

Research Article

Methyl Esters Selectivity of Transesterification Reaction with Homogenous Alkaline Catalyst to Produce Biodiesel in Batch, Plug Flow, and Continuous Stirred Tank Reactors

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Selectivity concept is essential in establishing the best operating conditions for attaining maximum production of the desired product. For complex reaction such as biodiesel fuel synthesis, kinetic studies of transesterification reaction have revealed the mechanism of the reaction and rate constants. The objectives of this research are to develop the kinetic parameters for determination of methyl esters and glycerol selectivity, evaluate the significance of the reverse reaction in transesterification reaction, and examine the influence of reaction characteristics (reaction temperature, methanol to oil molar ratio, and the amount of catalyst) on selectivity. For this study, published reaction rate constants of transesterification reaction were used to develop mathematical expressions for selectivities. In order to examine the base case and reversible transesterification, two calculation schemes (Case 1 and Case 2) were established. An enhanced selectivity was found in the base case of transesterification reaction. The selectivity was greatly improved at optimum reaction temperature (60°C), molar ratio (9:1), catalyst concentration (1.5 wt.%), and low free fatty acid feedstock. Further research might explore the application of selectivity for specifying reactor configurations.

1. Introduction

Biodiesel, a major renewable fuel to replace fossil fuel, is clean, environmental friendly, and derived from readily available sources such as vegetable oils and animal fats. In the biodiesel production, transesterification reaction is used to convert triglycerides to esters. It can be defined as alcoholysis of oil and fat with an alcohol to form esters and glycerol [1]. Various types of catalysts such as acidic and basic catalysts, which are either homogeneous or heterogeneous, as well as enzymes, can catalyse the reaction.

Transesterification of the oil often represented by triglycerides, T, with methanol, A, in the presence of a catalyst, usually alkaline, yields esters of fatty acids, E, and glycerol, G.

Monoglyceride, M, and diglyceride, D, are the intermediates. The overall reaction is written typically as

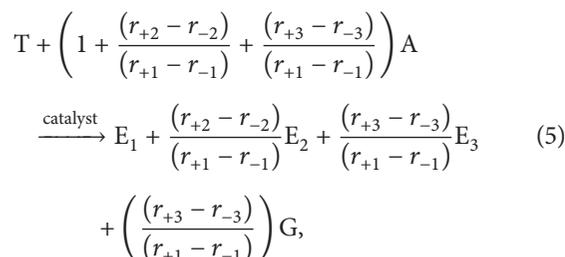


However, (1) is misleading because the rates of the forward reactions are not equal. The transesterification reaction is known to occur in three stages, where D produced from methanolysis in the first stage reaction becomes the reactant for the second stage methanolysis and the M produced from the second stage reaction becomes the reactant for the third stage reaction. The third stage reaction produces G as a byproduct. All three reactions produce different types of

methyl esters, collectively designated by E. The reactions are shown in (2) to (4), where k_{+1} - k_{-3} are rate constants:



A stoichiometric balance of the above three reversible reactions yield the correct form of the overall reaction, which is given below:



where r_{+1} is the rate of the forward reaction in reaction 1, r_{-1} is the rate of the backward reaction in reaction 1, r_{+2} is the rate of the forward reaction in reaction 2, r_{-2} is the rate of the backward reaction in reaction 2, r_{+3} is the rate of the forward reaction in reaction 3, and r_{-3} is the rate of the backward reaction in reaction 3. Equation (5) reduces to (1) if and only if all the net rates of reactions are equal or $(r_{+1} - r_{-1}) = (r_{+2} - r_{-2}) = (r_{+3} - r_{-3})$.

Kinetic studies of the chemical reactions in biodiesel production provide parameters that are used to predict the extent of the reactions at any time under any condition. Published kinetic data of biodiesel production are mostly dependent on the type of oil feed stock and the type of catalyst used as well as on the reaction conditions such as reaction temperature and catalyst concentration [2-4]. Previous evidence suggests that an important factor in the transesterification process is the degree of mixing between the alcohol, A, and the triglyceride, T, phases. As T and A phases are not miscible and they form two liquid layers upon their initial introduction into the reactor, mechanical mixing is typically applied to increase the contact between the reactants, resulting in an increase in mass transfer rate [5].

Many works have studied the kinetics of the transesterification reaction mechanism and determined its reaction rate constants [2-11]. Leevijit et al. [3] who conducted batch transesterification reaction and evaluated the reaction rate constants k_{+1} - k_{-3} found that the forward reactions are faster than the reverse reactions. The rate constants are presented as dataset 10 in Table 1. Similar kinetic study of palm oil methanolysis was conducted by Narv ez et al. [9] in order to investigate the effects of temperatures and concentration of NaOH catalyst. His results also suggest that the reaction kinetics for the forward reactions dominate over the reverse. From the result of their study on overall reaction of transesterification, the energy of activation for the forward reaction

(16.4 kcal gmol⁻¹) is greater than the energy of activation for the reverse reaction (13.6 kcal gmol⁻¹).

A kinetic study on the transesterification of *Jatropha curcas* oil by Jain and Sharma [4] using a two-step acid-base catalyst process in a batch system found that the esterification reaction was slower than the transesterification reaction because the process was assisted by the esterification reaction. Apart from that, recent studies reported the kinetics of transesterification reaction in the absence of a catalyst using soybean oil, palm oil, and rapeseeds oil [6-8, 10]. The rate constants, conversion, and yield of E showed an increasing trend with the reaction temperature, but the E content in the reaction product decreased as the reaction temperature was increased.

Reactor design uses information, knowledge, and experience from a variety of areas such as thermodynamics, chemical kinetics, fluid mechanics, heat transfer, mass transfer, and economics [12]. A considerable research has been devoted into the determination of the reaction rate constants of transesterification reactions of various types of edible and inedible vegetable oils. The published reaction rate constants at various conditions can be further used to determine the selectivity of E and G, providing opportunities for specifying reactor configurations using process system engineering tools such as the attainable region method. Selectivity can be described in a number of different ways, such as the production of the desirable component divided by the amount of limiting reactant converted or the production of desired component divided by the production of the undesired component [13]. The objectives of this present work are to develop the kinetic models of transesterification reaction and determine the selectivity of E and G using published reaction kinetic constants of the transesterification reactions and to investigate the effect of reaction conditions on them. In addition, this paper evaluates the significance of the reverse reactions in transesterification reaction on the E and G selectivities.

2. Methodology

2.1. Selectivity of Methyl Esters and Glycerol in Plug Flow Reactor. The amount of free fatty acids (FFAs) in oil feedstock could vary from 3 to 40% depending on types of oil used [14]. The saponification may occur in alkali-catalyzed transesterification reaction due to the reaction of acids with catalyst to produce soaps [15]. The transesterification reaction with the resulting soap formation tends to become viscous or forms a gel, and it is difficult to separate the glycerol from the mixture [16]. The saponification reaction is undesirable because it binds the catalyst into a form that does not contribute to accelerating the reaction [14]. For feedstock having a high free fatty acid content, pretreatment to the oil can be performed with methanol [17] or glycerol [18, 19] to decrease its acidity and thus reducing the potential for saponification to occur during the reaction. The presence of water in catalyzed transesterification reaction is also undesirable because water can consume the catalyst and reduce catalyst efficiency [20]. The saponification reaction can be taken into account while

TABLE 1: Reaction rate constants data for transesterification reaction in biodiesel production.

