KINETIC MODELING OF TRANSESTERIFICATION OF REFINED PALM OIL
TO PRODUCE BIODIESEL USING STRONTIUM OXIDE (SrO) AS A
HETEROGENEOUS CATALYST

by

MUHAMMAD FAIS BIN HARON

A thesis submitted to the Faculty of Chemical and Natural Resource Engineering in
partial fulfillment of the requirement for the Degree of Bachelor of Engineering in
Chemical Engineering (Biotechnology)

Faculty of Chemical and Natural Resources Engineering

Universiti Malaysia Pahang

FEBRUARY 2013

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREATIONS

Abbreations

BD	Biodiesel
DG	Diglyceride
ER	Eley-Rideal
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
GC	Gas Chromatography
LHHW	Langmuir-Hinshelwood-Hougen-Watson
ME	Methyl Ester
MeOH	Methanol
MG	Monoglyceride
MHDN	Methyl heptadecanoate
SSE	Sum of Square Errors
TG	Triglyceride

LIST OF SYMBOLS

Symbols

D Molecular diffusion coefficient (m^2/s)

K Adsorption coefficient ($Lmol^{-1}$)

k_1 Forward rate constant for the reaction of triglyceride to diglyceride ($Lmol^{-1}$ min^{-1})

k_2 Backward rate constant for the reaction of triglyceride to diglyceride ($Lmol^{-1}$ min^{-1})

k_3 Forward rate constant for the reaction of diglyceride to monoglyceride ($Lmol^{-1}$ min^{-1})

k_4 Backward rate constant for the reaction of diglyceride to monoglyceride ($Lmol^{-1}$ min^{-1})

k_5 Forward rate constant for the reaction of monoglyceride to glycerol ($Lmol^{-1}$ min^{-1})

k_6 Backward rate constant for the reaction of monoglyceride to glycerol ($Lmol^{-1}$ min^{-1})

M_T Thiele Modulus

Re Reynolds Number

V True pore volume (cm^3/g)

ε_p Catalyst particle porosity

τ_p Catalyst particle tortuosity

PEMODELAN KINETIC DARI TRANSESTERIFICATION MINYAK KELAPA SAWIT BERTAPIS SUPAYA MENGEMUKAKAN BIODIESEL MENGGUNAKAN STRONTIUM OKSIDA (SrO) SEBAGAI PEMANGKIN HETEROGEN

ABSTRAK

Biodiesel adalah satu sumber tenaga alternative untuk menggantikan bahan api. Pada asasnya, biodiesel adalah minyak sayuran dan lemak haiwan yang menjalani proses untuk menghasilkan gliserol dan asid lemak alyl ester. Dalam kajian ini proses transesterification telah dilakukan menggunakan Strontium Oksida (SrO) sebagai pemangkin heterogen. Objektifnya adalah untuk mengkaji model kinetic transesterification minyak sawit ditapis untuk menghasilkan biodiesel menggunakan SrO sebagai pemangkin heterogen. Keputusan menunjukkan bahawa kesan kepekatan pemangkin untuk 3.0% kepekatan SrO menghasilkan kepekatan methyl ester tertinggi, 0.78 mol/L, manakala kesan suhu menunjukkan suhu pada 60°C menghasilkan kepekatan methyl ester tertinggi iaitu pada 0.84 mol/L pada akhir eksperimen. Fungsi 'fminsearch' digunakan demi meminimumkan SSE data. Data eksperimen paling sesuai dimuatkan dengan ER model dengan nilai SSE yang terkecil iaitu 0.857 untuk kesan kepekatan pemangkin dan 4.471 bagi kesan suhu. Oleh itu, keputusan eksperimen menyokong bahawa kinetic ER sebagai model yang paling sesuai untuk digunakan.

