DETERMINATION OF KINETIC PARAMETERS FOR THE REACTIONS INVOLVED IN BIODIESEL PRODUCTION VIA OPTIMIZATION APPROACH

by

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15053

Dissertation submitted in partial fulfilment
of the requirement for the

Bachelor of Engineering (Hons) (Chemical Engineering)

JANUARY 2015

Universiti Teknologi PETRONAS,

32610 Bandar Seri Iskandar,

Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

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BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

_____

(DR. ABRAR INAYAT)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK

JANUARY 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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KUGAANESAAN A/L MURTHY

ABSTRACT

The search for alternative source of energy has become important as many believe that fossil fuel is not going to last for long and it is time to change to renewable source of energy. Biodiesel, produced from vegetable oil and alcohol commonly through the process of transesterification has become the most reliable biofuel that is widely used in the world today (Okullo, Temu and Ntalikwa, 2010). The reaction kinetic model for the biodiesel has been developed in the past years with limitation of specific reactions for each model. There is need to study and obtain generalized reaction kinetic model that can be used for all the reactions involved in the biodiesel production. This study is about developing general reaction kinetic model for all the reactions involved in the biodiesel production using simulation software called MATLAB by the means of OPTIMIZATION TOOLBOX to obtain the optimum kinetic data which will be compared to the experimental data for accuracy. The optimized value of activation energy and the pre-exponential factor values are general values that can be used at any temperature to calculate the concentration of the product yield. This will enable to use the optimized values to calculate the rate constants at any temperature. A general kinetic model and parametric study of the kinetics of the reaction involved in the synthesis of biodiesel developed in this project through the use of MATLAB OPTIMIZATION TOOLBOX have shown promising results whereby it has the potential to yield the similar set of results as compared to experimental results. Despite the increase in concentration of glycerol and the rate constants, the methyl esters yielded at any temperature are similar to that of experimental results with minimal error below 5 %. The objective of this project is achieved.

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CHAPTER 1: INTRODUCTION

1.1 Background

Fossil fuel is organic or covalently bonded carbon containing substances in the form of solid, liquid or gas that been produced by plants and animal remains which have undergone chemical and physical transformation over hundreds of years. Fossil fuels have become the world's primary source of energy. It is estimated about 85% of energy production was contributed by fossil fuel in 2010 (Dewallef, 2014). Fossil fuel is considered as non-renewable energy as the process of production of fossil fuel takes over geological time periods.

Table 1: World production and cumulative reserves of fossil fuels (1944-2010)

	1944	1945-1960	1961-1970	1971-1980	1981-1993	Total 1944-1993	Year 2010
OPEC							
Cummulative production	-	26	55	103	100	284	34.3
	-	219	251	128	434	1032	0
Gross reserve	22	215	412	436	770	770	1068
NON-OPEC							
Cummulative production	-	51	64	102	407	407	34.3
	-	98	187	114	607	607	6.1
Gross reserve	29	76	200	212	229	229	188.7
TOTAL WORLD							
Cummulative production	-	77	119	205	690	690	82.1
	-	318	439	242	1639	1639	7.7
Gross reserve	51	291	611	648	999	999	1382

Table 1 shows that supply of fossil fuel is limited. As population growth and development in industry increases, the world energy demand will eventually increase over time. This means the current fossil fuel supply will not be able to meet the energy demand in the future (The Colorado River Commission of Nevada, 2002)

Therefore, alternative source of energy have to be developed in order to curb the depletion of fossil fuel. Alternative source of energy simply means fuels from renewable sources such biomass. Biofuels are one of several alternative renewable energy source that being developed nowadays. Bio-fuels mainly derived from bio-mass which consist of organic waste such as agricultural waste, biological waste and forest waste (Zhang W. 2009).

In Malaysia, there are different types of biomass present in Malaysia which includes empty fruit branches, sugarcane bagasse, sawdust, rice husk, manure, grass crops, forest residues and municipal solid waste. These types of biomass is used to derive different types of product including natural palm oil fibre strand, geotextiles, biomass wood pellet, briquette from straw and hay, cork flooring and compost from municipal solid waste for agriculture.

Biodiesel is a type of biofuel produced from vegetable oil and fats with the addition of alcohol and the use of catalyst through the process of trans-esterification producing glycerol (ethyl esters) as co-product. There are many reactions involved in production of biodiesel. The most common reaction used to produce biodiesel is based on trans-esterification of vegetable oils and fats through the addition of methanol (or other alcohols) and a catalyst, giving glycerol as a co-product. Feedstock includes rapeseeds, sunflower seeds, soy seeds and palm oil seeds from which the oil is extracted chemically or mechanically (IEA, 2007).

Biodiesel can be produced mainly from palm oil as it does not increase the level of carbon dioxide in the atmosphere as the amount of carbon dioxide released is the almost equal or lower in some cases compared to the amount of carbon dioxide absorbed earlier through the photosynthesis process. Thus, palm oil biofuels are considered carbon neutral.

1.2 Problem Statement

At present, about 80% of all primary energy in this world is derived from fossil fuel with oil accounting for 32.8%, coal for 27.2% and natural gas for 20.9% (IEA, 2011). For the alternatives source of energy only contributes approximately 20 % to world energy source. The biofuels could not fully replace current fossil fuels as biofuels are combined with fossil fuels to be used in current technologies. There is need to carry out more studies to optimize the efficiency of biofuels in current technologies. Biodiesel, a type of biofuel has been studied and optimized to obtain kinetic reaction model. However, currently the kinetic reaction models present for biodiesel production are limited to specific reactions involved in biodiesel production. Therefore, study of reactions involved in the biodiesel production is very important. There is need of development of a general reaction kinetic model by which we can calculate the reaction kinetics data for reactions involved in biodiesel production.

1.3 Objective

- Development of general reaction kinetic model for biodiesel production.
- To calculate the reaction kinetics for reactions involved in the production of biodiesel using optimization approach.
- To carry out parametric study of reactions involved in biodiesel production.

1.4 Scope of Study

The study will involve developing general reaction kinetic model to calculate the optimum reaction constants using optimization method. The study will focus on production of biodiesel produced by different methods to obtain the optimum reaction kinetics data. The study will be conducted using MATLAB software to develop the general reaction kinetic model using OPTIMIZATION TOOLBOX in MATLAB. The general reaction kinetic model developed will be compared with the experimental data from previous studies to validate the reaction kinetics data calculated to ensure the reliability of the study. The parameter will be varying to get the best and optimum production process. The parametric study will focus more on temperature.

CHAPTER 2: LITERATURE REVIEW

2.1 Chemical Building Block

Fatty acids are a component of both vegetable oil and biodiesel. In chemical terms, they are carboxylic acids of the form:

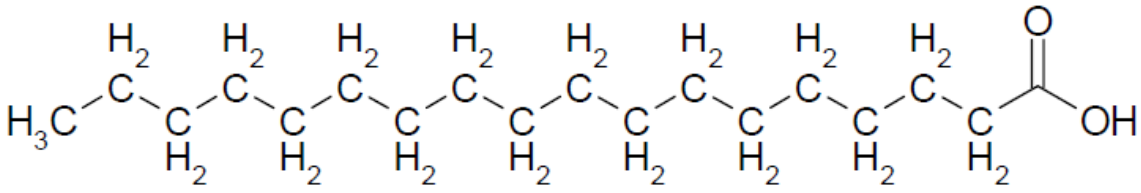


Figure 1: Molecular Structure of Idealized Fatty Acid

Fatty acids which are not bound to some other molecule are known as free fatty acids. When reacted with a base, a fatty acid loses a hydrogen atom to form soap.

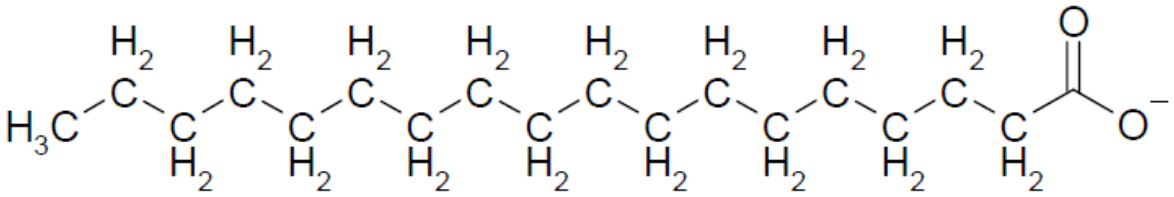


Figure 2: Molecular Structure of Soap

Chemically, soap is the salt of fatty acid. The structures of fatty acids shown in this section are highly idealized. Real fatty acids vary in the number of carbon atoms, and in the number of double bonds. Glycerol, a component of vegetable oil and a by-product of biodiesel production, has the following form:

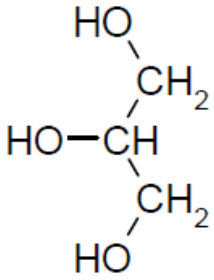


Figure 3: Molecular Structure of Glycerol

Alcohols are organic compounds of the form *R-OH*, where *R* is a hydrocarbon. Typical alcohols used in biodiesel-making are methanol, ethanol, 1-propanol, and 1-butanol:

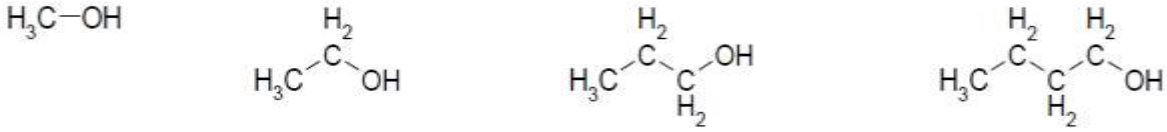


Figure 4: Molecular structure of methanol, ethanol, 1-propanol, and 1-butanol

Among these, methanol is the most commonly used to make biodiesel. Since ethanol is easily obtained from plant sugars, while methanol is commonly produced from natural gas, using ethanol makes for a more sustainable fuel. Ethanol is harder to use because it forms emulsions easily, making the separation of end products more difficult.