Sr. number	1	2	3	4	5	6	7	8	9	10
k_{+1} (L/mol.s)	0.0500	0.0920	0.1650	0.0060	0.0063	0.0021	0.0031	0.1672	0.2251	0.634
k_{-1} (L/mol.s)	0.1100	0.1750	0.2710	0.0016	0.0007	0.0035	0.0000	0.9373	0.4711	0
k_{+2} (L/mol/s)	0.2150	0.5440	1.3050	0.0442	0.0092	0.0072	0.0123	0.3553	0.1317	7.1040
k_{-2} (L/mol/s)	1.2280	2.4350	4.6410	0.0127	0.0023	0.0102	0.1224	0.2674	0.3917	4.9120
k_{+3} (L/mol/s)	0.2420	0.3270	0.4340	0.0050	0.0070	0.0231	0.0092	1.9608	0.1190	7.8600
k_{-3} (L/mol/s)	0.0070	0.0110	0.0170	0.0003	0.0027	0.0035	0.0000	0.0077	0.0181	0.1210
Temperature (°C)	50	60	70	65	65	30	30	60	60	60
Molar ratio M_R	6:1	6:1	6:1	9:1	3:1	9:1	9:1	6:1	6:1	6:1
Catalyst concentration (wt.%)	0.2	0.2	0.2	1.5	1.5	1.5	0.5	1.0	1.0	1.0
Oil feed stock	Soybean	Soybean	Soybean	Castor	Castor	Castor	Castor	Rapeseed	Waste Sunflower	Palm
Reference	[5]	[5]	[5]	[28]	[28]	[28]	[28]	[27]	[27]	[3]

developing the kinetic model of alkali-catalyzed transesterification reaction [21]. However, the kinetics parameter for alkali-catalyzed transesterification in the present work is developed by assuming that triglycerides were pretreated earlier. Also, this work represents a preliminary design of reactors for a biodiesel plant. Therefore, some important issues such as the existence of competing reaction along with the transesterification such as saponification reaction and the presence of water in the oil, the transport process, heterogeneity of the reaction, and loss of polarity of an alkaline catalyst were not considered.

The kinetic model was developed by first performing stoichiometric mole balance of each species in a plug flow reactor (PFR) using the reaction kinetics in (2) to (4). However, since a simpler mole balance of each species in a batch reactor produces the same solution as in Section 3, the batch reactor balance is used instead.

Mole balance of T is as follows:

$$-\frac{dC_T}{dt} = k_{+1}C_T C_A - k_{-1}C_D C_{E1}. \quad (6)$$

Mole balance of D is as follows:

$$\begin{aligned} -\frac{dC_D}{dt} &= -(k_{+1}C_T C_A - k_{-1}C_D C_{E1} - k_{+2}C_D C_A + k_{-2}C_M C_{E2}). \end{aligned} \quad (7)$$

Mole balance of M is as follows:

$$\begin{aligned} -\frac{dC_M}{dt} &= -(k_{+2}C_D C_A - k_{-2}C_M C_{E2} - k_{+3}C_M C_A + k_{-3}C_G C_{E3}). \end{aligned} \quad (8)$$

Mole balance of E1 is as follows:

$$-\frac{dC_{E1}}{dt} = -(k_{+1}C_T C_A - k_{-1}C_D C_{E1}). \quad (9)$$

Mole balance of E2 is as follows:

$$-\frac{dC_{E2}}{dt} = -(k_{+2}C_D C_A - k_{-2}C_M C_{E2}). \quad (10)$$

Mole balance of E3 is as follows:

$$-\frac{dC_{E3}}{dt} = -(k_{+3}C_M C_A - k_{-3}C_G C_{E3}). \quad (11)$$

Mole balance of A (methanol) is as follows:

$$\begin{aligned} -\frac{dC_A}{dt} &= k_{+1}C_T C_A - k_{-1}C_D C_{E1} + k_{+2}C_D C_A \\ &\quad - k_{-2}C_M C_{E2} + k_{+3}C_M C_A - k_{-3}C_G C_{E3}. \end{aligned} \quad (12)$$

Mole balance of G is as follows:

$$-\frac{dC_G}{dt} = -(k_{+3}C_M C_A - k_{-3}C_G C_{E3}). \quad (13)$$

Published reaction rate constants (k_{+1} - k_{x-3}) are listed in Table 1. In this work, methanol is assumed in excess while triglyceride is the limiting reactant.

Closed form simultaneous solution of ordinary differential equations (6) to (13) by analysis is possible if only the forward reactions are considered significant but the backward reactions are neglected. On the other hand, if both forward and reverse reactions are equally significant, closed form solution for (6) to (13) cannot be found and they have to be solved numerically using a 4th order Runge-Kutta algorithm, which is available in MATLAB. The solution generates the molar concentrations of all species, C_i , as functions of the design variables, that is, the conversion of the limiting reactant, X_T , and the molar ratio of the excess variable, M_R . Conversion is defined as

$$\text{conversion} = \frac{\text{loss of reactant}}{\text{feed of reactant}}. \quad (14)$$

For reactant T, the conversion is

$$X_T = \frac{N_{T0} - N_T}{N_{T0}} = 1 - \frac{N_{T0}/V}{N_{T0}/V} = 1 - \frac{C_T}{C_{T0}}. \quad (15)$$

Selectivity is defined as the ratio of the desired product to the amount of limiting reactant that has undergone chemical change [22]. That is,

$$\begin{aligned} \text{Selectivity} &= \frac{\text{amount of desired product}}{\text{amount of limiting reactant that has undergone chemical change}}. \end{aligned} \quad (16)$$

In this study, the total methyl ester is defined as

$$\begin{aligned} \text{Total methyl ester} &= \text{methyl ester 1} + \text{methyl ester 2} \\ &\quad + \text{methyl ester 3}. \end{aligned} \quad (17)$$

The selectivity of the total methyl ester, S_E , and of glycerol, S_G , defined as the moles of total methyl ester or glycerol produced, respectively, per moles of the limiting reactant T that have reacted is then formulated as functions of the conversion of triglyceride, X_T , as shown in

$$\begin{aligned} S_E &= \frac{C_{E1} + C_{E2} + C_{E3}}{C_{T0} X_T}, \\ S_G &= \frac{C_G}{C_{T0} X_T}. \end{aligned} \quad (18)$$

2.2. Selectivity of Methyl Esters and Glycerol in Continuous Stirred Tank Reactor. The kinetic model for continuous stirred tank reactor (CSTR) is much simpler. The stoichiometric mole balance of each species in a CSTR, using the reaction kinetics in (2) to (4), yields a set of nonlinear equations in (19) to (26).

Mole balance of T is as follows:

$$\begin{aligned} C_{T0} - C_T &= \frac{V}{F_T} (k_{+1}C_T C_A - k_{-1}C_D C_{E1}) \\ &= \tau (k_{+1}C_T C_A - k_{-1}C_D C_{E1}). \end{aligned} \quad (19)$$

Mole balance of D is as follows:

$$\begin{aligned} C_{D0} - C_D \\ = -\tau (k_{+1}C_T C_A - k_{-1}C_D C_{E1} - k_{+2}C_D C_A + k_{-2}C_M C_{E2}). \end{aligned} \quad (20)$$

Mole balance of M is as follows:

$$\begin{aligned} C_{M0} - C_M \\ = -\tau (k_{+2}C_D C_A - k_{-2}C_M C_{E2} - k_{+3}C_M C_A + k_{-3}C_G C_{E3}). \end{aligned} \quad (21)$$

