SIMULATION STUDY OF BIODIESEL PRODUCTION VIA TRANSESTERIFICATION PROCESS FROM WASTE COOKING OIL

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by

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TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CI	Compression ignition
DG	Diglyceride
E	Alkyl ester
FFA	Free fatty acid
GHG	Green house gaseous
LMA	Law of mass action
MG	Monoglyceride
ODE45	Ordinary differential equation 45
ROH	Alcohol
SDG	Sustainable development goal
TG	Triglyceride
WCO	Waste cooking oil

LIST OF SYMBOLS

A	Pre-exponential factor
C02	Carbon dioxide
CDG	Concentration diglyceride
CE	Concentration Ester
CG	Concentration glycerol
CMG	Concentration monoglyceride
CROH	Concentration alcohol
CTG	Concentration triglyceride
DAG	Diacylglycerols
Ea	Activation energy
H20	Water
k	reaction constant
k1	Reaction rate constant for equation 1
K1	Equilibrium constant
k10	Reaction rate constant for equation 10
k11	Reaction rate constant for equation 11
k12	Reaction rate constant for equation 12
k1r	Reaction rate constant for reversible equation 1
k2	Reaction rate constant for equation 2
k2r	Reaction rate constant for reversible equation 2
k3	Reaction rate constant for equation 3
k3r	Reaction rate constant for reversible equation 3
k4	Reaction rate constant for equation 4
k4r	Reaction rate constant for reversible equation 14
k6	Reaction rate constant for equation 10
k6r	Reaction rate constant for reversible equation 6
k8	Reaction rate constant for equation 8
k9	Reaction rate constant for equation 9
KOH	Potassium Oxide
MAG	Monoacylglycerols
NaOH	Natrium Oxide
OH-	Hydroxide
R	Universal gas constant
RO-	Alkoxide ion
T	Temperature
t	Time
TAG	Triacylglycerols

SIMULASI PENGHASILAN BIODIESEL MELALUI PROSES TRANSESTERIFIKASI DARIPADA MINYAK MASAK TERBUANG

ABSTRAK

Biodiesel adalah bahan bakar cair yang mesra alam dan satu alternatif yang dapat digunakan untuk menggantikan diesel konvensional. Ia boleh dihasilkan oleh pelbagai bahan makanan seperti lemak haiwan, minyak yang tidak boleh dimakan dan produk sampingan dari minyak sayuran penapisan. Biodiesel menjadi tumpuan sebagai bahan bakar yang boleh diperbaharui, yang tidak beracun dan boleh terbiodegradasi. Biasanya biodiesel disintesis oleh transesterifikasi minyak sayuran atau lemak haiwan bersama alcohol rantai pendek seperti methanol atau etanol. Tambahan lagi, kandungan oksigennya yang tinggi menjadikannya pilihan yang lebih baik untuk enjin diesel. Sisa minyak masak merupakan salah satu bahan makanan yang boleh diubah menjadi biodiesel. Oleh itu, dalam kajian ini sisa minyak masak telah diperkenalkan sebagai bahan mentah yang bertindakbalas dengan metanol. Kajian ini dijalankan dengan menggunakan perisian Matlab. Kesan parameter yang berbeza seperti suhu, nisbah alkohol dan minyak serta kepekatan pemangkin dikaji untuk mengoptimumkan keadaan reaksi. Didapati pada suhu 60℃, metil ester yang terhasil adalah yang tertinggi. Kajian ini juga mengkaji kesan nisbah minyak dan alkohol serta berat pemangkin terhadap hasil, penukaran dan selektiviti. Selain itu, model kinetik telah dikembangkan dan susunan keseluruhan reaksi transesterifikasi oleh sisa minyak masak adalah reaksi pesanan pertama. Keputusan simulasi yang diperoleh adalah munasabah dengan keputusan sorotan literasi dan dalam jurang yang sama dengan kajian yang dilakukan oleh pengkaji terdahulu.