Transesterification is sometimes called alcoholysis, or if by a specific alcohol, by corresponding names such as methanolysis or ethanolysis. Chemically, biodiesel is a fatty acid alkyl ester:

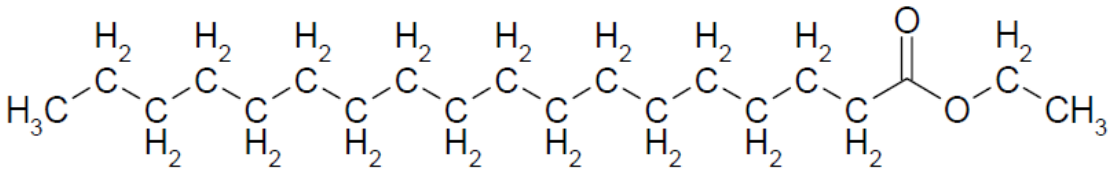


Figure 5: Biodiesel Molecule: Ethyl Ester

An ester is a compound of the form:

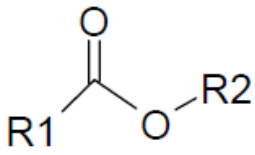


Figure 6: Form of Ester Compound

The biodiesel ester contains a fatty acid chain on one side, and a hydrocarbon called an alkane on the other. Thus, biodiesel is a fatty acid alkyl ester. Usually, the form of the alkane is specified, as in "methyl ester" or "ethyl ester". Vegetable oil is a mixture of many compounds, primarily triglycerides and free fatty acids. A triglyceride is a tri-ester of glycerol and three fatty acids:

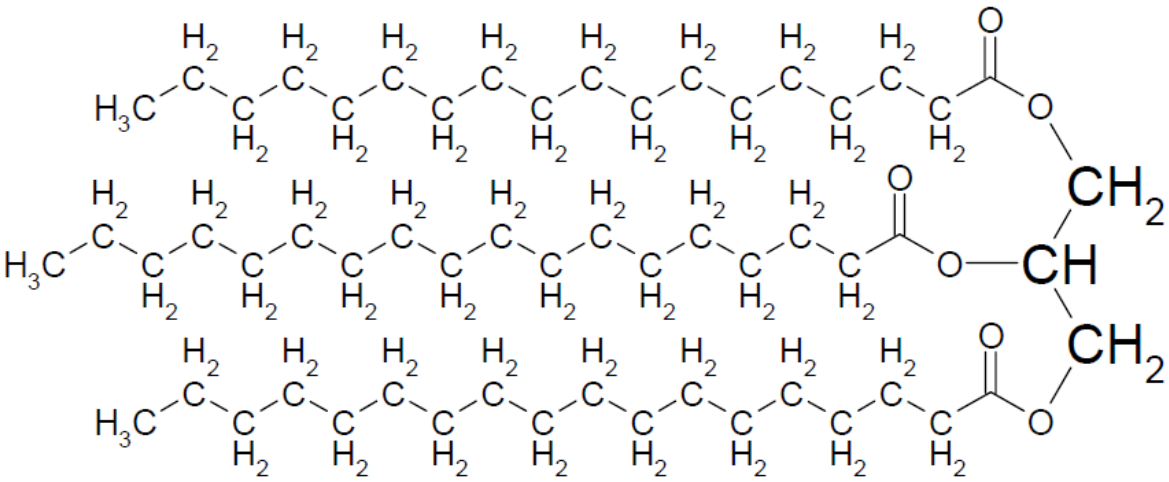


Figure 7: Molecular Structure of Triglyceride

2.2 Biodiesel Production

Biodiesel or ethyl ester is a type of biofuel produced from vegetable oil and fats with the addition of alcohol and the use of catalyst through primarily the process of trans-esterification producing glycerol (ethyl esters) as co-product. Trans-esterification reaction can be represented as follows:

$$DG + ROH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} MG + RCO_2R_1$$

$$DG + ROH \underset{k_4}{\overset{k_3}{\rightleftharpoons}} MG + RCO_2R_2$$

$$MG + ROH \underset{k_6}{\overset{k_5}{\rightleftharpoons}} GL + RCO_2R_3$$

Overall Reaction is:

$$TG + 3ROH \rightleftharpoons 3ME + GL$$

Where k_1, k_2 and k_5 are the rate constants for forward reactions; k_2, k_4 and k_6 are rate constants for reverse reactions; **ROH** is alcohol; RCO_2R_1, RCO_2R_2 and RCO_2R_3 are fatty acid esters; **TG** is Triglyceride; **DG** is Diglyceride; **MG** is monoglyceride; **ME** is Methyl Ester and **GL** is Glycerol (Okullo, Temu and Ntalikwa, 2010)

2.3 Development of Kinetic Reaction Model for Trans-esterification Reaction

There were several kinetic models developed in the past years based on specific trans-esterification reactions. The development of kinetic reaction model began by Freedman and colleagues at USDA in the early 1980's about the trans-esterification reaction of soybean oil and other vegetable oils with butanol and alcohols. The effects of the type of alcohol, molar ratio, type and amount of catalyst and reaction temperature on rate constants and kinetic order (Liu, 2013). Kinetic study was also carried out under non-catalytic conditions. Kusdiana and Saka (Kusdiana & Saka 2001) studied the kinetics of transesterification of rapeseed oil to biodiesel fuel without the application of a catalyst in supercritical methanol.

Table 2: Summarization of different kinetic models (Liu, 2013)

Model	Reactions	Order	Ref.
Three steps, reversible, alkaline as catalyst	$MG + MeOH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} GL + ME$ $MG + MeOH \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} GL + ME$ $MG + MeOH \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} GL + ME$	Second order	(Darnoko & Cheryan, 2000, Noureddini & Zhu, 1997, Wenzel et al., 2006,Shahbazi, M.R., et al.,2012)
Three steps, irreversible, no catalyst	$TG + MeOH \overset{k_1}{\longrightarrow} DG + ME$ $DG + MeOH \overset{k_2}{\longrightarrow} MG + ME$ $MG + MeOH \overset{k_3}{\longrightarrow} GL + ME$	First order	(Diasakou et al., 1998)
One step, reversible, no catalyst	$TG + 3MeOH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} GL + 3ME$	First order	(Kusdiana & Saka, 2001, He et al., 2007)
One step reversible, different base catalysts	$TG + 3MeOH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} GL + 3ME$	First order, or third order, depends on	(Singh & Fernando, 2007)

CHAPTER 3: METHODOLOGY

3.1 Project Flow Chart

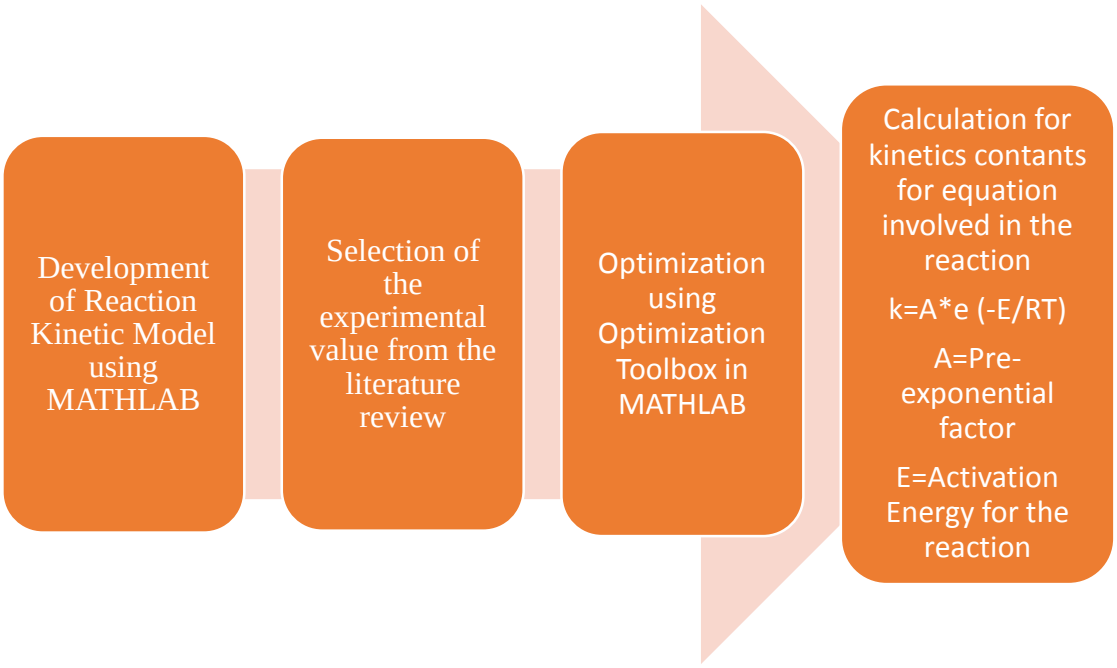
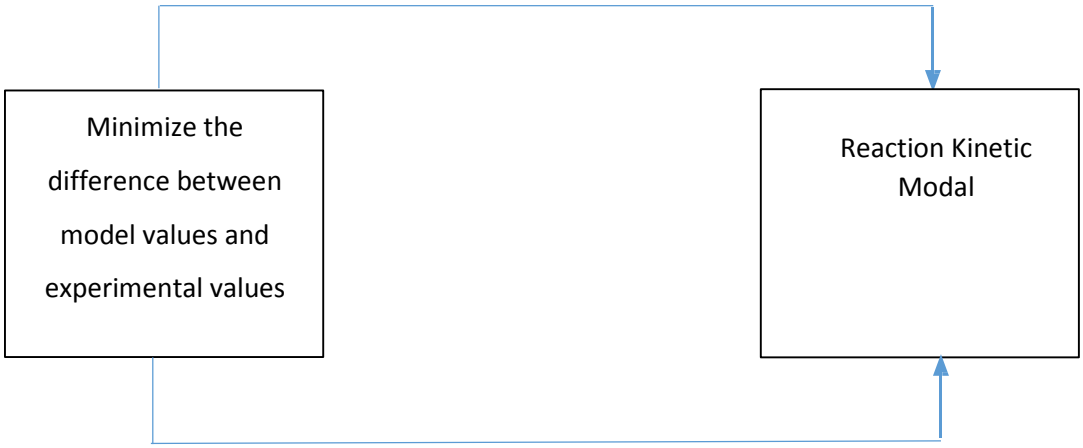


Figure 8: Research Process Flow Chart

Kinetics of All Reactions [K (A1, E1, A2, E2, A3,..)]