Mole balance of E1 is as follows:

$$C_{E10} - C_{E1} = -\tau (k_{+1}C_T C_A - k_{-1}C_D C_{E1}). \quad (22)$$

Mole balance of E2 is as follows:

$$C_{E20} - C_{E2} = -\tau (k_{+2}C_D C_A - k_{-2}C_M C_{E2}). \quad (23)$$

Mole balance of E3 is as follows:

$$C_{E30} - C_{E3} = -\tau (k_{+3}C_M C_A - k_{-3}C_G C_{E3}). \quad (24)$$

Mole balance of A (methanol) is as follows:

$$\begin{aligned} C_{A0} - C_A \\ = \tau (k_{+1}C_T C_A - k_{-1}C_D C_{E1} + k_{+2}C_D C_A - k_{-2}C_M C_{E2} \\ + k_{+3}C_M C_A - k_{-3}C_G C_{E3}). \end{aligned} \quad (25)$$

Mole balance of G is as follows:

$$C_{G0} - C_G = -\tau (k_{+3}C_M C_A - k_{-3}C_G C_{E3}). \quad (26)$$

Closed form simultaneous solution of nonlinear equations (19) to (26) by analysis is not possible. They have to be solved numerically using a matrix inversion algorithm, which is available in MATLAB. The solution generates the molar concentrations of all species, C_i , as functions of the design variables, that is, the conversion of the limiting reactant, and the molar ratio of the excess variable, A.

3. Solution of the PFR and CSTR

3.1. Removal of Temporal Dependence. Equations (6) to (13) cannot be solved in their time dependent forms because of the single degree of freedom of the problem. In order to solve the equations simultaneously, the degree of freedom is reduced to zero by changing the independent variable from time to the conversion or concentration of the limiting reactant using the chain rule and the mole balance equation for T (6). Consider the following:

$$\frac{dC_i}{dC_T} = \left(\frac{dC_i}{dt} \right) \left(\frac{dt}{dC_T} \right). \quad (27)$$

Hence, (7) to (13) can be rewritten with concentration of T as their independent variable as follows:

$$\begin{aligned} \frac{dC_D}{dC_T} &= - \left(1 - \frac{\alpha_2 C_D C_A - \alpha_3 C_M C_{E2}}{C_T C_A - \alpha_1 C_D C_{E1}} \right), \\ \frac{dC_M}{dC_T} &= - \left(\frac{\alpha_2 C_D C_A - \alpha_3 C_M C_{E2} - \alpha_4 C_M C_A + \alpha_5 C_G C_{E3}}{C_T C_A - \alpha_1 C_D C_{E1}} \right), \\ \frac{dC_{E1}}{dC_T} &= -1, \\ \frac{dC_{E2}}{dC_T} &= - \left(\frac{\alpha_2 C_D C_A - \alpha_3 C_M C_{E2}}{C_T C_A - \alpha_1 C_D C_{E1}} \right), \\ \frac{dC_{E3}}{dC_T} &= - \left(\frac{\alpha_4 C_M C_A - \alpha_5 C_G C_{E3}}{C_T C_A - \alpha_1 C_D C_{E1}} \right), \\ \frac{dC_A}{dC_T} &= 1 + \frac{\alpha_2 C_D C_A - \alpha_3 C_M C_{E2} + \alpha_4 C_M C_A - \alpha_5 C_G C_{E3}}{C_T C_A - \alpha_1 C_D C_{E1}}, \\ \frac{dC_G}{dC_T} &= - \left(\frac{\alpha_4 C_M C_A - \alpha_5 C_G C_{E3}}{C_T C_A - \alpha_1 C_D C_{E1}} \right), \end{aligned} \quad (28)$$

where

$$\begin{aligned} \alpha_1 &= \frac{k_{-1}}{k_{+1}}, & \alpha_2 &= \frac{k_{+2}}{k_{+1}}, & \alpha_3 &= \frac{k_{-2}}{k_{+1}}, \\ \alpha_4 &= \frac{k_{+3}}{k_{+1}}, & \alpha_5 &= \frac{k_{-3}}{k_{+1}}. \end{aligned} \quad (29)$$

Similarly, (28) cannot be solved in their time dependent forms because of the single degree of freedom of the problem. In order to solve the equations simultaneously, the degree of freedom is reduced to zero by changing the independent variable from time to the conversion or concentration of the limiting reactant using algebraic manipulation and the mole balance equation for T (19). Consider the following:

$$\frac{C_{i0} - C_i}{C_{T0} - C_T} = - \left(\frac{C_{i0} - C_i}{\tau} \right) \left(\frac{\tau}{C_{T0} - C_T} \right). \quad (30)$$

Hence, (28) can be rewritten with concentration of T as their independent variable as follows:

$$\begin{aligned} \frac{C_{D0} - C_D}{C_{T0} - C_T} &= - \left(1 - \frac{\alpha_2 C_D C_A - \alpha_3 C_M C_{E2}}{C_T C_A - \alpha_1 C_D C_{E1}} \right), \\ \frac{C_{M0} - C_M}{C_{T0} - C_T} &= - \left(\frac{\alpha_2 C_D C_A - \alpha_3 C_M C_{E2} - \alpha_4 C_M C_A + \alpha_5 C_G C_{E3}}{C_T C_A - \alpha_1 C_D C_{E1}} \right), \\ \frac{C_{E10} - C_{E1}}{C_{T0} - C_T} &= -1, \end{aligned}$$

$$\begin{aligned} \frac{C_{E2o} - C_{E2}}{C_{To} - C_T} &= - \left(\frac{\alpha_2 C_D C_A - \alpha_3 C_M C_{E2}}{C_T C_A - \alpha_1 C_D C_{E1}} \right), \\ \frac{C_{E3o} - C_{E3}}{C_{To} - C_T} &= - \left(\frac{\alpha_4 C_M C_A - \alpha_5 C_G C_{E3}}{C_T C_A - \alpha_1 C_D C_{E1}} \right), \\ \frac{C_{Ao} - C_A}{C_{To} - C_T} &= 1 + \frac{\alpha_2 C_D C_A - \alpha_3 C_M C_{E2} + \alpha_4 C_M C_A - \alpha_5 C_G C_{E3}}{C_T C_A - \alpha_1 C_D C_{E1}}, \\ \frac{C_{Go} - C_G}{C_{To} - C_T} &= - \left(\frac{\alpha_4 C_M C_A - \alpha_5 C_G C_{E3}}{C_T C_A - \alpha_1 C_D C_{E1}} \right). \end{aligned} \quad (31)$$

Two main cases are considered: the base case where the reactions (2) to (4) are irreversible and the alternative case where the reactions are reversible.

3.2. Case 1: Base Case: Irreversible Reactions. In Case 1, the base case is considered by assuming (2) to (4) to be irreversible reactions. In other words, the forward reactions are so dominant that the reverse reaction can be neglected and the overall effect is that the reactions are irreversible. The results of the base case can then be compared with that of the alternative Case 2, where the reactions are all reversible, in order to verify the importance of the reverse reaction and its implication to the maximum attainable molar concentration of methyl ester. Since the reverse reactions are omitted, the value of α_1 , α_3 , and α_5 is zero. Hence, (28) for PFR can be rewritten as follows:

$$\frac{dC_D}{dC_T} = - \left(1 - \frac{\alpha_2 C_D}{C_T} \right), \quad (32)$$

$$\frac{dC_M}{dC_T} = - \left(\frac{\alpha_2 C_D - \alpha_4 C_M}{C_T} \right), \quad (33)$$