SIMULATION STUDY OF BIODIESEL PRODUCTION VIA TRANSESTERIFICATION PROCESS FROM WASTE COOKING OIL

ABSTRACT

Biodiesel is an environmental-friendly and alternative liquid fuel that can be used to substitute conventional diesel. It can be produced by a variety of feed stocks such as animal fats, non-edible oils and by-product of the refining vegetable oils. Biodiesel becomes a spotlight as a renewable fuel that is non-toxic and is biodegradable. It is usually synthesised by the transesterification of vegetable oil or animal fat with short chain alcohol such as methanol or ethanol. Its high oxygen content makes it a better choice for diesel engines. Waste cooking oil is one of the feedstocks that can be converted into biodiesel. Therefore, in this simulation study, waste cooking oil has been used as the raw material that reacted with methanol. This study was done by using Matlab software to observe how the operating conditions affect on the yield, conversion and selectivity of biodiesel. It was found that the temperature of 60˚C exhibited the highest yield of methyl ester. Oil to alcohol ratio of 1:15 gives the highest yield at 59%and catalyst weight of 1.4 wt % leads to the maximum yield of biodiesel. The simulation results obtained reasonable with the literature results and within the range studied by the previous researchers.

CHAPTER 1

INTRODUCTION

1.1 Research background

Increasing environmental issues due to the utilization of fossil fuels by the current generation, rapidly growing uncertainty about global energy production and the high fluctuations in cost of petroleum products are the main cause to adopt for alternative fuel energy sources. Over the next 25 years, the global supply of conventional fuel sources is not likely to satisfy the global energy demand. By this outlook, notable amount of awareness has been given towards biodiesel production as an alternative for diesel. Further, due to the certainty that animal fats, plant oils and vegetable oils are all renewable and eco-friendly biomass sources, biodiesel has brought more attention (Hamzah et al., 2020).

Biodiesel is a renewable, non-toxic and biodegradable fuel that can be implied in internal combustion engines with compression ignition (CI). Biodiesel has been defined by ASTM (American Society for Testing and Materials) as monoalkyl esters of fatty acids which being derived from renewable lipid feed stocks such as vegetable oils or animal fats (Hamzah et al., 2020). The physicochemical properties of these fatty acid esters have a similarity with mineral diesel specifications. Therefore, they can be partially or completely replace petroleum-based diesel. The use of biodiesel in diesel engines as a pure fuel or blended in any proportion to fossil-diesel should requires no engine changes and can maintains their durability and reliability (Nazari et al., 2020).

The global warming may be reduced by using this alternative fuel which considered it as a promising fuel. Biodiesel provides significant reductions in particulates and carbon monoxide as compared to mineral diesel fuel. Thus, implying biodiesel as an alternative fuel is a way to minimize global air pollution and particularly reduces the emission levels that are potential and probable threats to human health (Nazari et al., 2020).

The economic effectiveness of the production of fatty acid methyl esters has been diminishing. One way of reducing the production costs for biodiesel fuels is the use of nonedible oils which tend to be considerably cheaper than edible vegetable oils. The technology of simultaneous transesterification of waste and fresh cooking oils were industrially introduced at the end of the ninety nineties (Buczek, 2014). Recycled or waste cooking oils have evolved as popular sources for the production of biodiesel as they are inexpensive and offer additional environmental benefits of using these substances which would otherwise need to be disposed (Buczek, 2014).

The first article which reported on successful engine test for methyl-, ethyl- and 1-butylesters produced from waste cooking oil appeared in 1983 (Nye et al., 1983). At the same time, recycle cooking oils were studied as raw materials by Mittelbach and Remschmidt who later developed a commercial process for converting waste cooking oils from households and restaurants as well as fatty waste from slaughter houses and sewage plants into biodiesel. Since dried, mechanical purified waste oil is sold about the half price of vegetable oils. Then, the use of such materials make sense from an economic point of view. In addition, the cost of the oil is about 85% of the operating cost of the process which makes this source of triglyceride a strong recommendation to diesel oil (Mittelbach et al., 2006).

1.2 Problem statement

Alternative energies such as biodiesel only contributes approximately 20 % to world energy source. The biodiesel could not fully replace current fossil fuels as biodiesel are combined with fossil fuels to be used in current technologies. There is a need to carry out more studies to optimize the efficiency of biodiesel in current technologies. Biodiesel production via transesterification reaction has been studied for its kinetic reaction model. Plus, the modelling and simulation study on various parameters involved in the transesterification will be carried out.