Biodiesel Product

Figure 9: Optimization Function

Please refer to APPENDICES for MATLAB Code on Reaction Kinetic Modal and Optimization

3.2 Key Milestone

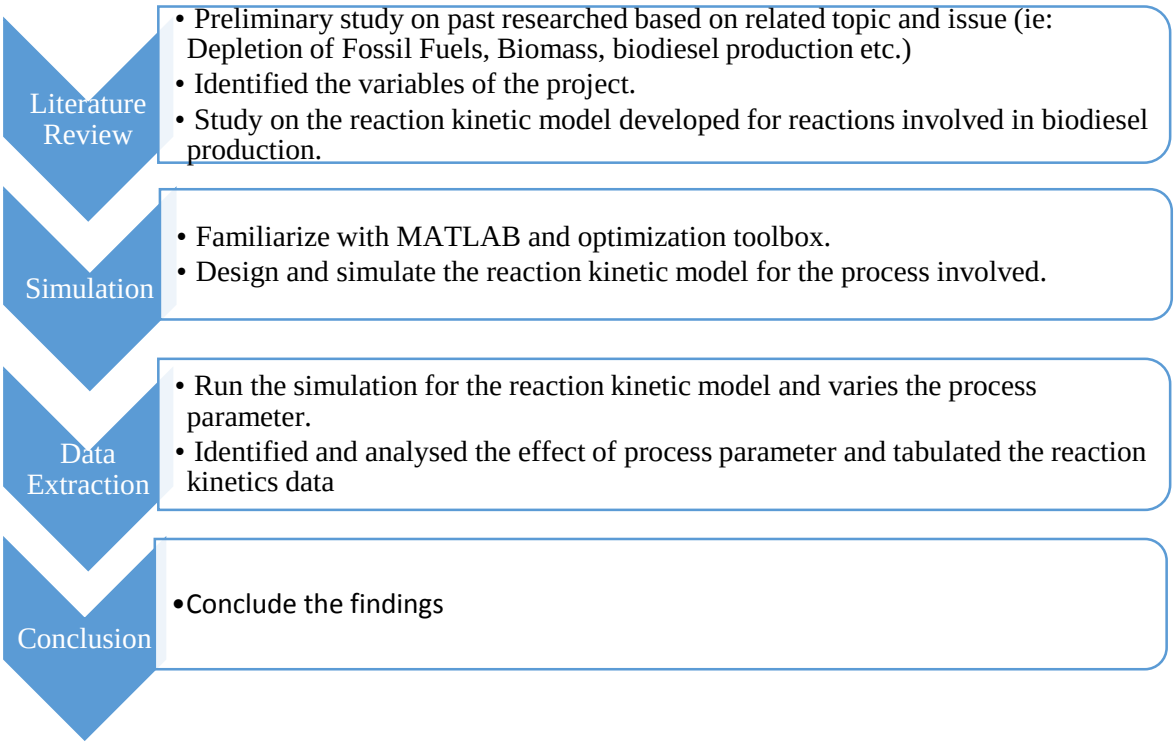


Figure 10: Key Milestone

3.3 Gantt Chart

Table 3: Gantt Chart

No	Details	Weeks													
		1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	Title and Supervisor Allocation														
2	Preliminary Research Work														
3	Preparing Extended Proposal														
4	Submission of Extended Proposal														
5	Proposal Defense														
6	Project Work Continues														
7	Submission of Interim Draft Report														
8	Submission of Final Interim Report														

CHAPTER 4: RESULTS AND DISCUSSION

Several experimental results were used as initial results to obtain optimized results from the simulation in MATLAB.

4.1.1 First Run

Experimental Results 1:

Triglyceride : 5.7 % w/w
Oil/Methanol Ratio : 6
Potassium Hydroxide : 1.0 % w/w (catalyst)

Table 4: Experimental Results 1 (Liu,2013)

Component	Unit	Temperature (K)		
		328	333	338
Diglyceride	% w/w	3.6	3.5	2.5
Monoglyceride	% w/w	2.6	2.4	2
Glycerol	% w/w	8.4	8.8	9.2
Methyl Esters	% w/w	79	81.5	82.5
Rate Constant (k) 1		0.024	0.036	0.048
Rate Constant (k) 2		0.051	0.07	0.098
Rate Constant (k) 3		0.158	0.161	0.191
Pre-exponential Factor (A) 1		0.025	0.038	0.050
Pre-exponential Factor (A) 2		0.453	0.845	1.888
Pre-exponential Factor (A) 3		0.935	1.002	2.471
Activation Energy (E) 1		14.7	14.7	14.7
Activation Energy (E) 2		14.2	14.2	14.2
Activation Energy (E) 3		6.4	6.4	6.4

MATLAB Simulation 1:

Table 5: Simulation Results 1 from MATLAB OPTIMIZATION TOOLBOX

Component	Unit	Temperature (K)		
		328	333	338
Diglyceride	% w/w	3.8	3.5	3.2
Monoglyceride	% w/w	2.6	2.4	2.2
Glycerol	% w/w	23.6	24.4	25.2
Methyl Esters	% w/w	79.7	81.5	83.3
Rate Constant (k) 1		5.264	5.316	5.366
Rate Constant (k) 2		0.872	0.884	0.897
Rate Constant (k) 3		0.901	0.910	0.920
Pre-exponential Factor (A) 1		10.071	10.071	10.071
Pre-exponential Factor (A) 2		2.266	2.266	2.266
Pre-exponential Factor (A) 3		1.856	1.856	1.856
Activation Energy (E) 1		212.781	212.781	212.781
Activation Energy (E) 2		313.254	313.254	313.254
Activation Energy (E) 3		237.098	237.098	237.098

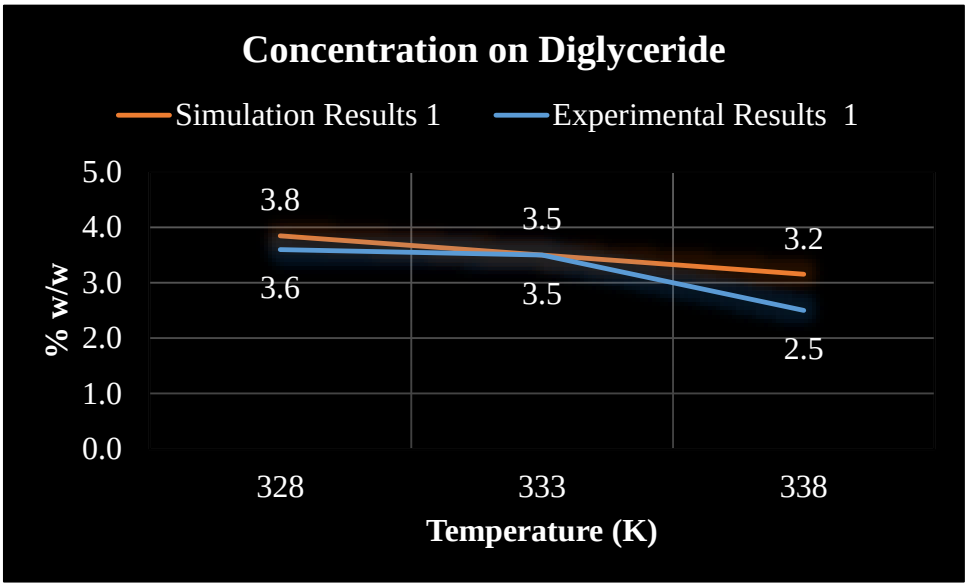


Figure 11: Graph of Comparison between Experimental Results 1 and Simulation Results 1 based on Composition of Diglyceride against Temperature

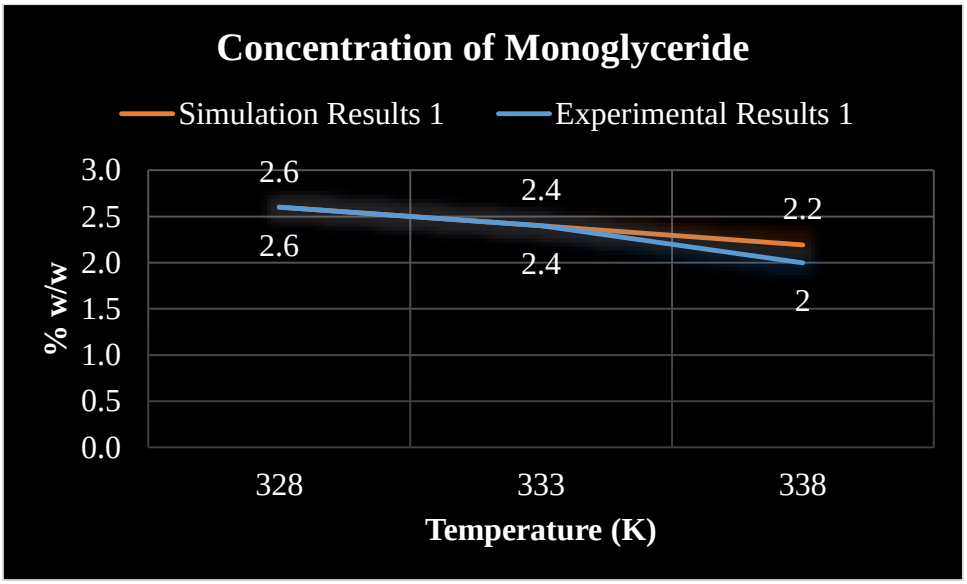


Figure 12: Graph of Comparison between Experimental Results 1 and Simulation Results 1 based on Composition of Monoglyceride against Temperature

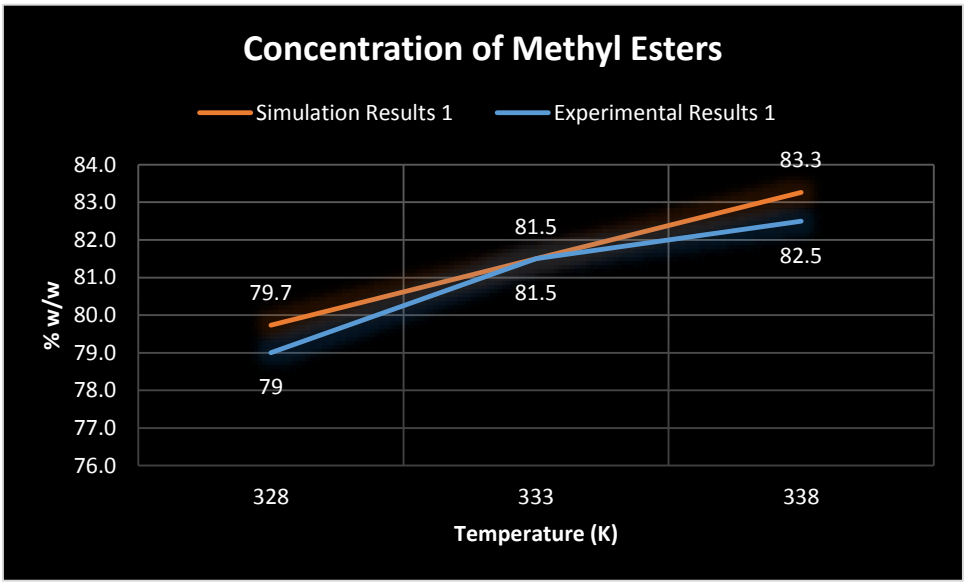


Figure 13: Graph of Comparison between Experimental Results 1 and Simulation Results 1 based on Composition of Methyl Esters against Temperature

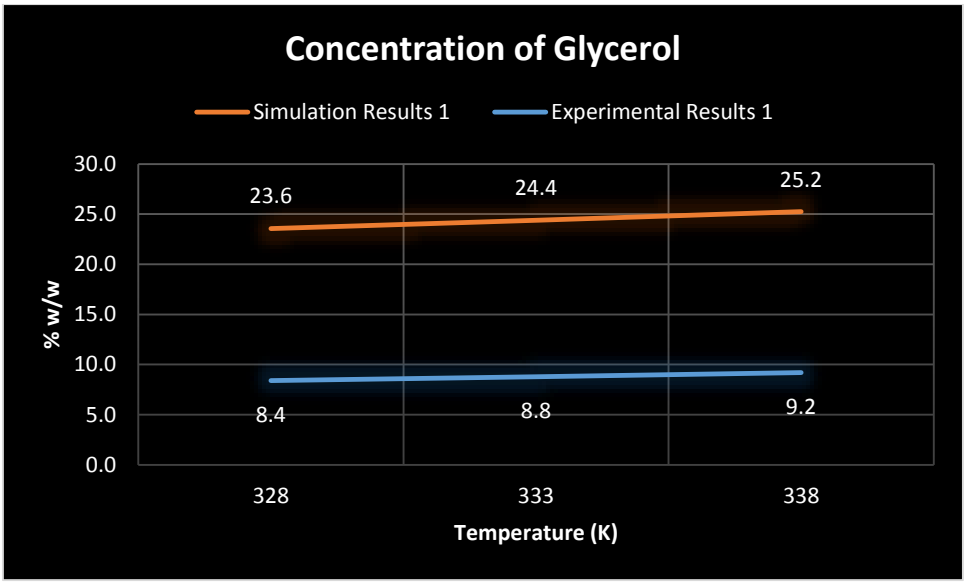


Figure 14: Graph of Comparison between Experimental Results 1 and Simulation Results 1 based on Composition of Glycerol against Temperature

Results from ***Figure 11, 12, 13 and 14*** show the Experimental Results 1 used as basis for simulation in MATLAB and the Simulation Results 1 obtained based on the new optimized general pre-exponential factors and activation energy generated from the MATLAB OPTIMIZATION TOOLBOX.