$$\frac{dC_{E1}}{dC_T} = -1, \quad (34)$$

$$\frac{dC_{E2}}{dC_T} = - \frac{\alpha_2 C_D}{C_T}, \quad (35)$$

$$\frac{dC_{E3}}{dC_T} = - \frac{\alpha_4 C_M}{C_T}, \quad (36)$$

$$\frac{dC_A}{dC_T} = 1 + \frac{\alpha_2 C_D + \alpha_4 C_M}{C_T}, \quad (37)$$

$$\frac{dC_G}{dC_T} = - \frac{\alpha_4 C_M}{C_T}. \quad (38)$$

The solution of the set of ordinary differential equations (32) can be found analytically by using the integrating factor method [23]. The concentrations of all the species generated

by the solution are then expressed in terms of the triglycerides conversion, X_T , as shown in

$$\begin{aligned} C_T &= C_{To} (1 - X_T), \\ C_D &= \frac{C_{To}}{\alpha_2 - 1} \left[\left(\frac{C_T}{C_{To}} \right) - \left(\frac{C_T}{C_{To}} \right)^{\alpha_2} \right] \\ &= \frac{C_{To}}{\alpha_2 - 1} \left[(1 - X_T) - (1 - X_T)^{\alpha_2} \right], \\ C_M &= C_{To} \left[\frac{\alpha_2}{1 - \alpha_2} \left[\frac{(1 - X_T)}{1 - \alpha_4} - \frac{(1 - X_T)^{\alpha_2}}{\alpha_2 - \alpha_4} \right] \right. \\ &\quad \left. + \frac{\alpha_2 (1 - X_T)^{\alpha_4}}{(1 - \alpha_4)(\alpha_2 - \alpha_4)} \right], \\ C_{E1} &= C_{To} \left(1 - \left(\frac{C_T}{C_{To}} \right) \right) = C_{To} (1 - (1 - X_T)) = C_{To} X_T, \\ C_{E2} &= C_{To} \left\{ 1 - \frac{\alpha_2}{\alpha_2 - 1} \left[(1 - X_T) - \frac{(1 - X_T)^{\alpha_2}}{\alpha_2} \right] \right\}, \\ C_{E3} &= \alpha_4 C_{To} \left[\frac{\alpha_2}{1 - \alpha_2} \left[\frac{X_T}{1 - \alpha_4} - \frac{[1 - (1 - X_T)^{\alpha_2}]}{(\alpha_2 - \alpha_4)\alpha_2} \right] \right. \\ &\quad \left. + \frac{\alpha_2 [1 - (1 - X_T)^{\alpha_4}]}{(1 - \alpha_4)(\alpha_2 - \alpha_4)\alpha_4} \right], \\ C_A &= C_{To} \left\{ M_R + \frac{\alpha_2}{(1 - \alpha_2)} \right. \\ &\quad \times \left[\left(\frac{(1 - \alpha_2)}{\alpha_2} + \frac{2\alpha_4 - 1}{(1 - \alpha_4)} \right) X_T \right. \\ &\quad \left. - \left(\frac{2\alpha_4 - \alpha_2}{\alpha_2(\alpha_2 - \alpha_4)} \right) [1 - (1 - X_T)^{\alpha_2}] \right. \\ &\quad \left. - \frac{(1 - \alpha_2)}{(1 - \alpha_4)(\alpha_2 - \alpha_4)} \right. \\ &\quad \left. \times [1 - (1 - X_T)^{\alpha_4}] \right] \left. \right\}, \\ C_G &= \alpha_4 C_{To} \left[\frac{\alpha_2}{1 - \alpha_2} \left[\frac{X_T}{1 - \alpha_4} - \frac{[1 - (1 - X_T)^{\alpha_2}]}{(\alpha_2 - \alpha_4)\alpha_2} \right] \right. \\ &\quad \left. + \frac{\alpha_2 [1 - (1 - X_T)^{\alpha_4}]}{(1 - \alpha_4)(\alpha_2 - \alpha_4)\alpha_4} \right]. \end{aligned} \quad (39)$$

For the CSTR, (31) can be manipulated algebraically and rewritten with conversion of T as their independent variable as follows:

$$C_D = \frac{C_{To} X_T (1 - X_T)}{(1 - (1 - \alpha_2) X_T)}, \quad (40)$$

$$C_M = \frac{\alpha_2 C_{T_0} X_T^2 (1 - X_T)}{(1 - (1 - \alpha_4) X_T) (1 - (1 - \alpha_2) X_T)}, \quad (41)$$

$$C_{E1} = C_{T_0} X_T, \quad (42)$$

$$C_{E2} = \frac{\alpha_2 C_{T_0} X_T^2}{(1 - (1 - \alpha_2) X_T)}, \quad (43)$$

$$C_{E3} = \frac{\alpha_2 \alpha_4 C_{T_0} X_T^3}{(1 - (1 - \alpha_4) X_T) (1 - (1 - \alpha_2) X_T)}, \quad (44)$$

$$C_A = C_{T_0} \left(M_R - 1 + \frac{\alpha_2 C_{T_0} X_T^2}{(1 - (1 - \alpha_2) X_T)} + \frac{\alpha_2 \alpha_4 C_{T_0} X_T^3}{(1 - (1 - \alpha_4) X_T) (1 - (1 - \alpha_2) X_T)} \right), \quad (45)$$

$$C_G = \frac{\alpha_2 \alpha_4 C_{T_0} X_T^3}{(1 - (1 - \alpha_4) X_T) (1 - (1 - \alpha_2) X_T)}. \quad (46)$$

3.3. *Case 2: Alternative Case: Reversible Reactions.* In Case 2, an alternative case was considered by assuming that the reactions in (2) to (4) are reversible. Together with the base case, where the reactions are irreversible, it can be used to discover the significance of the reverse and forward reactions.

Since the values of all α_i 's in (28) for the PFR and (31) for the CSTR are not zero, no closed form solution to them can be found because they are too complex for analytical solution. The solution of both sets of equations can be achieved by numerical methods using a computer simulation software. Equations (28) for the PFR are solved by using the ordinary differential equation 45, (ODE 45) in MATLAB. Concentration of each species is obtained using Rungge-Kutta numerical integration algorithm. On the other hand, (31) for the CSTR are solved by using the simultaneous nonlinear equations solver in MATLAB. Concentration of each species is obtained using the multivariable Newton-Raphson algorithm.

3.4. *Selectivity of Methyl Esters and Glycerol for Case 1 and Case 2.* The net concentration of methyl esters is the sum of concentration of ester 1, ester 2, and ester 3. In Case 1, the net concentration of methyl esters in the PFR is given by

$$\begin{aligned} & C_{E1} + C_{E2} + C_{E3} \\ &= C_{T_0} \left\{ 1 + X_T - \frac{\alpha_2}{\alpha_2 - 1} \left[(1 - X_T) - \frac{(1 - X_T)^{\alpha_2}}{\alpha_2} \right] \right. \\ & \quad + \alpha_4 \left[\frac{\alpha_2}{1 - \alpha_2} \left[\frac{X_T}{1 - \alpha_4} - \frac{[1 - (1 - X_T)^{\alpha_2}]}{(\alpha_2 - \alpha_4) \alpha_2} \right] \right. \\ & \quad \left. \left. + \frac{\alpha_2 [1 - (1 - X_T)^{\alpha_4}]}{(1 - \alpha_4) (\alpha_2 - \alpha_4) \alpha_4} \right] \right\}. \end{aligned} \quad (47)$$

Similarly, the net concentration of methyl esters in the CSTR for Case 1 is given by

$$\begin{aligned} & C_{E1} + C_{E2} + C_{E3} \\ &= C_{E1_0} + C_{E2_0} + C_{E3_0} \\ & \quad + \left[C_{T_0} X_T + \frac{\alpha_2 C_{T_0} X_T^2}{(1 - (1 - \alpha_2) X_T)} \right. \\ & \quad \left. + \frac{\alpha_2 \alpha_4 C_{T_0} X_T^3}{(1 - (1 - \alpha_4) X_T) (1 - (1 - \alpha_2) X_T)} \right]. \end{aligned} \quad (48)$$