1.3 Research objectives

The objectives of this study are as the following:

i. To study the effect of reaction temperature on biodiesel via transesterification reaction in terms of conversion, selectivity and yield.
ii. To study the molar stoichiometric ratio of methanol to oil in transesterification reaction.
iii. To study the effect of catalyst weight that will affect the yield, conversion and selectivity of the end product in transesterification reaction.

1.4 Scope of study

The study will involve developing reaction kinetic model of transesterifcation to calculate the yield, conversion and selectivity in biodiesel production. The study will be conducted using MATLAB software to develop the reaction kinetic model which will be compared with the experimental data from previous studies to validate the reaction kinetics data calculated in order to ensure the reliability of the study. The parameter will be varying to get the best and optimum production process. The parametric study will includes temperature, alcohol to oil ratio and catalyst weight.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel chemical buildings block

Biodiesel is a fatty acid alkyl ester which typically produced from the reaction of vegetable oil with an alcohol chemically in the presence of a catalyst. In order to understand how biodiesel is being produced, one should understand first the chemical building foundations of biodiesel making.

2.1.1 Fatty Acids

Fatty acids are carboxylic acids that are present in biodiesel. From Figure 1 it shows the idealized molecular structure of a fatty acid. The terms free fatty acids (FFA) indicates to fatty acids that are not bound to other molecules (Turner, 2005).

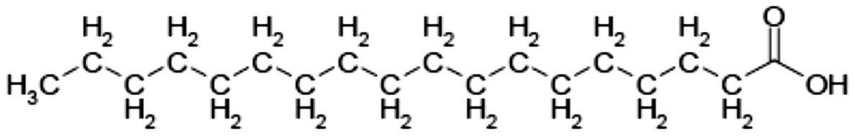

Figure 1: Molecular structure of fatty acids

The major drawbacks with oils that contain high free fatty acid (FFA) content is that it leads to formation of soap under base catalysis. This is because FFA tends to react with the base catalyst. Figure 2 shows a molecular structure of soap.

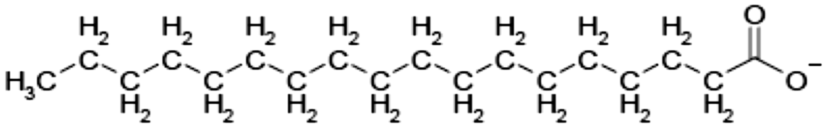

Figure 2: Molecular structure of soaps

2.1.2 Glycerol

Glycerol is a by-product in the biodiesel production process. It presents in dark coloration. The number of these impurities can vary from 20% to 60% depending on the raw material, efficiency of the catalytic process and the stages of preparation and purification of biodiesel (Monteiro et al., 2018). The molecular structure of glycerol is shown in Figure 3.

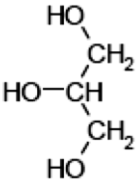

Figure 3: Molecular structure of glycerol

2.1.3 Alcohols

Alcohols are organic compounds that reacted with triglyceride to produce biodiesel alkyl esters. Methanol and ethanol are the most commonly used alcohol for the alcoholysis of vegetable oils in biodiesel production. Among these two kinds of alcohols, methanol is more widely used compared to ethanol. This is because ethanol is likely to forms emulsions which makes the separation of end products more difficult. Figure 4 and Figure 5 show the molecular structure of methanol and ethanol.

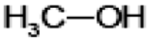

Figure 4: Molecular structure of methanol

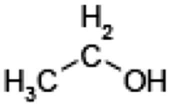

Figure 5: Molecular structure of ethanol

2.1.4 Alkyl Esters

Biodiesel is a fatty acid alkyl ester. The type of ester is dependent on the alcohol used during the reaction. The alkyl ester under methanolysis is a methyl ester. Figure 6 is the molecular structure of methyl ester