The results obtained from ***Figure 11, 12, and 13*** show that the simulation results yield the similar set of results compared to experimental results in terms of composition of Diglycerides, Monoglycerides and Methyl Esters in the transesterification reaction of palm oil with potassium hydroxide (KOH) as catalyst in the reaction. The set of results generated from MATLAB Simulation vary from the experimental results with minimal error which is below 5% error.

Figure 14 shows that there have been increase in terms of composition percentage of glycerol as the experimental results shows concentration values of 8.4, 8.8 and 9.2 for temperatures of 328K, 333K and 338K respectively whereas MATLAB Simulation 1 shows concentration values of 23.6, 24.4, and 25.2 for temperatures 328K, 333K and 338K respectively.

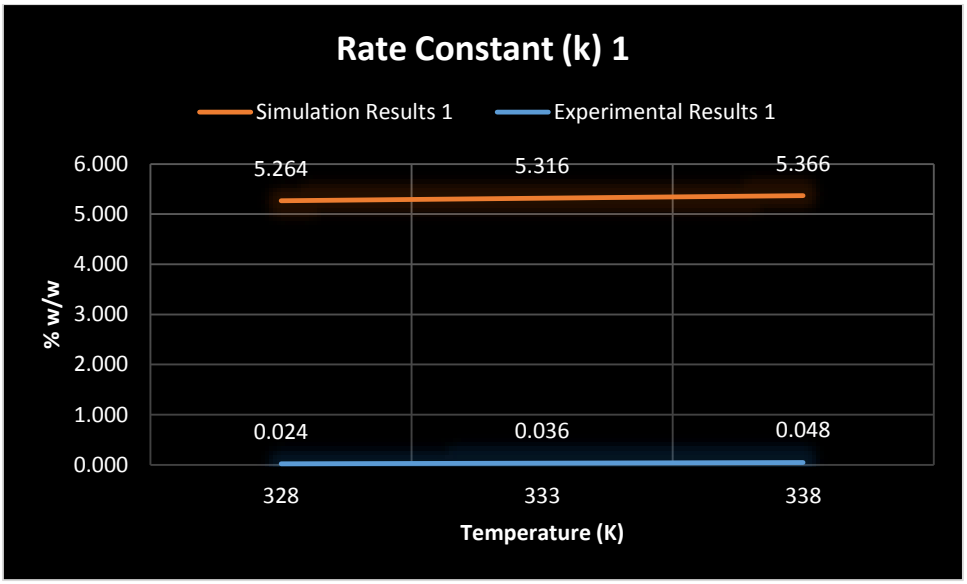


Figure 15: Graph of Comparison between Experimental Results 1 and Simulation Results 1 based on Rate Constant (k) 1

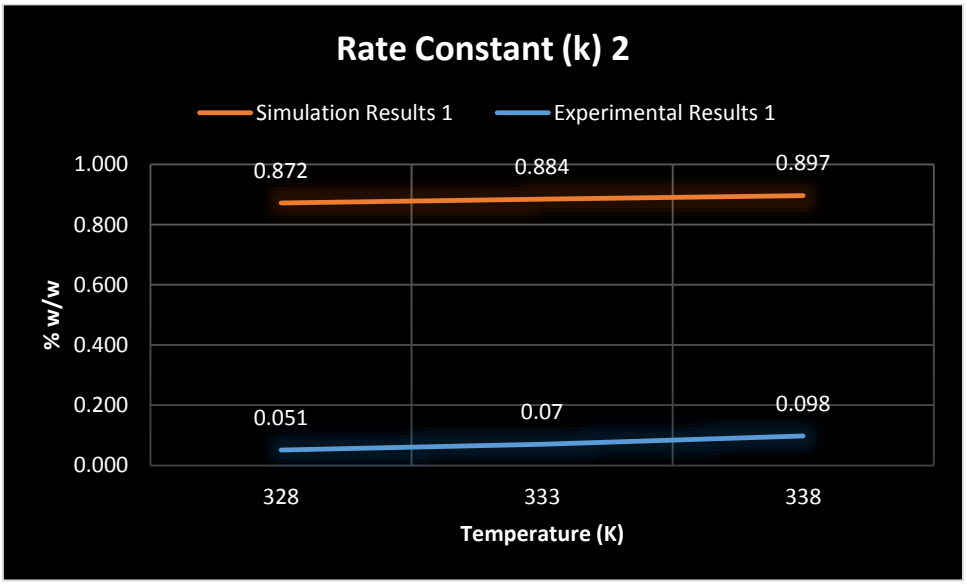


Figure 16: Graph of Comparison between Experimental Results 1 and Simulation Results 1 based on Rate Constant (k) 2

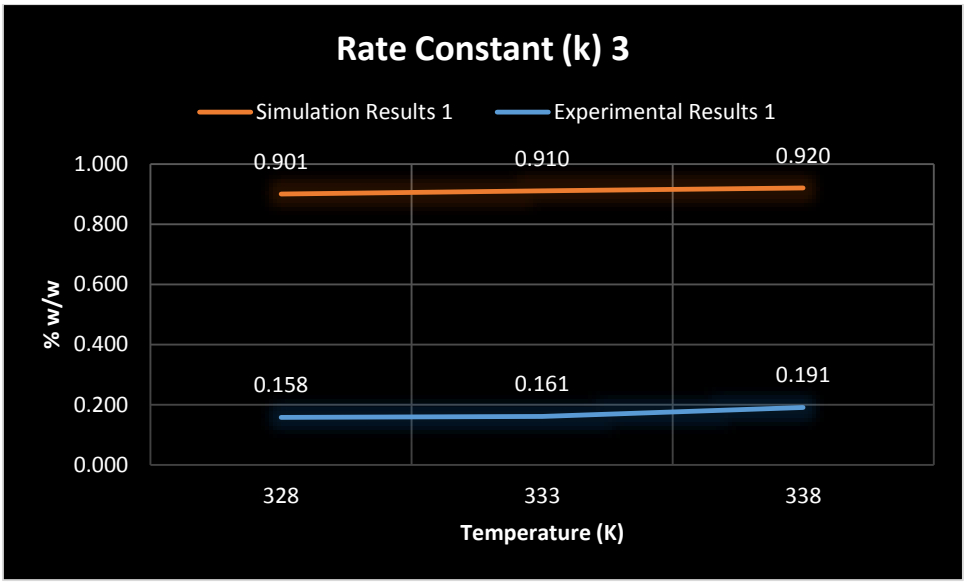


Figure 17: Graph of Comparison between Experimental Results 1 and Simulation Results 1 based on Rate Constant (k) 2

Figure 15, 16 and 17 show the rate constants from Experimental Results 1 and rate constants developed for each step of reaction from new MATLAB optimization values of activation energy and pre-exponential. The results show that rate constants from MATLAB Simulation Results 1 have significant increase compared to the actual Experimental Results 1.

4.1.2 Second Run

Experimental Results 2:

Triglyceride : 6.7 % w/w
Oil/Methanol Ratio : 6
Potassium Hydroxide : 0.45 % w/w (catalyst)

Table 6: Experimental Results 2 (Krishnan, 2012)

Component	Unit	Temperature (K)		
		328	333	338
Diglyceride	% w/w	4.6	3.8	3.2
Monoglyceride	% w/w	3.6	2.1	1.2
Glycerol	% w/w	6.9	7.2	9.1
Methyl Esters	% w/w	78	80.2	82
Rate Constant (k) 1		0.0188	0.0208	0.0244
Rate Constant (k) 2		0.042	0.061	0.0801
Rate Constant (k) 3		0.1431	0.1528	0.1682
Pre-exponential Factor (A) 1		0.019	0.021	0.025
Pre-exponential Factor (A) 2		0.042	0.061	0.081
Pre-exponential Factor (A) 3		0.189	0.215	0.252
Activation Energy (E) 1		2.53	2.53	2.53
Activation Energy (E) 2		1.93	1.93	1.93
Activation Energy (E) 3		1.29	1.29	1.29

Simulation Results 2:

Table 7: Simulation Results 2 from MATLAB OPTIMIZATION TOOLBOX

Component	Unit	Temperature (K)		
		328	333	338
Diglyceride	% w/w	4.6	3.4	2.8
Monoglyceride	% w/w	3.6	2.1	1.5
Glycerol	% w/w	20.8	21.0	21.6
Methyl Esters	% w/w	81.8	82.0	82.3
Rate Constant (k) 1		1.187	1.199	1.210
Rate Constant (k) 2		0.772	0.792	0.812
Rate Constant (k) 3		0.189	0.200	0.210
Pre-exponential Factor (A) 1		2.214	2.214	2.214
Pre-exponential Factor (A) 2		4.269	4.269	4.269
Pre-exponential Factor (A) 3		6.392	6.392	6.392
Activation Energy (E) 1		204.33	204.33	204.33
Activation Energy (E) 2		561.073	561.073	561.073
Activation Energy (E) 3		1154.072	1154.072	1154.072