KINETIC MODELLING OF TRANSESTERIFICATION OF REFINED PALM OIL TO PRODUCE BIODIESEL USING STRONTIUM OXIDE (SrO) AS A HETEROGENEOUS CATALYST

ABSTRACT

Biodiesel is an alternative source of energy to replace the fuel. Basically, biodiesel are vegetable oils and animal fats which undergoes a process to produce glycerol and fatty acid alkyl esters. In this study the transesterification process was performed using Strontium Oxide (SrO) as heterogeneous catalyst. The objective is to study the kinetic modeling of the transesterification of refined palm oil to produce biodiesel using SrO as a heterogeneous catalyst. The result show that the effect of catalyst concentration for 3.0 wt% of SrO concentration produced the highest concentration of methyl ester, 0.78 mol/L while the effect of temperature, the temperature of 60°C obtained the highest concentration of methyl ester, 0.84 mol/L at the end of the experiment. The function of 'fminsearch' was able to minimize the SSE of the data. The experimental data fit the ER model with the smallest value of SSE which 0.857 for effect of the catalyst concentration and 4.471 for effect of temperature. Therefore, the result supports that ER kinetics to be considered as the most appropriate model to use.

CHAPTER 1

INTRODUCTION

1.1   Background of Study

Petroleum diesel reserved is currently decreasing. On the other hand, the demand of this energy source is increasing day by day. Therefore, many studies have been done in finding a replacement for petroleum diesel. One of it is biodiesel. Biodiesel is an alternative energy source that has been introduced to replace the petroleum diesel. Biodiesel is more environmental friendly as it produces from natural resources and from the waste. Basically, biodiesel are vegetable oils and animal fats which undergo a process known as transesterification to produce glycerol and fatty acid alkyl esters.

1.2   Problem Statement

There are many types of catalyst which are homogeneous or heterogeneous acid-catalysts and base-catalysts and biocatalysts. Most of the previous studies used homogeneous base-catalyst as the catalyst in the process but there are some disadvantages. The disadvantages are listed below (Lopez *et al.*, 2005)

i)   the catalyst cannot be recovered,

ii)   the use of homogeneous catalyst necessitates the neutralization of glycerol at the end of the reaction,

iii)   there are limited use of continuous processing methodology and

iv)   the processes involved are very sensitive to the presence of water and free fatty acids.

The main problem of this study is to determine which of the two listed mechanisms of Langmuir-Hinshelwood-Hougen-Watson and Eley-Rideal is dominant.

1.3 Objective of the Study

The objective is to study the kinetic modeling of the transesterification of refined palm oil to produce biodiesel using SrO as a heterogeneous catalyst.

1.4 Research Scope

To achieve the objective of this study, two aims were identified:

1) To evaluate the use of SrO as a heterogeneous catalyst of transesterification in a batch reactor.

   i) Effect of Temperature

   ii) Effect of Catalyst Concentration

2) To identify the kinetic model based on matlab programming with kinetic model of Langmuir-Hinshelwood-Hougen-Watson and Eley-Rideal.

CHAPTER 2

LITERATURE REVIEW

2.1   Introduction

In this chapter, the literatures that are related to this study were sorted and cited to see the connection among various opinions of other articles. This chapter contains information relevant according to each sub headings and directly related to the topic of the study.

2.2   Sources of Triglycerides

There are several sources of vegetable oils use as feedstock for biodiesel production. The common vegetable oils used are rapeseed, sunflower, soybean and palm oil. The later was used as the source of triglycerides in this present study. Palm oil production has higher production yield compared to other vegetable oils

(Mekhilef *et al.,* 2011). Besides that, palm oil is easy to obtain because Malaysia is one of palm oil producing countries.

2.3   Biodiesel Production

This study uses the common process in producing a biodiesel from vegetable oil which is known as transesterification or alcoholysis. The reaction takes place when one mole of triglyceride reacts with three moles of alcohol to form one mole of glycerol and three moles of the respective fatty acid (Mittlebach and Remschmidt, 2006). Glycerol is being produce from triglyceride by three reversible reactions. Firstly, triglyceride reacts with methanol (methanolysis) to convert into diglyceride. Then, diglyceride will convert to monoglyceride and finally glycerol. The steps are shown in Figure 2.1.