The selectivity of methyl esters in Case 1 for PFR is given by

$$\begin{aligned} S_E &= \left\{ \frac{X_T + 1}{X_T} - \frac{\alpha_2}{\alpha_2 - 1} \left[\frac{(1 - X_T)}{X_T} - \frac{(1 - X_T)^{\alpha_2}}{\alpha_2 X_T} \right] \right. \\ & \quad + \alpha_4 \left[\frac{\alpha_2}{1 - \alpha_2} \left[\frac{1}{1 - \alpha_4} - \frac{[1 - (1 - X_T)^{\alpha_2}]}{(\alpha_2 - \alpha_4) \alpha_2 X_T} \right] \right. \\ & \quad \left. \left. + \frac{\alpha_2 [1 - (1 - X_T)^{\alpha_4}]}{(1 - \alpha_4) (\alpha_2 - \alpha_4) \alpha_4 X_T} \right] \right\}. \end{aligned} \quad (49)$$

The selectivity of glycerol in Case 1 for PFR is given by

$$\begin{aligned} S_G &= \frac{\alpha_4}{X_T} \left[\frac{\alpha_2}{1 - \alpha_2} \left[\frac{X_T}{1 - \alpha_4} - \frac{[1 - (1 - X_T)^{\alpha_2}]}{(\alpha_2 - \alpha_4) \alpha_2} \right] \right. \\ & \quad \left. + \frac{\alpha_2 [1 - (1 - X_T)^{\alpha_4}]}{(1 - \alpha_4) (\alpha_2 - \alpha_4) \alpha_4} \right]. \end{aligned} \quad (50)$$

On the other hand, the selectivity of methyl esters in Case 1 for CSTR is given by

$$\begin{aligned} S_E &= \left[1 + \frac{\alpha_2 X_T}{(1 - (1 - \alpha_2) X_T)} \right. \\ & \quad \left. + \frac{\alpha_2 \alpha_4 X_T^2}{(1 - (1 - \alpha_4) X_T) (1 - (1 - \alpha_2) X_T)} \right]. \end{aligned} \quad (51)$$

The selectivity of glycerol in Case 1 for CSTR is given by

$$S_G = \frac{\alpha_2 \alpha_4 X_T^2}{(1 - (1 - \alpha_4) X_T) (1 - (1 - \alpha_2) X_T)}. \quad (52)$$

For Case 2, there is no closed form expression for selectivity of methyl esters and glycerol. The selectivities of methyl esters and glycerol have to be calculated using (18) from the concentration of the species generated by the numerical solution.

4. Results and Discussion

4.1. *Comparison of Selectivities for Cases 1 and 2.* This study has shown the development of kinetic parameters for determining methyl esters and glycerol selectivity in a biodiesel

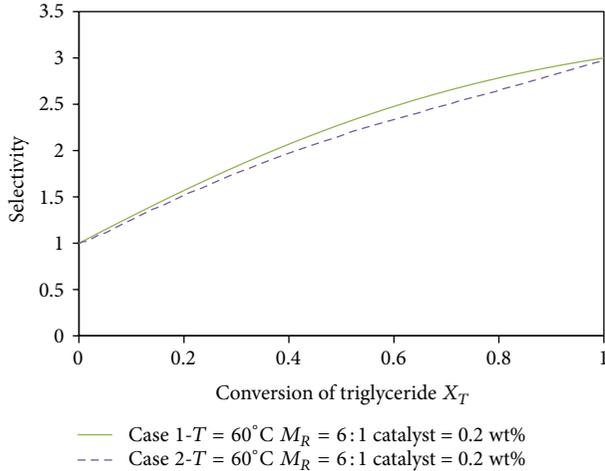


FIGURE 1: Selectivity plots of Cases 1 and 2 at reaction temperature 60°C, molar ratio 6 : 1, and catalyst concentration 0.2 wt.%.

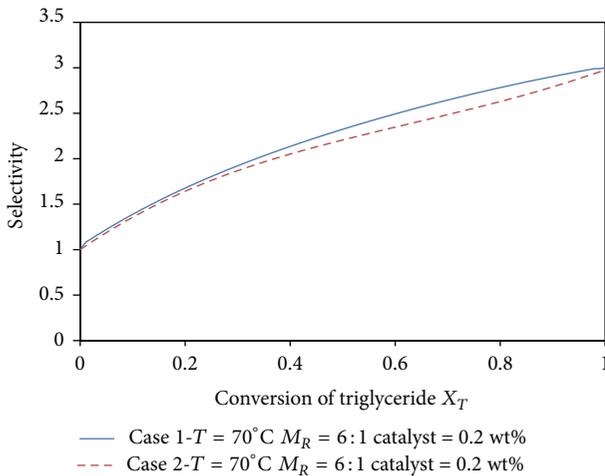


FIGURE 2: Selectivity plots of Cases 1 and 2 at reaction temperature 70°C, molar ratio 6 : 1, and catalyst concentration 0.2 wt.%.

transesterification reaction; it has also established several mathematical equations for the same. Furthermore, a particularly important parameter for designing a reactor, that is, product selectivity, was determined for each case and condition. For comparing the base case and an alternative case, datasets 2 and 3 were evaluated using each calculation schemes. The difference in the selectivity between Case 1 and Case 2, which were investigated under the same conditions, is very significant and is attributed to the reversibility factor of the reaction, as illustrated in Figures 1 and 2. The results of the base case show that when all the reactions are irreversible, it implies that the maximum attainable molar concentration and selectivity of methyl ester have been reached. This verifies the significant role of the forward reactions in (2)–(4).

For a simple reversible reaction, we can see the effects of thermodynamic parameter like temperature on the reversibility of the reaction whereas the reversibility of a reaction is controlled by reaction equilibrium constant.

TABLE 2: Selectivity at 0.7–0.9 triglycerides conversion for datasets (1–3) and (6–7).

Conversion, X_T	Dataset	Methyl esters selectivity	
		Case 1	Case 2
0.7	1	2.610	2.526
	2	2.643	2.511
	3	2.630	2.470
	6	2.610	2.613
	7	2.493	2.313
0.8	1	2.766	2.675
	2	2.784	2.666
	3	2.769	2.629
	6	2.764	2.766
	7	2.682	2.480
0.9	1	2.895	2.832
	2	2.903	2.816
	3	2.892	2.788
	6	2.893	2.879
	7	2.852	2.655

The reaction equilibrium constant, K , is defined as the forward rate constant divided by the reverse rate constant and affected by temperature [12]. This transesterification reaction is a complex reaction which consists of three reversible and consecutive reactions. Therefore, for simplification and preliminary design purpose, selectivity is effectively used to determine the effect of temperature and role of catalyst on the reversibility. Figures 1 and 2 show significant changes of the selectivity plots for conversion of triglycerides from 0.7 to 0.9 and the plots finally reach the equilibrium at the end of the reaction. In order to access the role of temperature and amount of catalyst on the reversibility of transesterification reaction, Table 2 was constructed by observing the methyl esters selectivity for conversion of triglycerides from 0.7 to 0.9. It presents the difference in selectivity for Case 1 and Case 2. Datasets (1–3) are used to determine the effects of different temperatures on the reversibility of the transesterification reaction which represent a temperature of 50, 60, and 70, respectively. Conversion of triglyceride at 0.9 is selected for analysis. From this data, we can see that the forward reaction alone is able to provide better selectivity than reverse reaction at any temperature. Datasets (6–7) are used to analyze the role catalyst on the reversibility of transesterification reaction whereas datasets 6 and 7 represent the amount of catalyst of 1.5% and 0.5%, respectively. A significant role of the forward reaction once again was determined at a higher catalyst concentration. The results obtained also indicate that a higher catalyst concentration controls the forward reactions and gives preferably product selectivity.