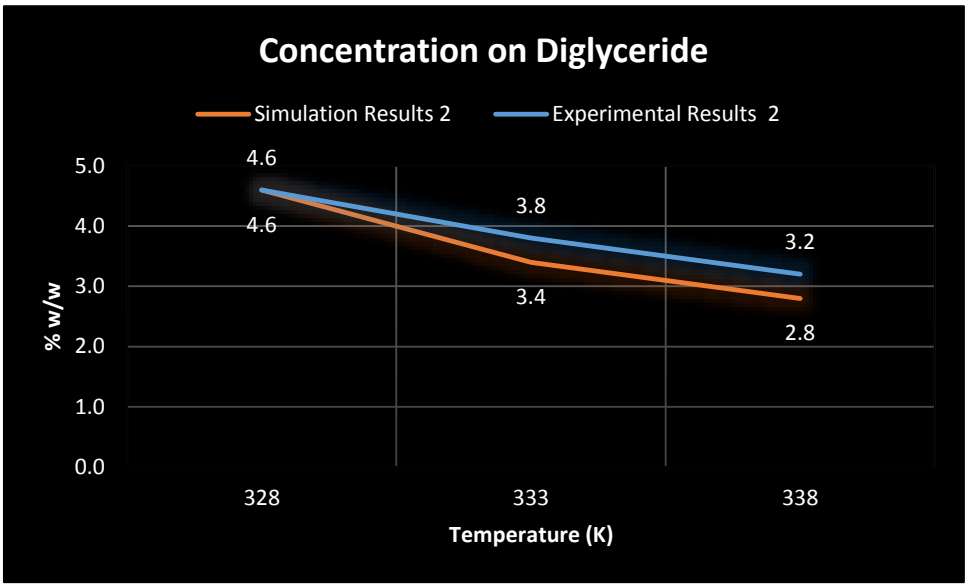


Figure 18: Graph of Comparison between Experimental Results 2 and Simulation Results 2 based on Composition of Diglyceride against Temperature

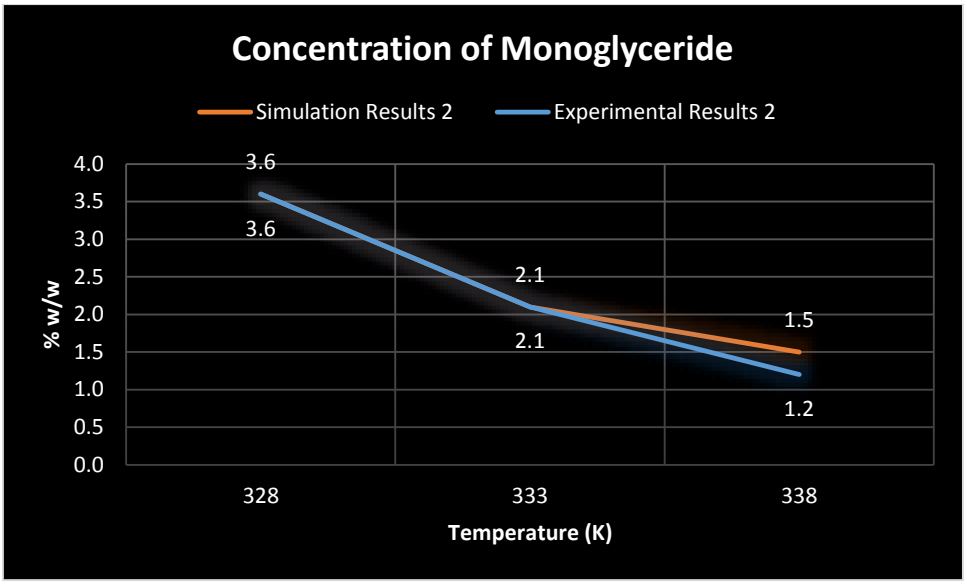


Figure 19: Graph of Comparison between Experimental Results 2 and Simulation Results 2 based on Composition of Monoglyceride against Temperature

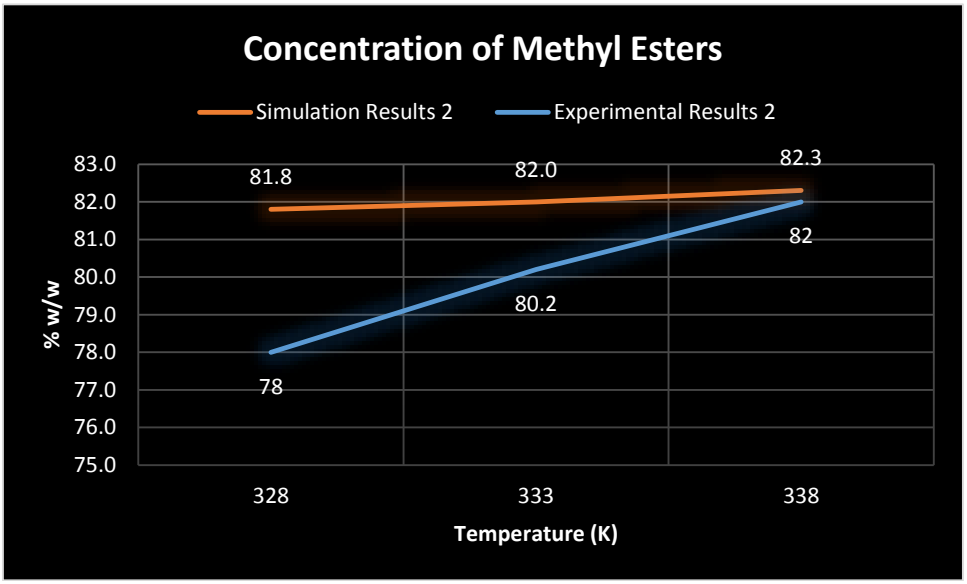


Figure 20: Graph of Comparison between Experimental Results 2 and Simulation Results 2 based on Composition of Methyl Esters against Temperature

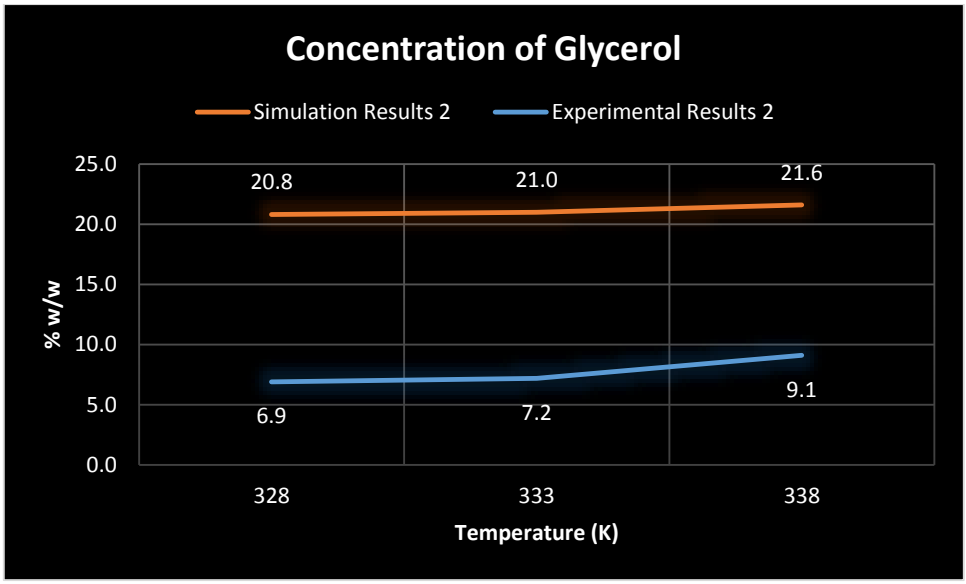


Figure 21: Graph of Comparison between Experimental Results 2 and Simulation Results 2 based on Composition of Glycerol against Temperature

Results from ***Figure 18, 19, 20 and 21*** show the experimental results 2 used as basis for simulation in MATLAB and the Simulation Results 2 obtained based on the new optimized general pre-exponential factors and activation energy generated from the MATLAB OPTIMIZATION TOOLBOX.

The results obtained from ***Figure 18, 19, and 20*** show the simulation results yield the similar set of results compared to experimental results in terms of composition of Diglycerides, Monoglycerides and Methyl Esters in the transesterification reaction of palm oil with potassium hydroxide (KOH) as catalyst in the reaction. The set of results generated from MATLAB Simulation vary from the experimental results with minimal error which is below 5% error.

Similarly, ***Figure 21*** shows that there have been increase in terms of composition percentage of glycerol as the experimental results shows concentration values of 6.9, 7.2 and 9.1 for temperatures of 328K, 333K and 338K respectively whereas MATLAB Simulation 1 shows concentration values of 20.8, 21.0 and 21.6 for temperatures 328K, 333K and 338K respectively.

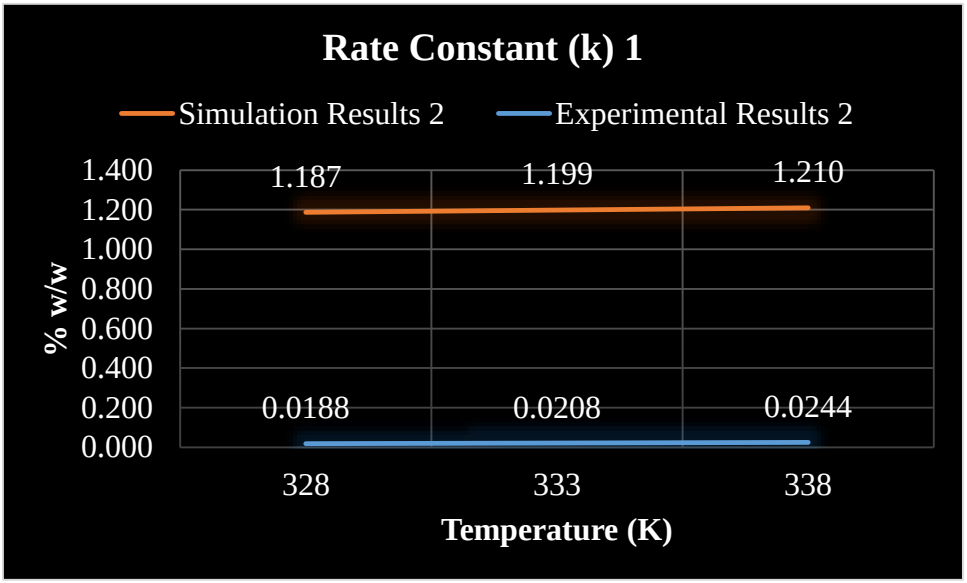


Figure 22: Graph of Comparison between Experimental Results 2 and Simulation Results 2 based on Rate Constant (k) 1

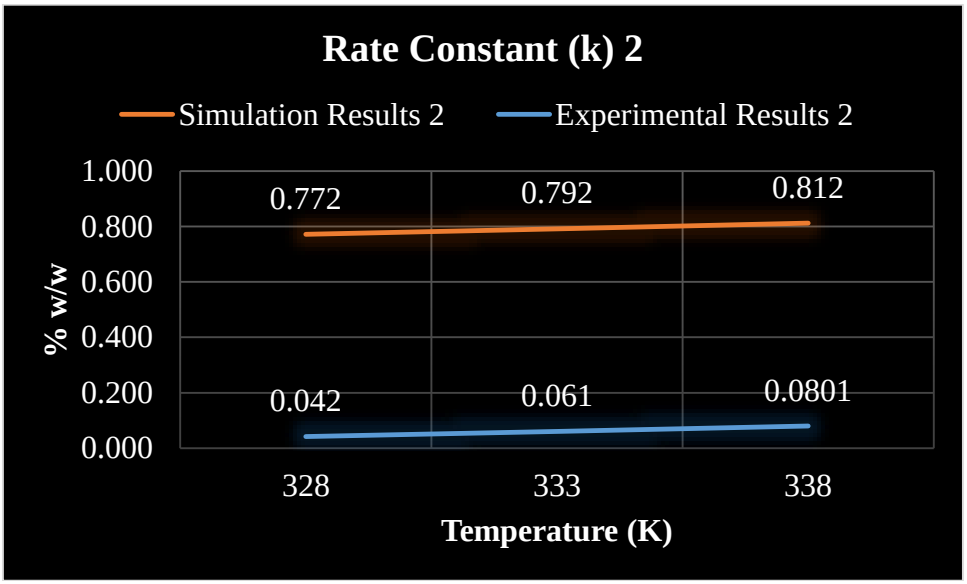


Figure 23: Graph of Comparison between Experimental Results 2 and Simulation Results 2 based on Rate Constant (k) 2