*R₁, R₂, and R₃: Carbon chain of fatty acid
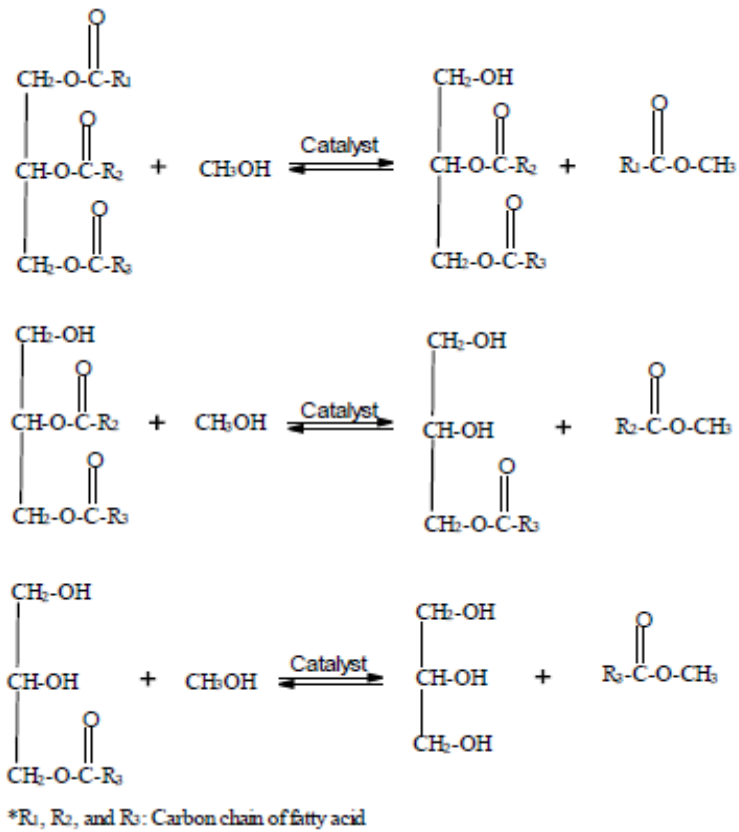
Figure 2.1: Stages of Transesterification Reaction

*R₁, R₂, and R₃: Carbon chain of fatty acid
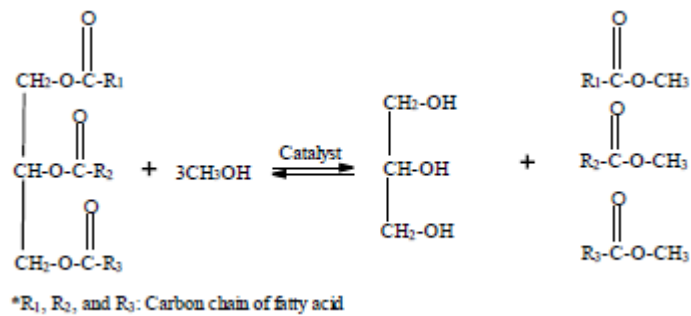
Figure 2.2: Overall Transesterification Reaction

2.4　Catalyst Application

There are several catalysts that can assist the transesterification reaction such as homogeneous or heterogeneous base-catalyst and acid-catalyst and biocatalyst. Mittelbach, (2006) stated that the reaction efficiency tends to be poor by using biocatalyst as the catalyst for the process because of low reaction rate, very high cost for industrial scale use and loss of activity within about 100 days of operation. Thus, it is either to use base catalysts or acid catalysts. By comparing both of the catalysts, base catalysts is more preferred to be use in the process because of the lower process temperature and the high reaction rates (Freedman *et al.*, 1986; Dossin *et al.,* 2006). Besides that, as stated in section 1.2, there are disadvantages in using a homogeneous catalyst. Neutralization and separation of the homogeneous catalysts from the reaction mixture is needed before it is being release to the environment so that it is acid free. Thus, this process will require large amount of solvents and energy (Dossin *et al.,* 2006).Therefore, by using a heterogeneous base catalyst can solve the all problems that had been faced by previous studies. Heterogeneous catalysts can easily be separated without using any solvents which leads to more cheaper and environmental friendly.