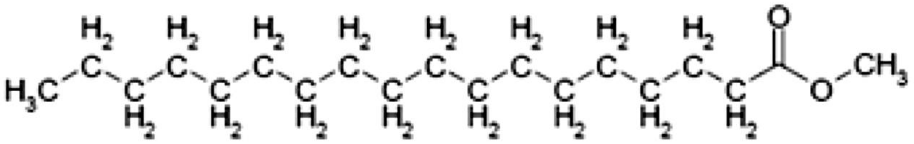

Figure 6: Molecular structure of alkyl ester

2.2 Potential of biodiesel

Biodiesel is the one of the alternative fuel with properties that make low concentration biodiesel-diesel fuel blends to run well in unmodified conventional compression ignition (CI) engines. Understanding these properties provides key toward evaluating and improving diesel engine performance and emissions. The benefits and technical challenge of the biodiesel as a fuel for diesel engine are revealed through the investigation of their properties relevant to engine performance and emissions (Nazari et al., 2020). The biodegradability of biodiesel has been proposed as a solution to waste problems. This biodegradable fuel has an expanding range of potential applications are environmentally friendly. Biodiesel degrades faster than mineral diesel due to its higher oxygen content which typically about 11% (Ahorsu et al., 2018).

The properties of biodiesel fuel that has high oxygen content improves the combustion efficiency results from the increase of the homogeneity of oxygen with the fuel during combustion. Therefore, the combustion efficiency of biodiesel is higher in value compared to the mineral diesel (Nazari et al., 2020). Another plus point of biodiesel is a good lubricant which means it has very low sulphur diesel. This characteristic is crucial in reducing wear on the engine parts and the injection system (Nazari et al., 2020).

Biodiesel is being produced from numerous feed stocks including refined vegetable oil, waste cooking oil and rendered animal fats. Different kind of feed stocks will produced biodiesel with distinct qualities that must be considered when replacing diesel fuel with biodiesel.

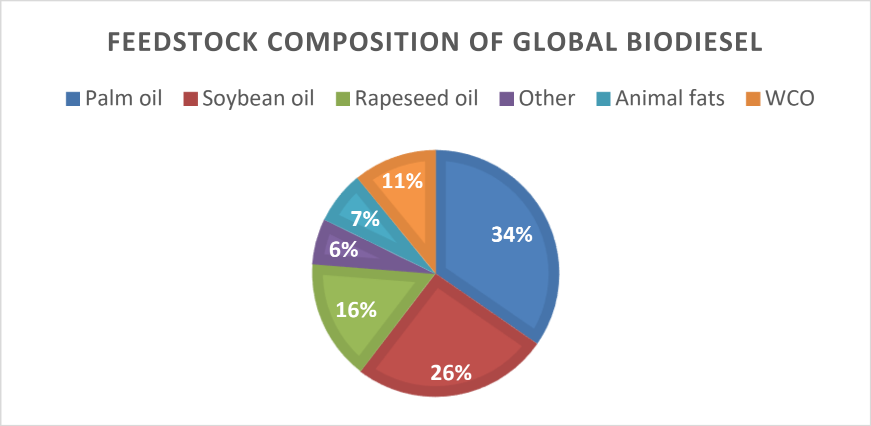

Figure 7: Feedstock composition of global biodiesel (Ahorsu et al., 2018)

Figure 7 shows the percentage of feed stocks used all around the world in 2019. These data remained virtually unchanged from year of 2017 but will likely increase in the years to come due to the rapid growth of biodiesel production.

2.3 Potential of waste cooking oil as feed stocks

Most biodiesel plants are using refined vegetable oils as their main feedstock. Therefore, the cost of refined vegetable oils contributed nearly 80% of the overall biodiesel production cost (Lam et al., 2009). Thus, it is undeniable that feedstock will be the most crucial variable affecting the price of biodiesel in the global market. In order to overcome this limitation, biodiesel manufacturer are focusing their attention on using low-cost feedstock such as waste cooking oil in order to ensure economic viability in biodiesel production. Waste cooking oil (WCO) is far less expensive than refined vegetable oils and therefore has become a promising alternative feedstock to produce biodiesel. In fact, generation of waste cooking oil in any country in the world is huge, and may result to environmental contamination if no proper disposal method is implemented (Lam et al., 2009).

Table 1 shows the estimation of waste cooking oil produced in selected countries (Gui et at., 2008). Based on the table below, waste cooking oil generated is more than 15 million tonnes. However, it is estimated that the WCO collected in Malaysia, is 0.5 million per year. This collected material is a good commercial choice to produce biodiesel due to its low cost. It should be noted that the actual amount of waste oil produced is much higher based on global production. It is recorded that biodiesel was relatively more expensive compared to the diesel fuel produced (Ahmad et al., 2017). This result moved most of the industrialist to utilise waste cooking oil (WCO) as a feedstock due to its relatively low price and availability.

