the values of SSE, RMSE, and R^2 that were determined at different reactant molar ratios and catalyst concentrations. Hence, based on Table 7, the proposed model's best fit was at a reactant molar ratio of 4:1, followed by 5:1, 6:1 and 7:1. As for the catalyst concentration, the proposed

model had best-fit values at 0.5 wt%, followed by 1.25 wt%, 0.75 wt%, and 1 wt%. Overall, the optimum proposed model has the following expression:

$$r_A = 0.0707 C_{cat} e^{\frac{0.1001P^{0.9} + 1}{RT}} C_{A0} \left[\frac{X_{Ae}^2 (1 - X_A)(M - X_A) - X_A^2 (1 - X_{Ae})(M - X_{Ae})}{X_{Ae}^2} \right]$$

5 Conclusion

The kinetic of transesterification of used frying oil and methanol was modeled by an analytical solution that relied heavily on the assumption of a 2nd order reversible reaction. A model simulation of the reaction kinetics was conducted and compared with experimental data taken from Hingu, *et al.* [1].

An excellent fit of the curve lines to the experimental data points indicates that the proposed simulated kinetic model can be used to adequately describe ultrasound assisted transesterification from waste cooking oil with a value of $R^2 > 0.9$ and a value of $RMSE < 1$.

6 Nomenclature

A,B,C,D	= component of triglyceride, methanol, methyl ester and glycerol	
a,b,c	= constants in equation	
C	= concentration	(mmol/ml)
C _{cat}	= catalyst concentration	% (w/w)
C _i	= concentration of i component	(mmol/ml)
C _{ie}	= concentration of i component in equilibrium	(mmol/ml)
C _{io}	= initial concentration of i component	(mmol/ml)
E _A	= activation energy	Joule
FAME	= fatty acid methyl ester	
K _e	= equilibrium constant	
k ₁	= reaction rate constant (formation of FAME)	(ml ³ .mmol ⁻³ . min ⁻¹)
k ₂	= reaction rate constant (decomposition of FAME)	(ml ³ .mmol ⁻³ . min ⁻¹)
M	= reactant molar ratio (C _{B0} /C _{A0})	
MeOH	= methanol	
P	= ultrasound power	Watt
R	= ideal gas law constant (1,98 cal/gmol.°K)	
R ²	= coefficient of determination	
RMSE	= root mean square error	
r _A	= reaction rate	
SSE	= sum of squares error	

SST	= sum of squares total	
T	= temperature	K
TG	= triglyceride	
X _A	= conversion of triglyceride	
X _{Ae}	= conversion of triglyceride in equilibrium	

References

- [1] Hingu, S.M., Gogate P.R. & Rathod, V.K., *Synthesis of Biodiesel from Waste Cooking Oil Using Sonochemical Reactors*, Ultrasonic Sonochemistry, **17**(5), pp. 827-832, 2010.
- [2] Ma, F., & Hanna, M.A, *Biodiesel Production: a Review*, Bioresource Technology, **70**, pp.1-15, 1999.
- [3] Han, M., Yi, W., Wu, Q., Liu, Y., Hong, Y. & Wang, D., *Preparation of Biodiesel from Waste Oils Catalyzed By A Brønsted Acidic Ionic Liquid*, Bioresource Technology, **100**, pp. 2308-2310, 2009.
- [4] Cao, F., Chen, Y., Zhai, F., Li, J., Wang, J., Wang, X., Wang, S. & Zhu, W., *Biodiesel Production from High Acid Value Waste Frying Oil Catalyzed by Superacid Heteropolyacid*, Biotechnology Bioengineering, **101**, pp. 93-100, 2008.
- [5] Kawashima, A.K., Matsubara, K. & Honda, *Development of Heterogeneous Base Catalysts for Biodiesel Production*, Bioresource Technology, **99**, pp. 3439-3443, 2008.
- [6] Ranganathan, S.V., Narasimhan, S.L. & Muthukumar, K., *An Overview of Enzymatic Production of Biodiesel*, Bioresource Technology, **99**, pp. 3975-3981, 2008.
- [7] Hawash, S., Kamal, N., Zaher, F., Kenawi, O. & Diwani, G.E., *Biodiesel Fuel from Jatropha Oil via Non-Catalytic Supercritical Methanol Transesterification*, Fuel, **88**(3), pp. 579-582, 2009.
- [8] Azcan, N. & Danisman, A., *Microwave Assisted Transesterification of Rapeseed Oil*, Fuel, **87**(10), pp. 1781-1788, 2008.
- [9] Stavarache, C., Vinatoru, M., Maeda, Y. & Bandow, H., *Ultrasonically Driven Continuous Process for Vegetable Oil Transesterification*, Ultrasonics Sonochemistry, **14**(4), pp. 413-417, 2007.
- [10] Teixeira, L.S.G., Assis, J.C.R., Mendonça, D.R., Santos, I.T.V., Guimarães, P.R.B., Pontes, L.A.M. & Teixeira, J.S.R., *Comparison between Conventional and Ultrasonic Preparation of Beef Tallow Biodiesel*, Fuel Processing Technology, **90**, pp. 1164-1166, 2009.
- [11] Widayat, Satriadi, H., Yuariski O. & Murwono, D. *Biodiesel Production from Bulk Frying Oil with Ultrasound Assisted*, Research Journal of Applied Sciences Engineering and Technology, **6**(10), pp. 1732-1739, 2013.