2.5　The Kinetic Modeling

There are several studies on kinetic modeling of transesterification using homogeneous bases catalysts and most of them have suggested that the reaction is second-order kinetics at the initial stages (Noureddini and Zhu, 1997; Vicente *et al.,*

2005; Karmee *et al,.* 2006) and followed by first-order or zero-order kinetics as the reaction proceeds (Darnoko and Cheryan. 2000).

However, there is less studies on kinetic modeling using heterogeneous bases catalysts. One of the literatures was Hattori *et al.* (2000) who proposed a five-step mechanism for transesterification of ethyl acetate using heterogeneous alkaline earth metal oxides by considering the rate-determining steps based on the basicity of the catalyst.

On the other hand, Dossin *et al.* (2006) studied the simulation of heterogeneously MgO-catalzed transesterification by comparing with three different models. The Langmuir-Hinshelwood-Hougen-Watson (LHHW), Eley-Rideal and the previous model proposed by Hattori *et al.* (2000). Dossin *et al.* (2006) proposed a kinetic model based on a three-step mechanism of Eley-Rideal and suggested that the rate-determining step for the MgO is methanol adsorption on its active sites.

Overall, Lopez *et al.* (2005) stated that the rate-determining step is either methanol adsorption on its active sites, or the reaction at the catalyst surface which is similar in both heterogeneous and homogeneous base-catalyzed transesterification.

2.5.1 Langmuir-Hinshelwood-Hougen-Watson (LHHW) Mechanism
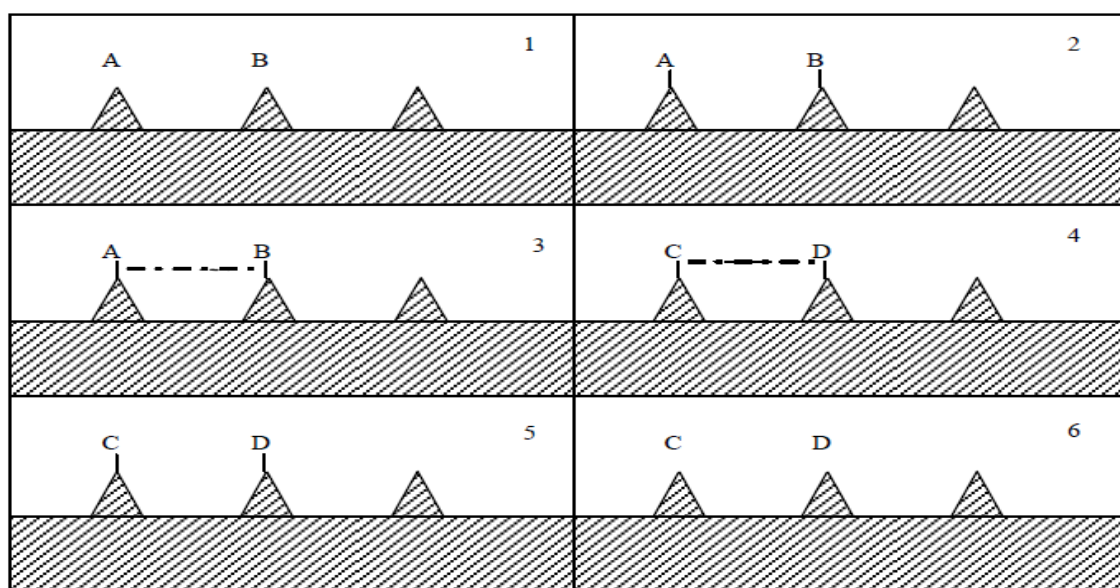
Figure 2.3: Langmuir-Hinshelwood-Hougen-Watson Mechanism