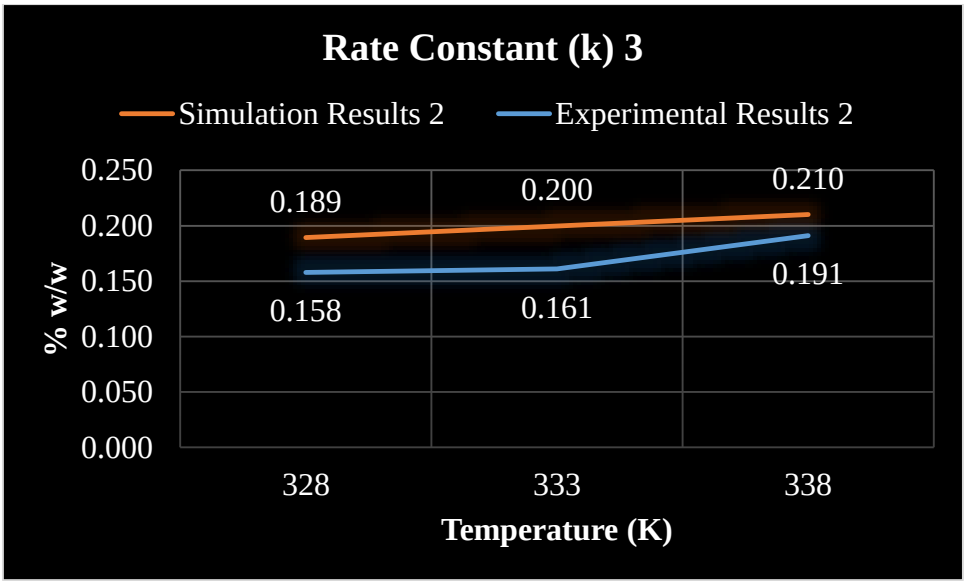


Figure 24: Graph of Comparison between Experimental Results 2 and Simulation Results 2 based on Rate Constant (k) 3

Figure 15, 16 and 17 show the rate constants from Experimental Results 2 and rate constants developed for each step of reaction from new MATLAB optimization values of activation energy and pre-exponential. The results show that rate constants from MATLAB Simulation Results 2 have significant increase compared to the actual experimental results.

4.1.3 Third Run

Experimental Results 3:

Triglyceride : 9.5 % w/w
Oil/Methanol Ratio : 6
Potassium Hydroxide : 0.50 % w/w (catalyst)

Table 8: Experimental Results 3 (Hitoshi, Shoji, Hiroshi, 2008)

Component	Unit	Temperature (K)		
		328	333	338
Diglyceride	% w/w	4.5	4	3.2
Monoglyceride	% w/w	2.6	2.3	2.1
Glycerol	% w/w	9.2	8.4	8.2
Methyl Esters	% w/w	74.7	77.9	80.1
Rate Constant (k) 1		0.031	0.051	0.056
Rate Constant (k) 2		0.188	0.205	0.302
Rate Constant (k) 3		0.415	0.527	0.711
Pre-exponential Factor (A) 1		0.032	0.052	0.057
Pre-exponential Factor (A) 2		0.191	0.208	0.307
Pre-exponential Factor (A) 3		1.016	1.443	2.505
Activation Energy (E) 1		6.61	6.61	6.61
Activation Energy (E) 2		5.52	5.52	5.52
Activation Energy (E) 3		4.03	4.03	4.03

Simulation Results 3

Table 9: Simulation Results 2 from MATLAB OPTIMIZATION TOOLBOX

Component	Unit	Temperature (K)		
		328	333	338
Diglyceride	% w/w	4.5	4.0	3.5
Monoglyceride	% w/w	2.6	2.4	2.1
Glycerol	% w/w	22.0	23.1	24.1
Methyl Esters	% w/w	75.7	77.9	80.1
Rate Constant (k) 1		1.915	1.936	1.956
Rate Constant (k) 2		0.528	0.540	0.551
Rate Constant (k) 3		0.559	0.567	0.575
Pre-exponential Factor (A) 1		3.923	3.923	3.923
Pre-exponential Factor (A) 2		2.260	2.260	2.260
Pre-exponential Factor (A) 3		1.453	1.453	1.453
Activation Energy (E) 1		235.248	235.248	235.248
Activation Energy (E) 2		476.756	476.756	476.756
Activation Energy (E) 3		313.264	313.264	313.264

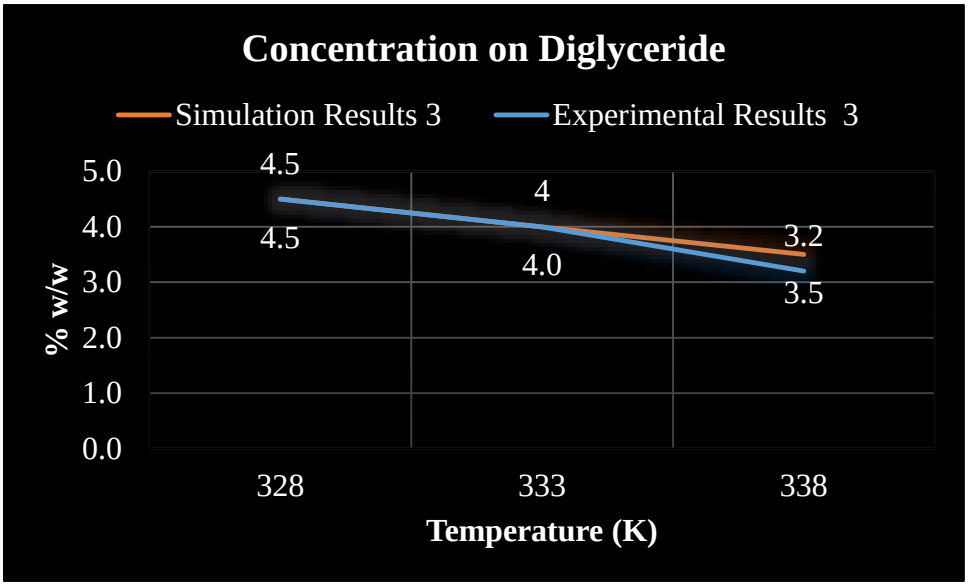


Figure 25: Graph of Comparison between Experimental Results 3 and Simulation Results 3 based on Composition of Diglyceride against Temperature

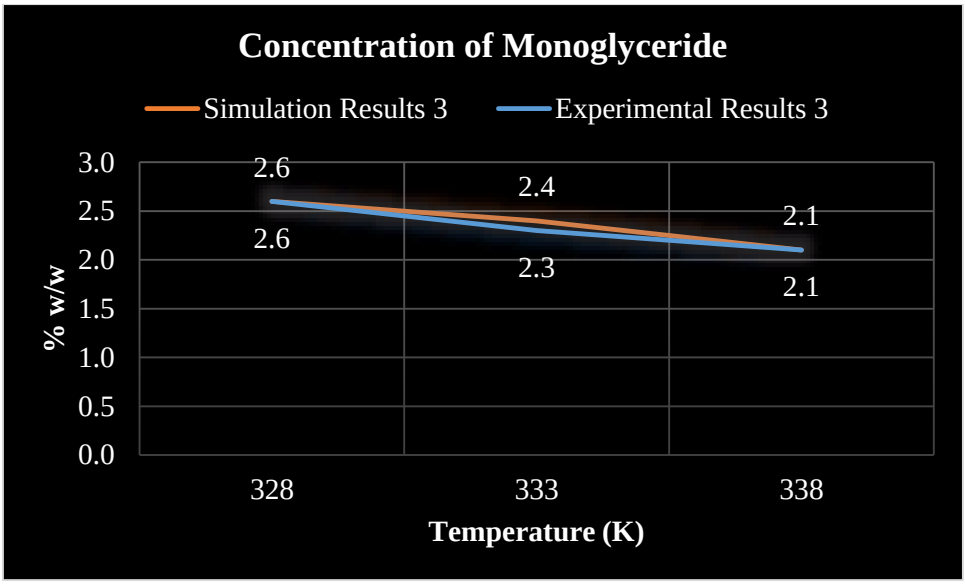


Figure 26: Graph of Comparison between Experimental Results 3 and Simulation Results 3 based on Composition of Monoglyceride against Temperature

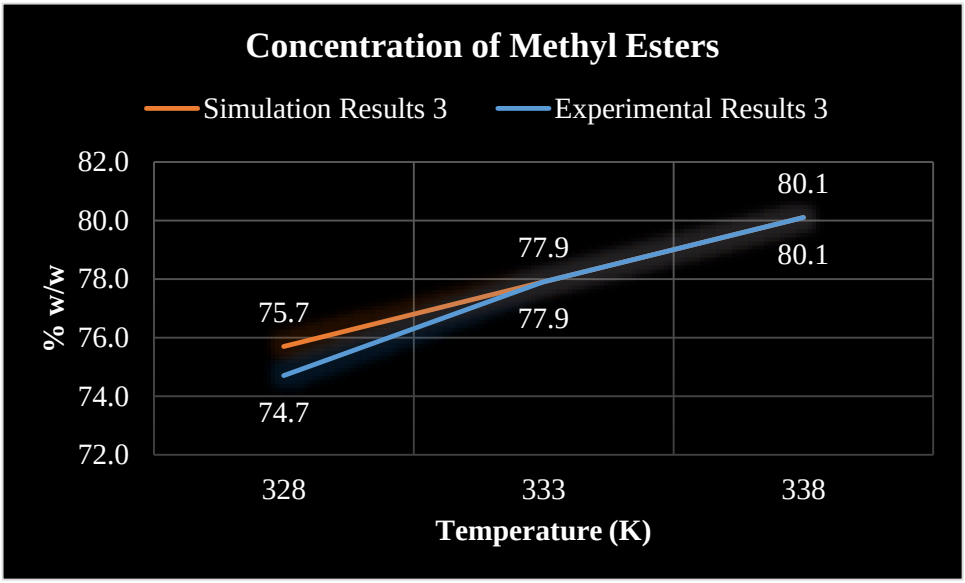


Figure 27: Graph of Comparison between Experimental Results 3 and Simulation Results 3 based on Composition of Methyl Esters against Temperature