According to Narváez et al. [9] and Nouredini and Zhu [5], the forward reactions in a transesterification reaction are the most important reactions. However, Diasakou et al. [7] claimed that the reverse reactions during a transesterification reaction do not influence the forward reactions. In this study, a lower concentration of methyl ester was found for Case 2,

TABLE 3: Activation energy.

Reaction	Activation energy (cal/mol)
T → D	13145
D → T	9932
D → M	19860
M → D	14639
M → G	6421
G → M	9588

which affects the selectivity and methyl ester conversion, which is likely due to the reverse nature of the reaction [4]. This result suggests that for establishing the optimal chemical process for biodiesel fuel production, it can be assumed that when irreversible reactions are employed, better selectivity can be obtained because of the absence of reverse reactions.

4.2. Effects of Reaction Characteristics on Selectivity. The reactor design stage for a biodiesel plant utilizes methyl ester selectivity for the material balances and stream costs. Attaining the appropriate operating conditions through product selectivity can eliminate material and energy recycling, thus reducing costs. The effects of the reaction temperature, molar ratio of methanol to oil, and the catalyst concentration on the selectivity of methyl esters and glycerol are analyzed for both Case 1 and Case 2 in the following subsections.

4.2.1. Effect of Reaction Temperature on Selectivity. An investigation on the effect of temperature on methyl ester selectivity was conducted using datasets (1-3), where the molar ratio of alcohol to oil and the catalyst concentration are fixed. The Arrhenius equation was used for this investigation:

$$k = k_0 \exp\left(-\frac{E}{RT}\right). \quad (53)$$

According to (53), the reaction rate, k , is an integral part of the selectivity expressions. It depends on the energy of activation (E) obtained from the Arrhenius equation [22]. For reactions at different temperatures, fixed molar ratios, and catalyst concentrations, the activation energy is constant. In this study, the kinetic data used to analyze the temperature effect were adapted from Nouredini and Zhu [5]. Because the data published in their research utilize the average reaction rate constants at 50°C and constant activation energy, (53) can be manipulated to obtain the other reaction rate constants (at 60°C and 70°C) listed in Table 1. The results of the activation energy investigated in their study are shown in Table 3.

Figures 3 and 4 show the effects of the reaction temperature on the selectivity of methyl esters and glycerol for Cases 1 and 2, respectively. The reaction temperature had a small but substantial effect on the selectivity. The figures show that the selectivity of methyl esters is high at a high temperature in the early conversion of T. However, in both figures, the selectivities of E for both Cases 1 and 2 at 70°C were found to decrease toward the completion of the reaction. As the boiling point of methanol is 64.7°C, an additional 5°C has

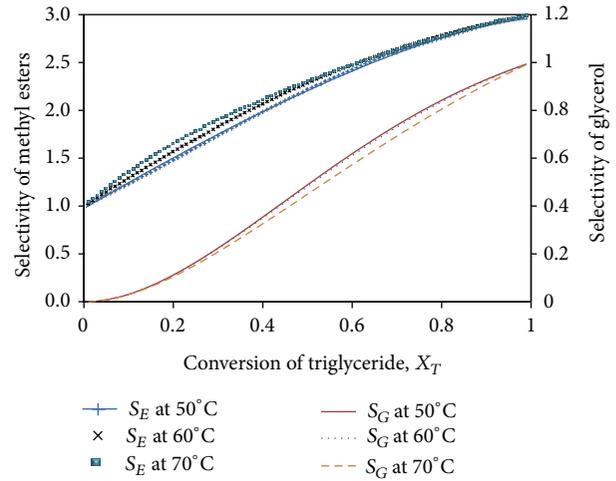


FIGURE 3: Selectivity of methyl ester at various temperatures and fixed molar ratio and catalyst concentration for Case 1.

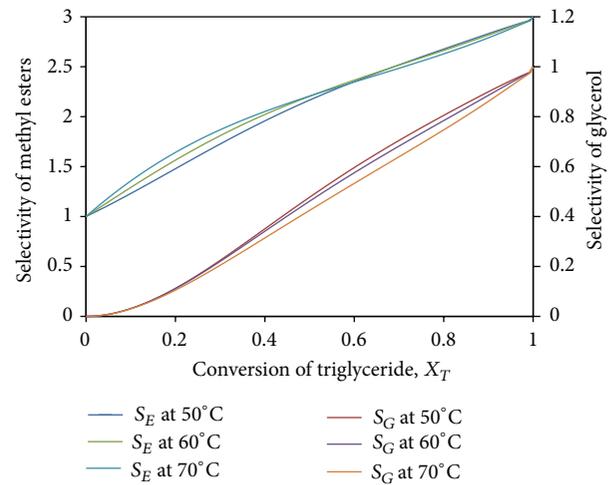


FIGURE 4: Selectivity of methyl ester at various temperatures and fixed molar ratio and catalyst concentration for Case 2.

the effect of lowering the product concentration and affecting the selectivity of E at the equilibrium. This temperature effect changes the slope of selectivity from a concave to a convex shape, which is also related with the reaction rate constant at different temperatures.

According to Darnoko and Cheryan [2], the transesterification reaction rates were increased at 65°C as compared with those at 50°C. The results of their research also showed an enhanced methyl ester yield at 65°C compared with that at 50°C, which was because of the higher viscosity of oil at 50°C. In addition, 55°C is a stable temperature that can maintain the oil liquidity. This result indicates that an optimum temperature promotes the formation of methyl esters and, thus, contributes to a higher selectivity of biodiesel products. It can also be suggested that the reaction rate constant, k , which is greatly dependent on the temperature and selectivity of E, is greatly improved at the optimum temperature.

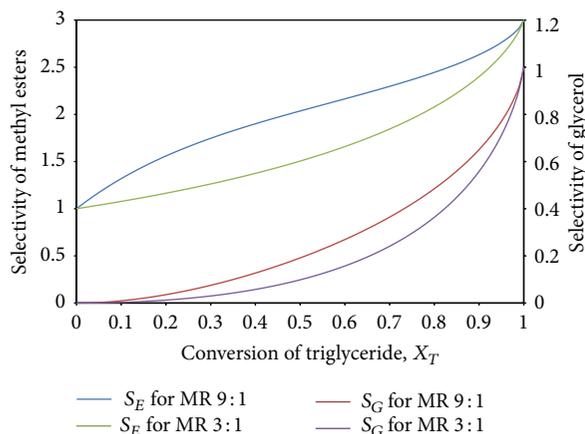


FIGURE 5: Selectivity of methyl ester at various molar ratios, constant temperature of 65°C, and catalyst concentration of 1.5 wt.% for Case 1.

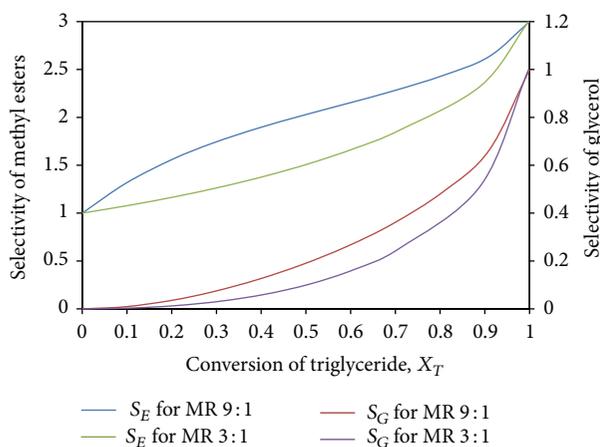


FIGURE 6: Selectivity of methyl ester at various molar ratios, constant temperature of 65°C, and catalyst concentration of 1.5 wt.% for Case 2.