Basically, the Langmuir-Hinshelwood-Hougen-Watson (LHHW) mechanism is a mechanism that involves adsorption and desorption of atoms and molecules on the surfaces. From the figure, it is proposed that both reactant molecule A (methanol) and B (triglyceride) are adsorbed at different free sites on the catalyst surface. Then, the reaction takes place between chemisorbed (chemical bond between the surface and an atom or a molecule) molecules to give the products C and D. Finally, the adsorbed products C and D are desorbed.

$$A + B \leftrightarrow C + D \qquad [2.1]$$
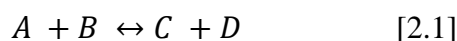
Based on Figure 2.3, the elementary steps of LHHW are derived in five-step sequence as presented in Equation 2.2 below. The 'S' represents the active site of catalyst surface and B represents tri-, di-, and monoglyceride molecules:

1. $A + S \leftrightarrow AS$ (chemisorption of A)

2. $B + S \leftrightarrow BS$ (chemisorption of B)

3. $AS + BS \leftrightarrow CS + DS$ (surface reaction)

4. $CS \leftrightarrow C + S$ (desorption of C)

5. $DS \leftrightarrow D + S$ (desorption of D)   [2.2]

If the surface reaction is assumed to be the rate-determining step (RDS), the final rate equation obtained is as follows (Hayes, 2001; Schwarzer, 2006; Hafizuddin, 2012):

$$(-r_A) = \frac{k_S K_A K_B ([A][B] - \frac{1}{K}[C][D]}{(1 + K_A[A] + K_B[B] + K_C[C] + K_D[D])^2} \qquad [2.3]$$

On the other hand, if step 1 or adsorption of A is the rate-determining step, the surface reaction is at equilibrium, as is the adsorption of B, C, and D. Therefore, the overall rate of reaction is influenced by the rate of adsorption, which is given by:

$$(-r_A) = r_{ads\,(A)} = k_{a\,(A)}[A]\theta_i - k_{d\,(A)}\frac{K_C K_D[C][D]}{K_S K_B[B]}\theta_i \qquad [2.4]$$

Further simplification of Equation 2.4 produces Equation 2.5 with the assumption that adsorption of A is the rate-determining step (Hayes, 2001; Hafizuddin, 2012).

$$(-r_A) = \frac{k_{a(A)}([A] - \frac{1}{K}\frac{[C][D]}{[B]})}{(1 + \frac{K_A[C][D]}{K\,[B]} + K_B[B] + K_C[C] + K_D[D]} \qquad [2.5]$$

The reaction scheme for LHHW in transesterification of triglycerides is given as follows (Macleod, 2008; Hafizuddin, 2012):

$$\frac{d[TG]}{dt} = -k_1\theta_{TG}\theta_A + k_2\theta_{DG}\theta_{BD} \qquad [2.6]$$

$$\frac{d[DG]}{dt} = k_1\theta_{TG}\theta_A - k_2\theta_{DG}\theta_{BD} - k_3\theta_{DG}\theta_A + k_4\theta_{MG}\theta_{BD} \qquad [2.7]$$

$$\frac{d[MG]}{dt} = k_3\theta_{DG}\theta_A - k_4\theta_{MG}\theta_{BD} - k_5\theta_{MG}\theta_A + k_6\theta_G\theta_{BD} \qquad [2.8]$$

$$\frac{d[BD]}{dt} = k_1\theta_{TG}\theta_A - k_2\theta_{DG}\theta_{BD} + k_3\theta_{DG}\theta_A - k_4\theta_{MG}\theta_{BD} + k_5\theta_{MG}\theta_A - k_6\theta_G\theta_{BD} \; [2.9]$$

$$\frac{d[A]}{dt} = -k_1\theta_{TG}\theta_A + k_2\theta_{DG}\theta_{BD} - k_3\theta_{DG}\theta_A + k_4\theta_{MG}\theta_{BD} - k_5\theta_{MG}\theta_A + k_6\theta_G\theta_{BD} \; [2.10]$$

$$\frac{d[G]}{dt} = k_5\theta_{MG}\theta_A - k_6\theta_G\theta_{BD} \qquad [2.11]$$