Table 1: Quantity of waste cooking oil produces in selected countries (Gui et al., 2008)

Country	**Quantity (million tonnes/year)**
China	4.5
European	0.7-1.0
United States	10.0
Japan	0.45-0.57
Malaysia	0.5
Canada	0.12
Taiwan	0.07

It has been reported that around 50,000 tonnes of WCO generated from vegetable oils and animal fats are disposed to the environment without proper treatment in Malaysia (Abdullah et al, 2013). This results in water and soil contamination, aquatic life distraction, sewer system blockages and overflow in a long run. It also consequently generates undesirable impact to the entire environmental system. Thus, due to the abundant of this waste, selecting WCO as a raw material in the production of biodiesel would be the best alternative which gives a lot more advantages to the process as well as environment itself.

2.4 Chemical reaction involved

The reactions associated with biodiesel production include transesterification of triglycerides and esterification of free fatty acids (under acid catalysis), usually accompanied by potentially competing hydrolysis and saponification reactions.

2.4.1 Transesterification reaction

The common method to produce biodiesel from waste cooking oils is transesterification of triglycerides with alcohol in the presence of either a base or strong acid catalyst. Chemical catalysts (base and acid) of alcoholysis can be either homogeneous or heterogeneous. Non-catalytic alcoholysis reactions occur at high temperatures and pressures and still do not have any practical application (Bankovicilic et al., 2012). The transesterification reaction of triglycerides (TG) is as follows:

$$\mathrm{TG} + 3\mathrm{ROH}\ \text{catalyst} \rightarrow 3\mathrm{E} + \mathrm{G} \qquad (2.1)$$

The transesterification reaction occurs in three steps as shown in equation (2.2) to (2.4). The triglyceride first reacts with alcohol to form a diglyceride and an alkyl ester. The diglyceride is then converted to monoglyceride thus releasing an additional alkyl ester and lastly the monoglyceride to glycerol, releasing a final alkyl ester is converted.

$$\mathrm{TG} + \mathrm{ROH} \leftrightarrow \mathrm{DG} + \mathrm{E} \qquad (2.2)$$

$$\mathrm{DG} + \mathrm{ROH} \leftrightarrow \mathrm{MG} + \mathrm{E} \qquad (2.3)$$

$$\mathrm{MG} + \mathrm{ROH} \leftrightarrow \mathrm{G} + \mathrm{E} \qquad (2.4)$$

Where MG, DG, TG, and E refer to monoglyceride, diglyceride, triglyceride and alkyl ester respectively. The alkyl esters produced depend on the type of alcohol used. Ethanol (R=CH2CH3) and methanol (R=CH3) are the most common alcohols of choice. The choice of a catalyst is driven by factors such as the free fatty acid (FFA) content, fatty acid composition, economics and maximum product yield (Jaun et al., 2011).

There are three categories of catalysts that are often used in the transesterification of triglycerides which are homogeneous catalysts (acid or base), heterogeneous catalysts (acid or base) and enzymatic catalysts (Turner, 2005). The homogeneously and heterogeneously catalysed processes can either have one step or two steps (Bankovicllic et al., 2012). The latter process is recommended if a feedstock contains more than 1% of FFA (Ghadge et al., 2005). Although some authors have recently suggested the limit as 3% of FFA (Bankovicllic et al., 2012).

2.4.1(a) Homogeneously catalyzed transesterification

Homogeneously catalysed transesterification is the most industrially applied method for biodiesel production from non-edible oil via one-step and two step processes (Bankovicllic et al., 2012). The choice of process is dependent mainly on the FFA content. For one-step process it can be either an acid or base catalyst where base catalysed transesterification reactions being economically feasible and having high catalytic activity and quality of the yield. However, the conversion of FFA to alkyl esters using a base catalyst becomes impossible due to the formation of soap. As a result, the soap formation decreases the yield of biodiesel and inhibits the separation of glycerol (Bankovicllic et al., 2012).