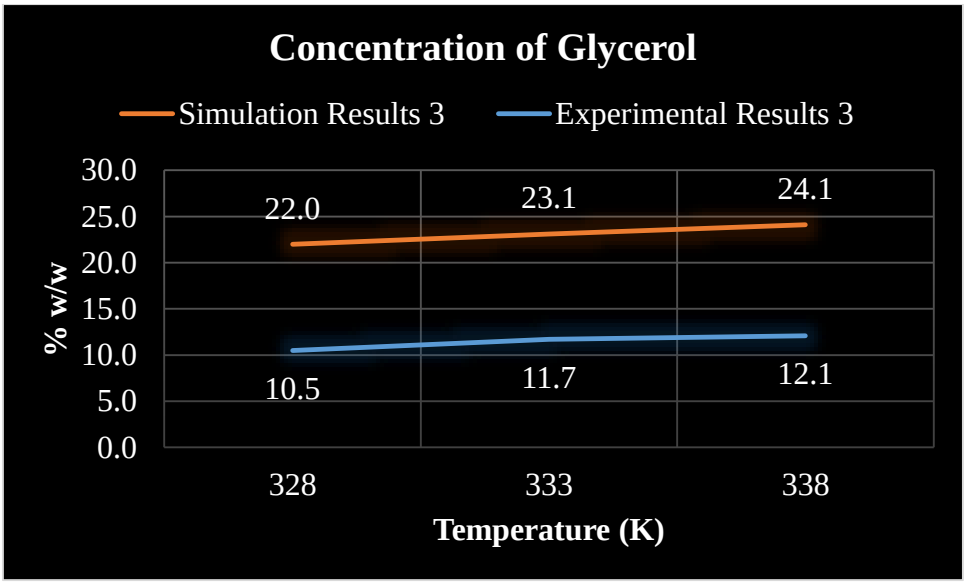


Figure 28: Graph of Comparison between Experimental Results 2 and Simulation Results 2 based on Composition of Glycerol against Temperature

Results from ***Figure 25, 26, 27 and 28*** show the Experimental Results 3 used as basis for simulation in MATLAB and the Simulation Results 3 obtained based on the new optimized general pre-exponential factors and activation energy generated from the MATLAB OPTIMIZATION TOOLBOX.

The results obtained from ***Figure 25, 26, and 27*** show that the simulation results yield the similar set of results compared to experimental results in terms of composition of Diglycerides, Monoglycerides and Methyl Esters in the transesterification reaction of palm oil with potassium hydroxide (KOH) as catalyst in the reaction. The set of results generated from MATLAB Simulation vary from the experimental results with minimal error which is below 5% error.

Figure 28 shows that there have been increase in terms of composition percentage of glycerol as the experimental results shows concentration values of 10.5, 11.7, and 12.1 for temperatures of 328K, 333K and 338K respectively whereas MATLAB Simulation 1 shows concentration values of 22.0, 23.1 and 24.1 for temperatures 328K, 333K and 338K respectively.

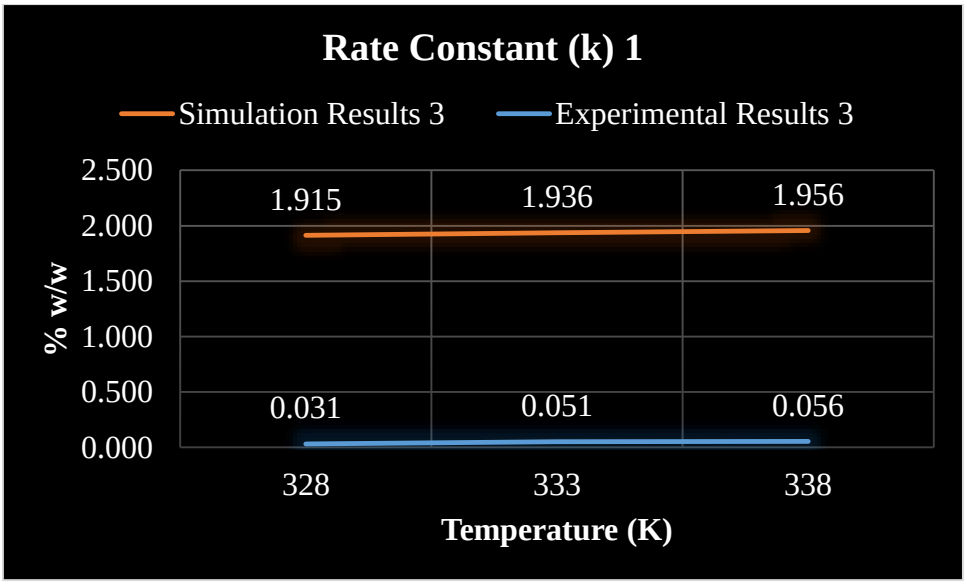


Figure 29: Graph of Comparison between Experimental Results 3 and Simulation Results 3 based on Rate Constant (k) 1

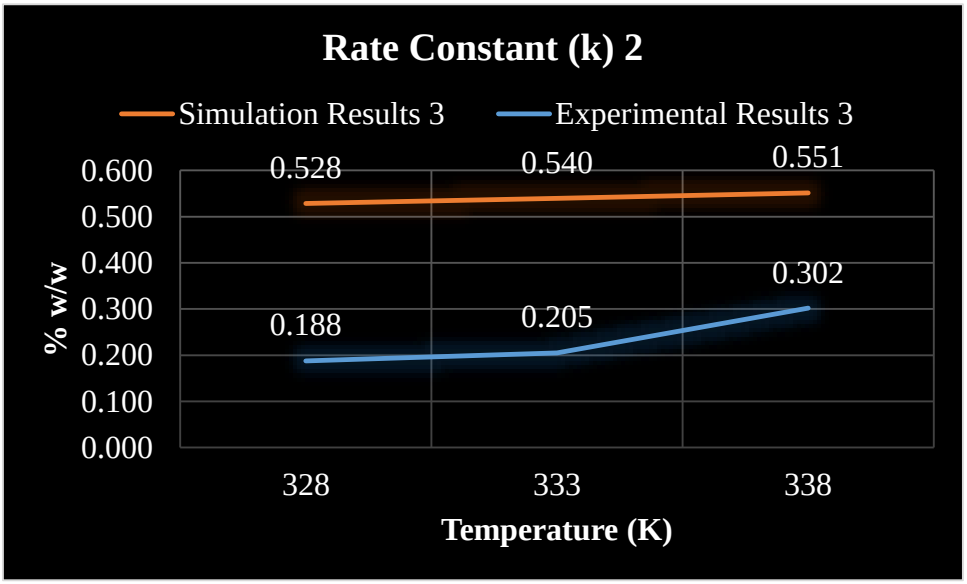


Figure 30: Graph of Comparison between Experimental Results 3 and Simulation Results 3 based on Rate Constant (k) 2

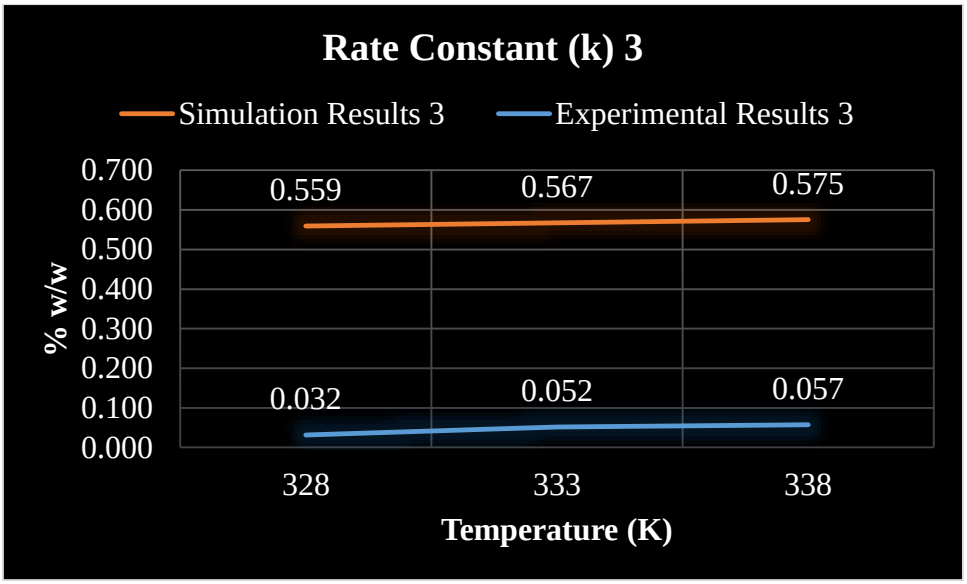


Figure 31: Graph of Comparison between Experimental Results 3 and Simulation Results 3 based on Rate Constant (k) 3

Figure 39, 30 and 31 show the rate constants from Experimental Results 1 and rate constants developed for each step of reaction from new MATLAB optimization values of activation energy and pre-exponential. The results show that rate constants from MATLAB Simulation Results 3 have significant increase compared to the actual Experimental Results 3.

4.2 Discussion

A total of three runs have been carried out in this project to develop and validate a general reaction kinetic modal. From the results obtained from the three runs in MATLAB OPTIMIZATION TOOLBOX, there have been similar set of results generated when compared to the actual experimental results with error of less than 5% in terms of production of methyl esters which is biodiesel.

Although, there have been slight increase in concentration in terms of composition of Glycerol in the product, the methyl esters which is the biodiesel yielded from the simulation in MATLAB shows similar results as compared to the experimental results in all the three runs. This shows that the product composition are tally with the experimental results and the reaction kinetic modal is providing accurate results for transesterification results.

Besides that, the rate constant of the reactions involved in transesterification which is the Reaction Constant (k) 1, 2 and 3 in all three runs show significant difference in values. The rate constants generated from MATLAB Simulation are higher compared to that of the experimental results in all three runs. Although the rate constants are higher, the product yield which is the methyl ester did not vary too much compared to the experimental results.

Furthermore, the optimized value of activation energy and the pre-exponential factor values are general values that can be used at any temperature to calculate the concentration of the product yield. This will enable to use the optimized values to calculate the rate constants at any temperature. This relates with the objective of this project which is to develop a general reaction kinetic modal with temperature as kinetic parametric study.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 Conclusion

As a conclusion, a general kinetic model and parametric study of the kinetics of the reaction involved in the synthesis of biodiesel developed in this project through the use of MATLAB OPTIMIZATION TOOLBOX have shown promising results whereby it has the potential to yield the similar set of results as compared to experimental results. Despite the increase in concentration of glycerol and the rate constants, the methyl esters yielded at any temperature are similar to that of experimental results with minimal error below 5 %. The objective of this project is achieved.

5.2 Recommendation

- Carry out real experiments to further prove the validity of the modal developed in this project.
- Expand the parametric study to other kinetics such as amount of catalyst, and the reaction time.
- Expand the model for other type of reactions of transesterification in producing biodiesel besides using palm oil.