The transesterification reaction can be presented by the following stoichiometric equations:

$$TG + A \underset{k3}{\overset{k1}{\longleftrightarrow}} DG + BD \qquad [2.12]$$

$$DG + A \underset{k4}{\overset{k2}{\longleftrightarrow}} MG + BD \qquad [2.13]$$

$$MG + A \underset{k6}{\overset{k5}{\longleftrightarrow}} G + BD \qquad [2.14]$$

where triglyceride is TG, diglyceride is DG, monoglyceride is MG, glycerol is G and fatty acid methyl ester (biodiesel) is BD. There are also k's which represent the rate of reaction. The $k1$, $k3$ and $k5$ are the forward reaction rate while $k2$, $k4$ and $k6$ are the backward reaction rate. The lowest value of k is believed to be the rate-determining step of the reaction.

2.5.2 Eley-Rideal (ER) Mechanism
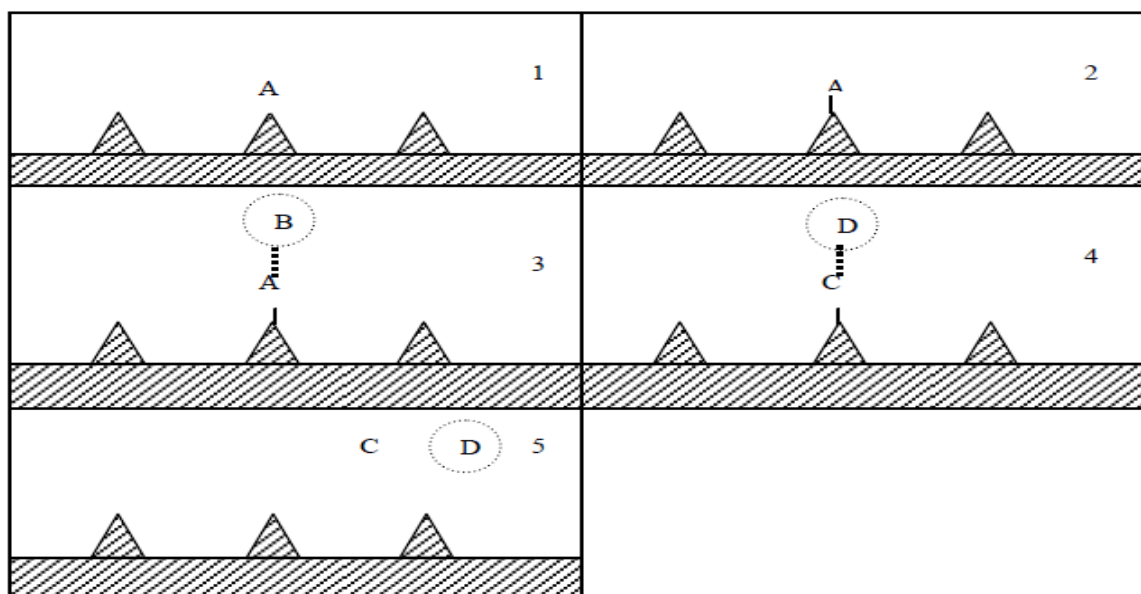
Figure 2.4: Eley-Rideal Mechanism

Similarly with the LHHW mechanism, the Eley-Rideal (ER) mechanism only differs on the early stage which is in the adsorption. It is assumed that only some of the molecules involved in the reaction are adsorbed onto the surface of the catalyst. From the figure, molecule A is the only molecule which chemisorbed onto the single site of the catalyst surface. Then, in step 3, the molecule B approaches the surface and without being adsorbed onto the surface, it reacts with the chemisorbed molecule A. Molecule A and B react to produce the chemisorbed C and molecule D, which attached to molecule C. Finally, the product C and D are desorbed.