Several studies have conflicting results when it comes to the percentage yield of biodiesel. For example a study by the Silva et al., (2009) shows a 99% ester yield when castor oil and ethanol were used to produce biodiesel at 16:1 alcohol to oil molar ratio in the presence of sodium ethoxide catalyst. However, other studies report relatively lower yields. For instance studies by Chitra et al., (2005) and Deng et al., (2010) report low yields when jatropha oil was used. The difference in percentage yield of biodiesel is due to the difference in FFA content of different oils.

The oil with low FFA content, alkyl ester yields of as high as 98% can be achieved in the presence of about 1% catalyst concentration under dry conditions to minimise soap formation (Bankovicllic et al., 2012). Sodium hydroxide (NaOH) and Potassium hydroxide (KOH) are commonly used base catalysts in base catalysed transesterification processes (Turner, 2005). The degree of conversion of triglycerides (TG) is highly influenced by the initial catalyst concentration and the optimal catalyst concentration has been reported to be 1% based on oil weight (Bankovicllic et al., 2012).

Savaranan et al., (2010) conducted studies that gave biodiesel yield of approximately 90% using acid catalysed transesterification. However, both acid and base catalysed reactions had their limitations with base catalysed reactions having longer reaction times and acid catalysed reactions requiring higher temperatures (Saravanan et al., 2010).

2.4.1(b) Heterogeneously catalyzed transesterification

Using a solid base catalyst has proven to be environmentally friendly as it provides a simpler means of recovery and purification (Bournay, 2005). This in turn results in the reduction of the amount of waste water. Furthermore, these catalysts can be regenerated for reuse in the process thus reducing operational costs. However, catalyst preparation is complex and diffusion inhibitions associated with the three phase mixture result in slow reaction rates (Meher et al., 2006).

Like homogeneously catalysed transesterification, the type of catalyst used is dependent on the FFA content of the non-edible oil (Bankovicllic et al., 2012). Solid acid catalyst is commonly used for the synthesis of fatty acid methyl esters from non-edible oils due to their ability to simultaneously perform esterification and alcoholysis (Lopez et al., 2007). There have been challenges in developing these with a completely heterogeneously catalysed two-step process (Bankovicllic et al., 2012).

2.4.2 Esterification reaction

An esterification reaction is an acid catalysed conversion of FFAs into alkyl esters. Esterification reaction is sometimes performed as a pre-treatment step for non-edible oils with high FFA content before base catalysed transesterification and it is also a resultant reaction for acid catalysed transesterification (Wang, 2007). Equation (2.5) shows the esterification of FFA to produce an alkyl ester and water. When used as a pre-treatment step in the presence of 2% ferric sulphate catalyst, 97% conversion of waste cooking oil with high FFA content was achieved in the study conducted by Wang et al. (2007).

$$\mathrm{FFA} + \mathrm{ROH\ Acid\ Catalyst} \leftrightarrow \mathrm{E} + \mathrm{H_2O} \quad (2.5)$$

2.4.3 Side Reactions of Saponification and hydrolysis

Depending on the quality of the non-edible oil, undesired side reactions may occured. Nonedible oil with excessive FFA content will be neutralised with excess base (NaOH or KOH) resulting in side reactions such as saponification and hydrolysis (Yazdani et al., 2007). A saponification reaction produces soap and water as shown in equation (2.6). During the saponification reaction water reacts with an alkyl ester under base catalysis to form FFA and alcohol as shown in equation (2.7).

$$\mathrm{FFA} + \mathrm{NaOH\ or\ KOH} \leftrightarrow \mathrm{A} + \mathrm{H_2O} \quad (2.6)$$

$$\mathrm{E} + \mathrm{H_2O\ Base\ Catalyst} \leftrightarrow \mathrm{FFA} + \mathrm{ROH} \quad (2.7)$$

Where: E stands for alkyl ester, and A stands for soap

2.5 Reaction kinetics

Reaction kinetics pertains to the rate of chemical reactions (reversible or irreversible). The kinetics for biodiesel production is largely dependent on the phase, reaction temperature, reactant concentration, and the type of catalyst used to lower the activation energy needed to start a reaction (He et al., 2007).