- [12] Endang, K., Setyawardhani, D.A., Widyawati, E.D. & Adi, W.K., *Pengaruh Temperatur terhadap Kinetika Reaksi Metanolisis Minyak Jelantah Menjadi Biodiesel (Ditinjau sebagai Reaksi Homogen)*, Jurnal Ekuilibrium, **6**(2), pp. 71-74, 2007. (Text in Indonesian).
- [13] Fachri, B.A., *Kinetika Reaksi Alkoholisis Minyak Dedak Padi dalam Metanol Dengan Katalis KOH pada Proses Pembuatan Biodiesel*, Jurnal Ilmu Dasar, **7**(2), pp. 98-105, 2006. (Text in Indonesian).
- [14] Sahirman, A., Suryani, D., Mangunwidjaja, D., Sukardi R. & Sudradjat R., *Kinetika Reaksi Transesterifikasi Minyak Biji Nyamplung (Calophyllum Inophyllum) pada Proses Produksi Biodiesel*, Jurnal Penelitian Hasil Hutan, pp. 84-91, 2008 (Text in Indonesian).
- [15] Berrios, M., Siles, J., Martin, M.A. & Martin, A., *A Kinetic Study of the Esterification of Free Fatty Acids (FFA) in Sunflower Oil*, Fuel, **86**(15), pp. 2383-2388, 2007.
- [16] Vujicic, D., Comic, D., Zarubica, A., Micic, R. & Baskovic, *Kinetics of Biodiesel Synthesis from Sunflower Oil Over CaO Heterogenous Catalyst*, Fuel, **89**(8), pp. 2054-2061, 2010.
- [17] Joelianingsih, Maeda, H., Hagiwara, S., Nabetani, H., Sagara, Y., Soerawidjaya, T.H., Tambunan, A.H. & Abdullah, K., *Biodiesel Fuels from Palm Oil Via The Non-Catalytic Transesterification in A Bubble Column Reactor at Atmospheric Pressure: A Kinetic Study*, Renewable Energy, **33**(7), pp. 1629-1636, 2008.
- [18] Zhang, L., Shang, B., Xin, Z., Liu, Q. & Sun, S., *Kinetics of Transesterification of Palm Oil and Dimethyl Carbonate for Biodiesel Production At The Catalysis of Heterogenous Base Catalyst*, Bioresource Technology, **101**, pp. 8144-8150, 2008.
- [19] Vyas, A.P., Verma, J.W. & Subrahmanyam, N., *Effects of Molar Ratio, Alkali Catalyst Concentration and Temperature on Transesterification of Jatropha Oil with Methanol under Ultrasonic Irradiation*, Advances in Chemical Engineering and Science, **1**, pp. 45-50, 2011.
- [20] Tania, S., Arbianti, R. & Nurhasman, D., *Kinetika Reaksi Transesterifikasi CPO terhadap Produk Metal Palmiat Dalam Reactor Tumpak*, Prosiding Seminar Nasional Fundamental dan Aplikasi Teknik Kimia ITS Surabaya, 2007. (Text in Indonesian).
- [21] Renita, M., *Kinetika Transesterifikasi Minyak Sawit menjadi Etil Ester (Biodiesel)*, Jurnal Teknologi Proses, pp. 39-44, 2007. (Text in Indonesian).
- [22] Murni, Y. & Karim, A.A., *Kinetika Reaksi Pembuatan Biodiesel dari Minyak Goreng Bekas (Jelantah) dan Metanol dengan Katalisator KOH*, Jurnal Teknologi IST AKPRIND, **2**(2), pp. 130-136, 2009. (Text in Indonesian).

- [23] Lopez, J.M., Cata, N.J.G., Monterrosas, E.E.G., Martinez, R.N., Gonzalez, V.M.C., Flores, J.L.A. & Ortega, Y.R, *Kinetic Study by H. Nuclear Magnetic Resonance Spectroscopy for Biodiesel Production from Castor Oil*, Chemical Engineering Journal, **178**, pp. 391-397, 2011.
- [24] Darnoko, D. & Cheryan, M., *Kinetics of Palm Oil Transesterification in A Batch Reactor*, JAOCS, **77**, pp. 1263-1267, 2000.
- [25] Pojanalai, C. & Sookkumnerd, T., *Kinetics of Homogeneous Transesterification Reaction of Palm Oil and Methanol*, Journal School of Chemical Engineering, 2005.
- [26] Nouredini, H. & Zhu, D., *Kinetics of Transesterification of Soybean Oil*, J. Am. Oil Chem. Soc., **74**, pp. 1457-63, 1997.
- [27] Avramovic, J.M., Stamenkovic, O.S., Todorovic, Z.B., Lazic, M.L. & Veljkovic, V.B., *Empirical Modeling of Ultrasound- Assisted Base-Catalyzed Sunflower Oil Methanolysis Kinetics*, CI & CEQ, **18**, pp. 115-127, 2012.