The findings confirm that methyl ester selectivity effects can be realistically obtained at the optimum temperature, which is 60°C in this study. As the reactor optimization requires the relationship between the conversion and selectivity in both cases (Case 1 and Case 2), the selectivity within the studied temperature indicates that the biodiesel reactor may work more efficiently in converting T to E at 60°C.

4.2.2. Effect of Molar Ratio of Methanol to Oil on Selectivity.

An investigation into the effects of the methanol-to-oil molar ratio involves datasets 4 and 5. Selectivity plots of methyl esters and glycerol are shown in Figures 5 and 6. For Cases 1 and 2, the selectivity of methyl esters and glycerol was relatively affected by the molar ratio of methanol to oil. It can be seen from the figures that the higher molar ratio of methanol to oil encourages the formation of transesterification reaction products, thus contributing to a higher selectivity.

The most striking result to emerge from the figures is the change in the shape of the selectivity plot from concave

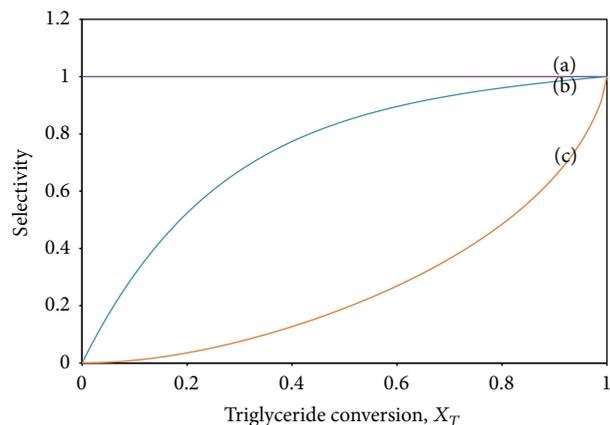


FIGURE 7: Selectivity plots: (a) methyl ester 1, (b) methyl ester 2, and (c) methyl ester 3 for dataset 4.

to convex for a molar ratio of 9:1. An increasing selectivity of methyl ester can be found in an early conversion of triglyceride, but toward equilibrium, the selectivity is found to slightly decrease. A possible explanation for this might be that the methyl ester concentration has both quadratic as well as cubic effects that can be explained by (42)–(44) and Figure 7.

According to (42), the selectivity of methyl ester 1 is constant at 1. Equation (43) is a quadratic equation, which gives a parabolic shape to the plot of methyl ester 2. Equation (44) clearly illustrates the selectivity of methyl ester 3 when the equation is a cubic one. In more detail, the power of two is more dominant at an X_T of less than 0.3, which means that the formation of E2 is more active under this condition. However, we can see an active formation of E3 at an X_T of 0.5–1 when the power of three is dominant. At the same time, E1 is formed linearly with a triglyceride conversion. The stepwise transesterification reaction in (2)–(4) shows that each E is formed consecutively. This means that to achieve the maximum yield, the maximum selectivity at the maximum T conversion is necessary, and each E must be formed during the process. Therefore, it can be assumed that the selectivity of methyl ester is more greatly affected by the quadratic and cubic functions at a higher molar ratio of methanol to oil than at a lower one.

In addition, Freedman et al. [11] reported that the best methyl ester conversion is achieved at a molar ratio of 6:1 with alkaline catalyst and that higher molar ratios do not increase the productivity but do increase the cost of alcohol recovery. At a high molar excess of methanol, a pseudo-first-order reaction appeared more likely than a second-order reaction. However, high molar ratio of methanol is used for noncatalytic and supercritical methanol reaction [6, 11, 20, 24]. Narv ez et al. [9] stated that when an excess amount of methanol is used, it can positively affect the reversible characteristic of the reaction and the displacement of the reaction toward the product. As a consequence, excess methanol does not necessarily contribute to an increase in the concentration of methyl ester and glycerol.

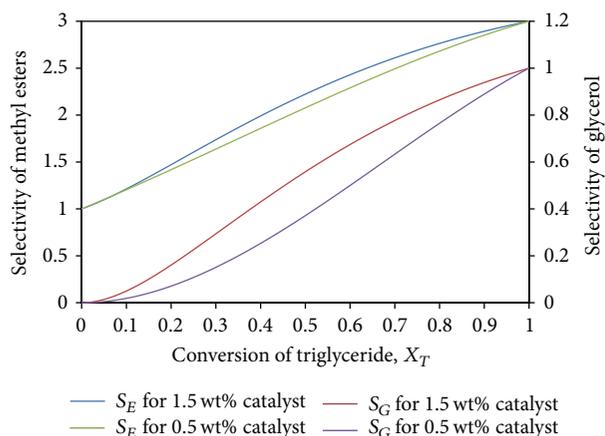


FIGURE 8: Selectivity of methyl ester at various catalyst concentrations, constant temperature of 30°C, and molar ratio 9 : 1 for Case 1.

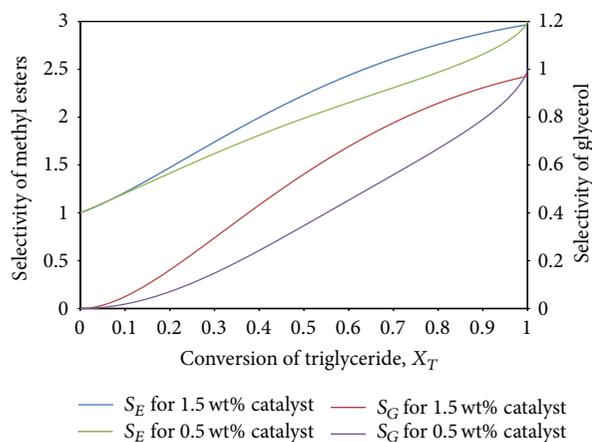


FIGURE 9: Selectivity of methyl ester at various catalyst concentrations, constant temperature of 30°C, and molar ratio 9 : 1 for Case 2.

4.2.3. *Effect of Catalyst Concentration on Selectivity.* Apart from the temperature and molar ratio, the parameters that affect the selectivity are the same as those influencing the reaction rates, namely, the catalyst. The effects of the catalyst concentration are studied through datasets 6 and 7, and the selectivity plots can be seen in Figures 8 and 9. When analyzing the figures, it can be seen that the selectivity of both products is higher at a higher catalyst concentration.

Toward the equilibrium of the reaction, the selectivity was observed to increase at a higher catalyst concentration, thus contributing to an increased amount of methyl ester formation. Vicente et al. [25] stated that the largest methyl ester conversions are obtained when a large catalyst concentration is employed (1.3%) at a mild temperature (20–50°C). This agrees with the resulting selectivity curves plotted, which indicates that the catalyst concentration has a positive effect on the selectivity of methyl esters and glycerol. However, a greater application of an alkali catalyst can lead to the production of large amounts of soap, and extra cost is required to remove the catalyst from the reaction system. Srivastava and Prasad [26] have stated that a catalyst

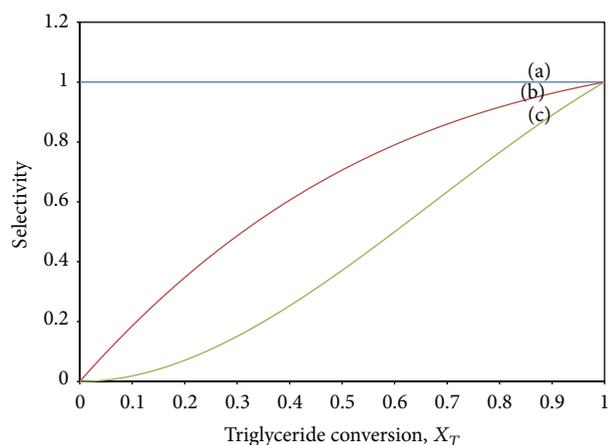


FIGURE 10: Selectivity plots: (a) methyl ester 1, (b) methyl ester 2, and (c) methyl ester 3 for dataset 6.

concentration of 0.5–1% can yield up to a 99% methyl ester conversion.