Rate equations are expressed in terms of reactant concentrations and are typically obtained by use of the law of mass action (LMA). LMA states that the rate of reaction is directly proportional to the products of reactant concentrations where each raised to the power of its coefficient in the reaction. The law only applies to elementary reactions; those depicting the mechanism at the molecular level and occurring as a single event (Turner, 2005). Simplicity tests are used to predict the order of the reaction, however these tests still need to be verified by experiment (Turner, 2005). Below are reactions of saponification, hydrolysis and transesterification and their rate equations under LMA.

Saponification reaction

$$\mathrm{FFA} + \mathrm{OH}^- \xrightarrow{\mathrm{k12}} \mathrm{A} + \mathrm{H2O} \tag{2.8}$$

Where k12 is the reaction rate constant

Saponification rate equation

$$\frac{\mathrm{dW}}{\mathrm{dt}} = \mathrm{k}_{12}[\mathrm{FFA}]^1\,[\mathrm{OH}^-]^1 \tag{2.9}$$

Hydrolysis reaction

$$\mathrm{ROH} + \mathrm{OH}^- \underset{\mathrm{k1r}}{\overset{\mathrm{k1}}{\leftrightarrow}} \mathrm{RO}^- + \mathrm{H2O} \tag{2.10}$$

The hydrolysis reaction is a reversible reaction, meaning it can proceed in either forward or backward direction depending on reaction conditions. The forward reaction rate is controlled by the reaction rate constant k1, and the reverse reaction is governed by k1r. When the rate of the forward reaction is the same as that of the reverse reaction, the reversible reaction is said to be in equilibrium. The equilibrium constant is given by equation (2.11) below

$$\mathrm{K1} = \frac{\mathrm{k1}}{\mathrm{k1r}} = \frac{[\mathrm{RO}^-][\mathrm{H}_2\mathrm{O}]}{[\mathrm{ROH}][\mathrm{OH}^-]} \tag{2.11}$$

Transesterification

Taking the first forward reaction of transesterification, as given by equation (2.2) and applying (law of mass action) LMA, the rate equation for transesterification of TG is found to be:

$$-\frac{\mathrm{d[TG]}}{\mathrm{dt}} = \mathrm{k1[TG][ROH]} \tag{2.12}$$

The reaction kinetics of biodiesel production changes with system temperature and pressure. According to (Freedman et al., 1986), transesterification follows pseudo first-order kinetics and the reverse reaction occurs as described by second-order kinetics. For methanol approximating at its critical point, (Warabi et al., 2004) considered kinetics to be first-order as described by equation (2.13).

$$-\ln \frac{x_t}{x_0} = kt \qquad (2.13)$$

The determination of reaction constant is necessary for the determination of activation energy required for the reaction to occur. Reaction constants are a function of temperature and are obtained by taking the slope of the plot ln (k) versus 1/T. The activation energy is then determined from the Arrhenius equation given in equation (2.14).

$$\ln k = \ln A - \frac{Ea}{RT} \qquad (2.14)$$

Where Ea is the activation energy; R is the universal gas constant; T is temperature.

2.5 Kinetic model

Kinetic models are necessary in predicting the extent of reactions that occur during the production of biodiesel and they also allow for optimization of process variables for better efficiency. Although the production of biodiesel has become rather crucial in the current trying times of the depletion of fossil fuel reserves and many other related challenges such as stricter air emissions standards, the kinetics of transesterification remain controversial. Two widely accepted kinetic models have been developed and will be discussed in the following sections.

2.6.1 Freedman's Kinetic Model

Freedman and his colleagues devised a chemical kinetic model for the alcoholysis of soy bean oil in the early 1980's at USDA and they used the overall reaction of TG to alkyl esters (equation 2.1) which occurs as a sequence of three steps as shown by equation 2.2, equation 2.3 and equation 2.4.

Freedman’s model seems to be devised from the law of mass action (LMA) because the first forward reaction proceeds according to equation (2.12). The overall order of the proposed forward reaction step is second-order and a condition called pseudo-first order occurs when the concentration of alcohol is assumed constant due to the very high molar ratio of alcohol to the TG (Freedman et al., 1986).