For ER mechanism, if the rate-determining step is methanol adsorption, the rate of reaction is given as below (Dossin*et al.,* 2005, Hafizuddin, 2012):

$$(-r) = \frac{k_1([A] - (\frac{1}{K})(\frac{[C][D]}{[B]})}{1 + (\frac{K_1}{K})(\frac{[C][D]}{[B]} + K_3[D]} \qquad [2.15]$$

However, when the surface reaction became the rate-determining, the reaction rate becomes (Hafizuddin, 2012):

$$(-r) = \frac{k_{sr}K_1([A][B] - (\frac{1}{K})([C][D])}{1 + K_1[A] + K_3[D]}$$ [2.16]

The reaction scheme for ER in the transesterification of triglycerides is given as follows (Macleod, 2008; Hafizuddin, 2012):

$$\frac{d[TG]}{dt} = -k_1[TG]\theta_A + k_2\theta_{DG}[BD]$$ [2.17]

$$\frac{d[DG]}{dt} = k_1[TG]\theta_A - k_2\theta_{DG}[BD] - k_3[DG]\theta_A + k_4\theta_{MG}[BD]$$ [2.18]

$$\frac{d[MG]}{dt} = k_3[DG]\theta_A - k_4\theta_{MG}[BD] - k_5[MG]\theta_A + k_6\theta_G[BD]$$ [2.19]

$$\frac{d[BD]}{dt} = k_1[TG]\theta_A - k_2\theta_{DG}[BD] + k_3[DG]\theta_A - k_4\theta_{MG}[BD] + k_5[MG]\theta_A - k_6\theta_G[BD]$$ [2.20]

$$\frac{d[A]}{dt} = -k_1[TG]\theta_A + k_2\theta_{DG}[BD] - k_3[DG]\theta_A + k_4\theta_{MG}[BD] - k_5[MG]\theta_A + k_6\theta_G[BD]$$ [2.21]

$$\frac{d[G]}{dt} = k_5[MG]\theta_A - k_6\theta_G[BD]$$ [2.22]

2.5.3 Diffusional Resistance

The study was conducted using an appropriate batch reactor design according to some factors that needed to be avoided. Factors that should be avoided in these experiments are mass transfer limitation and also factors that can lead to saponification. By using a variable-speed and specific type of stirrer as shown in Figure 2.5, influence of the mass transfer can then be eliminated by following slurry process in case of reaction in a multiple phase system. According to Perry and Walas (1997), only a single impeller is required when the height ratio of the liquid to tank diameter is ≤ 1. In addition, for radial impellers, the ratio between impeller diameter, d to tank diameter, D_t should be $0.3 \leq d/D_t \leq 0.6$ (Perry and Walas, 1997).

It is very important to get rid of the mass transfer limitation in studying the kinetics of the reaction because the purpose of kinetics study was to identify the rate of determining of the reaction directly between the catalyst and the reactant. If external mass transfer resistance occurs, the rate of reaction is controlled by the mass transfer of the reactant from the bulk liquid phase to the surface of the catalyst particles (Veljkovic *et al.,* 2009). The evaluation of the effect of an external mass transfer limitation on the reaction rate can be performed by varying agitation rate, under the same reaction conditions. Normally, a high agitation speed is applied to establish a turbulence flow at high Reynolds number, which eliminates external mass transfer limitations. It also ensures that the catalyst is distributed widely in the reactor, and reduces the presence of dead zones (Lopez *et al.,* 2007). The Reynolds number can be estimated using the given equation:

$$Re = \frac{\rho D^2 N}{\mu} \qquad [2.23]$$