In Figures 8 and 9, there is a clear increasing trend of the selectivity of methyl ester for a 1.5 wt.% catalyst concentration during the early conversion of the reactant, which decreases at the end of the reaction. The same transition trend has been found when analyzing the influence of the molar ratio on methyl ester selectivity. A further detailed analysis showed that the quadratic and cubic effects are more significant at a higher catalyst concentration than at a lower catalyst concentration. As shown in Figure 10, the selectivity of E2 has a quadratic plot, whereas the selectivity of E3 has a parabolic shape. Referring to (42)–(44), we can see that E1 is linearly formed with a T conversion. E2 is produced more at a T conversion of lower than 0.35, where we can see that the power of two in (43) is more dominant at this stage. At a T conversion of over 0.5, the effect of the power of three in (44) is dominant, causing a higher formation of E3. Because the transesterification reaction is a reversible and consecutive equation, the formation of three Es is important to achieve a better selectivity. With an optimum amount of catalyst, the reactor becomes more efficient in converting the reactant into the products.

4.3. *Comparison of Methyl Ester Selectivities from Different Oil Feedstocks.* To compare the selectivities of methyl esters and glycerol from different feedstocks, datasets (8–10) were used. Figure 11 presents the selectivity of methyl esters derived from rapeseed oil, waste sunflower oil, and palm oil for Case 1 and Case 2. As can be seen from the graph, the methyl esters and glycerol were more likely to form if palm oil is used as the feedstock compared to the other two oil feedstocks. The present finding also suggests that the selectivity of methyl ester was much lower when using low cost feedstock such as waste sunflower oil. Waste oil contains large amounts of free fatty acids (FFAs) (about 20%) which affect the yield of fuel from that process. The amount of FFAs in palm oil is 0.64% [3], but for rapeseed oil, the author used fresh oil [27] which is estimated less than 1%.

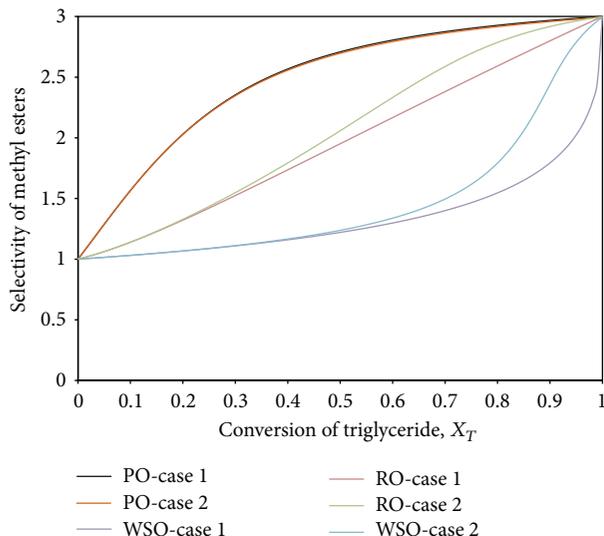


FIGURE 11: Selectivity plots of methyl ester from various feedstock for Cases 1 and 2.

As discussed before, these free fatty acids will react with alkali catalysts to produce soaps that will inhibit the transesterification reaction. Soaps will allow emulsification that causes the phase separation of methyl ester and glycerol to be less sharp. It produces water that can hydrolyze the triglycerides and contribute to the formation of more soap [14]. The effect of reversibility of transesterification can be seen significantly when analysing the selectivity of methyl ester derived from palm oil. In Figure 11, methyl ester derived from palm oil shows a higher selectivity plot for base case. This finding suggests that forward reaction dominates the reaction and contributes to a better selectivity when low FFAs feedstock is used in biodiesel production. As there are many low cost feedstocks available for biodiesel production, a pretreatment to these feedstocks can be carried out in order to ensure the value of FFAs is within the allowable range.

5. Conclusions

This paper has presented a comprehensive kinetic modeling of a transesterification reaction for biodiesel with homogeneous alkaline catalyst. The purpose of the study was to develop the kinetic models of transesterification reaction, determine the selectivity of methyl ester and glycerol, and evaluate the significance of the reverse reactions in the transesterification reaction. This study has shown that a process model solution was found for two types of common biodiesel reactors. The concentration of each species during transesterification was found, leading to a selectivity determination during the biodiesel production. In addition, the reversible and irreversible effects of a transesterification reaction were discovered. The forward reaction is more dominant than the reverse reaction, and the maximum selectivity can be found if a base case of transesterification reaction is assumed to have occurred in the biodiesel reactor system. For the various reaction characteristics under investigation, the selectivities

are influenced by the temperature, molar ratio of methanol to oil, catalyst concentration, and type of oil used as the feedstock. Furthermore, an analysis of the selectivity plots indicates an enhanced effect of the reaction characteristics on the selectivity. This research has shown that the selectivity of methyl ester is maximized at 60°C, a 9:1 molar ratio of methanol to oil, and a catalyst concentration of 1.5%. This investigation into the effects of the molar ratio of methanol to oil and the catalyst concentration on the selectivity can be made more interesting if several more curves are plotted at a molar ratio of methanol to oil between 3:1 to 9:1 and a catalyst concentration between 0.5 and 1.5%. However, a limitation of this research remains in the availability of the reaction rate constants under various reaction conditions. In addition, a comparison should be made through mutual reaction conditions. The findings from this study will enhance the concept of selectivity and its applications in the evaluation of complex transesterification reactions when the goal is to attain the maximum production of methyl esters and glycerol. It is recommended that further research is undertaken in exploring the selectivity data for specifying the reactor configurations and may be used in the synthesis of reactor network for biodiesel production.

Nomenclature

k_{+1}, k_{-1}, k_{+2}	Reaction constant
k_{-2}, k_{+3}, k_{-3}	
C_T, C_D, C_M, C_G	Molar concentration of triglyceride,
C_{E1}, C_{E2}, C_{E3}	diglyceride, monoglyceride, glycerol,
C_A, C_E	ester 1, ester 2, ester 3, methanol, and methyl ester
X_T	Conversion of triglyceride
M_R	Molar ratio
C_{T0}	Initial molar concentration of triglyceride
S_E, S_G	Selectivity of methyl ester, glycerol
α	Reaction rate constant factor
wt. %	Weight percent
T	Triglyceride
D	Diglyceride
M	Monoglyceride
A	Methanol
G	Glycerol
E	Methyl ester
E1	Methyl ester 1
E2	Methyl ester 2
E3	Methyl ester 3
PFR	Plug flow reactor
CSTR	Continuous stirred tank reactor
N_{T0}	Initial amount of triglyceride at $t = 0$
N_T	The amount of triglyceride present at time, t
V	Volume
PO	Palm oil
RO	Rapeseed oil
WSO	Waste sunflower oil
NaOH	Sodium hydroxide.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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