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APPENDICES

APPENDIX I: REACTION KINETIC MODAL

Reaction Kinetic Model using MATLAB was developed on the reaction rate and reactions constants.

The reactions involved are:

$$DG + ROH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} MG + RCO_2R_1$$

$$DG + ROH \underset{k_4}{\overset{k_3}{\rightleftharpoons}} MG + RCO_2R_2$$

$$MG + ROH \underset{k_6}{\overset{k_5}{\rightleftharpoons}} GL + RCO_2R_3$$

Equations used to develop Kinetic Model and Function Files using MATLAB:

$$R_1 = k_1 * C_{ROH} * C_{TG}$$

$$R_2 = k_2 * C_{ROH} * C_{DG}$$

$$C_{DG} = R_1$$

$$R_2 = k_2 * C_{ROH} * R_1$$

$$R_3 = k_3 * C_{ROH} * C_{MG}$$

$$C_{MG} = R_2$$

$$R_3 = k_3 * C_{ROH} * R_2$$

** The reversible reaction is not considered for the development of the Reaction Kinetic Model*

APPENDIX II: GENERAL RATE OF REACTION

General Rate of Reaction for First Order Reaction:

$$K = A * \exp((-E) / (R*T))$$

$$R = K C_1 * C_2$$

$$R = A * \exp((-E) / (R*T)) * C_1 * C_2$$

Matlab Function for the above equation:

```
function [r] = run_reaction_rate(A,E,G,T,C1,C2)

% input (T,A,E,C1,C2)
% T : temperature
% G : Gas Constant
% E : Activation Energy
% A : Pre-exponential Factor
% C1: Concentration of Reactant 1
% C2: Concentration of Reactant 2

% Calculate Rate of Reaction
r = A * exp((-E)/(G*T))*C1*C2;

end
```

Figure 32: MATLAB Function File for General Rate of Reaction for First Order Reaction

APPENDIX III: CONCENTRATION OF THE REACTANT AND PRODUCT

Concentration of the Reactant and Product of Transesterification Reaction:

$$R_{ROH} = - R_1 - R_2 - R_3$$

$$R_{TG} = - R_1$$

$$R_{DG} = R_1 - R_2$$

$$R_{MG} = R_2 - R_3$$

$$R_{GL} = R_3$$

$$R_{RCO2R} = R_1 + R_2 + R_3$$

$$R_{TOTAL} = R_{DG} + R_{MG} + R_{GL} + R_{RCO2R}$$

Matlab Function for the above equation:

```
function [RDG, RMG, RGL, RBD] = calc_product_rate(r1,r2,r3)


%Diglyceride
RDG = r1-r2;

%Monoglyceride
RMG = r2-r3;

%Glycerol
RGL = r3;

%Biodiesel (Metyl Ester)
RBD = r1+r2+r3;
```

Figure 33: MATLAB Function File for Concentration of Reactant and Product of Transesterification Reaction

APPENDIX IV: PERCENTAGE CONCENTRATION

Percentage Concentration of the Reactant and Product of Transesterification Reaction:

$$\% R_{DG} = R_{DG} / R_{TOTAL}$$

$$\% R_{MG} = R_{MG} / R_{TOTAL}$$

$$\% R_{GL} = R_{GL} / R_{TOTAL}$$

$$\% R_{RCO2R} = R_{RCO2R} / R_{TOTAL}$$

Matlab Function for the above equation:

```
function [PRDG, PRMG, PRGL, PRBD] = run_perc_product(RDG, RMG, RGL,
RBD, RT)

%Total Concentration
RT = RDG + RMG + RGL + RBD;

%Percentage of Diglyceride
PRDG = RDG / RT;

%Percentage of Monoglyceride
PRMG = RMG / RT;

%Percentage of Glcerol
PRGL = RGL / RT;

%Percentage of Biodiesel (Metyl Esters)
PRBD = RBD / RT;

end
```

Figure 34: MATLAB Function File for Percentage Concentration of the Reactant and Product of Transesterification Reaction

APPENDIX V: REACTION KINETIC MODAL

Reaction Kinetic Modal Developed for Transesterification Process:

```
function [PRDG, PRMG, PRGL,
PRBD]=run_reaction_kinetics_model_kinetics_parameters(T,A1,E1,A2,E2,
A3,E3,G,C1,C2)

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%function file for reaction kinetics model of Integrated catalytic
%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%

    %Concentration of Triglyceride
    CTG = C1;

    %Concentration of Alcohol
    CAL = C2;

    %Rate of First Step Esterification Reaction
    [r1]=run_reaction_rate(A1,E1,T,CTG,CAL);

    %Concentration of Diglyceride
    CDG = r1;

    %Rate of Second Step Esterification Reaction
    [r2]=run_reaction_rate(A2,E2,T,CDG,CAL);

    %Concentration of Monoglyceride
    CMG = r2;

    %Rate of Third Step Esterification Reaction
    [r3]=run_reaction_rate(A3,E3,T,CMG,CAL);

    %Rate of Product
    [RDG, RMG, RGL, RBD] = calc_product_rate(r1,r2,r3);

    %Percetage of Product
    [PRDG, PRMG, PRGL, PRBD] = run_perc_product(RDG, RMG, RGL, RBD);

end
```

Figure 35: MATLAB Function File for Kinetic Reaction Modal of Transesterification Process

APPENDIX VI: CONSTRAINT CONDITIONS FOR OPTIMIZATION

Constraint Conditions for Optimization:

```
function [c,ceq] = kinetics_constants_constraints(X)

A1=X(1);
E1=X(2);
A2=X(3);
E2=X(4);
A3=X(5);
E3=X(6);

% global for parameter fitting approach

global C1;      %Average Concentration of Triglyceride
global C2;      %Concentration of Alcohol

global CDGa;    %Concentration of Diglyceride at 328K
global CDGb;    %Concentration of Diglyceride at 333K
global CDGc;    %Concentration of Diglyceride at 338K

global CMGa;    %Concentration of Monoglyceride at 328K
global CMGb;    %Concentration of Monoglyceride at 333K
global CMGc;    %Concentration of Monoglyceride at 338K

global CGLa;    %Concentration of Glycerol at 328K
global CGLb;    %Concentration of Glycerol at 333K
global CGLc;    %Concentration of Glycerol at 338K

global CBDa;    %Concentration of Biodiesel (Metyl Esters) at 328K
global CBDb;    %Concentration of Biodiesel (Metyl Esters) at 333K
global CBDc;    %Concentration of Biodiesel (Metyl Esters) at 338K


n = 3;  % Number of intervals
T = linspace(328,338,n);
    %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
for i=1:n

     [RDG(i), RMG(i), RGL(i),
RBD(i)]=run_reaction_kinetics_model_kinetics_parameters(A1,E1,A2,E2,A3,E3,T(i),C1,C2);

end

ceq=[];

c(1)=CDGa - RDG(1);
c(2)=CDGb - RDG(2);
c(3)=CDGc - RDG(3);

c(4)=CMGa - RMG(1);
c(5)=CMGb - RMG(2);
c(6)=CMGc - RMG(3);


c(7)=CGLa - RGL(1);
c(8)=CGLb - RGL(2);
c(9)=CGLc - RGL(3);

c(10)=CBDa - RBD(1);
c(11)=CBDb - RBD(2);
c(12)=CBDc - RBD(3);

end
```

Figure 36: MATLAB Function File for Constraint Conditions for Optimization

APPENDIX VII: CONSTANTS FOR OPTIMIZATION

Constants for Optimization of Transesterification Reaction:

```
function [PT]= run_kinetics_constants(X)

A1=X(1);
E1=X(2);
A2=X(3);
E2=X(4);
A3=X(5);
E3=X(6);

global C1;        %Average Concentration of Triglyceride

global C2;        %Concentration of Alcohol

global RT;        %Total Percentage of Product in Experimental
Results

n = 3;  %change this to number of intervals
T = linspace(328,338,n);

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
%%%%
for i=1:n

      [RDG(i), RMG(i), RGL(i),
RBD(i)]=run_reaction_kinetics_model_kinetics_parameters(A1,E1,A2,E2,
A3,E3,T(i),C1,C2);

      PT(i) = C1 + C2 + RDG(i) + RMG(i) + RGL(i) + RBD(i);

end

      PT = PT(1)+PT(2)+PT(3)-RT;

end
```

Figure 37: MATLAB Function File for Constants for Optimization of Transesterification Reaction

APPENDIX VIII: OPTIMIZATION OF TRANSESTERIFICATION REACTION

Optimization of Transesterification Reaction:

```
% Script file for Parameters Modelling Fitting approach
% global for kinetics modelling

global C1;      %Average Concentration of Triglyceride
global C2;      %Concentration of Alcohol
global RT;      %Total Percentage of Product in Experimental Results

% global for parameter fitting approach
global CDGa;    %Concentration of Diglyceride at 328K
global CDGb;    %Concentration of Diglyceride at 333K
global CDGc;    %Concentration of Diglyceride at 338K

global CMGa;    %Concentration of Monoglyceride at 328K
global CMGb;    %Concentration of Monoglyceride at 333K
global CMGc;    %Concentration of Monoglyceride at 338K

global CGLa;    %Concentration of Glycerol at 328K
global CGLb;    %Concentration of Glycerol at 333K
global CGLc;    %Concentration of Glycerol at 338K

global CBDa;    %Concentration of Biodiesel (Metyl Esters) at 328K
global CBDb;    %Concentration of Biodiesel (Metyl Esters) at 333K
global CBDc;    %Concentration of Biodiesel (Metyl Esters) at 338K

C1 = 6.7;
C2 = 1.1;
RT = 300;

CDGa = 4.6;
CDGb = 3.8;
CDGc = 3.2;

CMGa = 3.6;
CMGb = 2.1;
CMGc = 1.2;

CGLa = 6.9;
CGLb = 7.2;
CGLc = 9.1;

CBDa = 78;
CBDb = 80.2;
CBDc = 82;

% define the initial guess independent variables for optimization
% [A1,E1,A2,E2,A3,E3]
X0=[0.019 2.53 0.042 1.93 0.189 1.29];
% define the lower bounds for independent variables
LB=[];
% define the upper bounds for independent variables
UB=[];

% define the coefficients for the linear inequality constraints
A = [];
B = [];

% define the coefficients for the linear equality constraints
Aeq = [];
Beq = [];

% The function NONLCON lists the nonlinear constraints
% define the options for the optimization solver
options = optimset('Algorithm','interior-point','Display', 'iter','MaxFunEvals',1e6,'MaxIter',1e6, ...
    'TolFun',1e-6,'TolConSQP',1e-6,'TolX',1e-6,'FunValCheck','on');

% solving the optimization problem
[X,FVAL,EXITFLAG,OUTPUT,LAMBDA,GRAD,HESSIAN]=fmincon(@run_kinetics_constants,X0,A,B,Aeq,Beq,LB,UB,@kinetics_constan
ts_constraints,options);
```

Figure 38: MATLAB File for Optimization of Transesterification Reaction