The aim of most kinetic models is to find the best fit of empirical data to models of simple reaction order; when the data doesn’t fit Freedman suggests what is called a shunt reaction which is a fourth-order reaction in which three alcohol molecules concurrently react with a TG (Freedman et al., 1986). The shunt reaction correlates to:

$$[\mathrm{TG}][\mathrm{ROH}]^3 \qquad (2.15)$$

Freedman studied the transesterification of soy bean oil using methanol and butanol with alcohol to oil ratios of 30:1 and 6:1 at temperatures varying from 20°C to 60°C (Freedman et al., 1986). Reverse reactions for the transesterification of soy bean oil were found to be second order for both methanol and butanol. When using butanol, the forward reactions were found to be second order at 6:1 alcohol to oil molar ratio, and pseudo-first-order at 30:1 alcohol to oil molar ratio. With methanol, the forward reactions were fourth order (shunt reaction) at 6:1 alcohol to oil molar ratio, and pseudo-first-order at 30:1 alcohol to oil molar ratio (Freedman et al., 1986).

The Arrhenius equation (equation 2.14) was used to find the rate constants and ultimately the activation energies by taking the slope of ln (k) vs. 1/T. There have been several investigations that used the application of the Freedman kinetic model. One study was conducted by Mittelbach, (1990) at the University of Karl Franzen

University, Austria and it was found that the reaction was not a single phase as previously suggested by Freedman. However, for the first two minutes a two phase system was observed. Another discrepancy found by Mittelbach, (1990) is that the reaction order of the forward reactions is not governed by second-order kinetics.

An investigation by Bikou et al., (1999) focused on the study of the effect of water on the kinetics of the transesterification of cotton oil with ethanol under the catalysis of potassium hydroxide. Contrast to Freedman's kinetic model, Bikou et al., (1999) found that each of the three transesterification reaction steps were third order with respect to methanol.

2.6.2 Komer's Kinetic Model

Komers' model is based on the transesterification of vegetable oil using methanol as a solvent and potassium hydroxide (KOH) as catalyst. Komers and his colleagues built a model from suggested mechanisms for all the competing reactions which are saponification, methanolysis and methoxide formation that occur during transesterification and is the only model that explicitly treats the amount of water and catalyst present (Komers, 2002).

The research on the negative effect of water on the equilibrium reactions by Bikou et al., (1999) is supported by this model. Komers proposed simplifying assumptions that resulted in a system of six rate equations including eight reaction species and ten rate constants (Komers, 2002). The simplifying assumptions are listed below:

a) The concentration of FFAs is negligible

b) Among all the theoretically possible reactions only two progress to form products which are the alcoholysis of acylglycerols and the saponification of TAG, DAG, MAG, or alkyl esters (E).

c) All the isomers of TAG, DAG, MAG, and E proceed at the same rate, with the same mechanism.

d) Alcoholysis is catalysed by OH or RO- (alkoxide) ions. Concentrations of OH and RO ions are much smaller than those of TAG and ROH.

The above mentioned assumptions give rise to the differential equations below:

$$\frac{-\,\mathrm{dTAG}}{\mathrm{dt}} = \mathrm{b.OH.}(\mathrm{k_2.TAG.ROH} - \mathrm{k_{2r}.DAG.E}) + \mathrm{a.OH.k_9.TAG} \qquad (2.16)$$

$$\frac{-\,\mathrm{dDAG}}{\mathrm{dt}} = \mathrm{b.OH.}(\mathrm{k_2.TAG.ROH} - \mathrm{k_{2r}.DAG.E} + \mathrm{k_4.DAG.ROH} - \mathrm{k_{4r}.MAG.E}) +$$
$$\mathrm{a.OH.}(\mathrm{k_9.TAG.} + \mathrm{k_{10}.DAG}) \qquad (2.17)$$

$$\frac{-\,\mathrm{dMAG}}{\mathrm{dt}} = \mathrm{b.OH.}(\mathrm{k_4.DAG.ROH} + \mathrm{k_{4r}.MAG.E} + \mathrm{k_6.MAG.ROH} - \mathrm{k_{6r}.G.E}) +$$
$$\mathrm{a.OH.}(-\mathrm{k_{10}.DAG.} + \mathrm{k_{11}.MAG}) \qquad (2.18)$$

$$\frac{\mathrm{dG}}{\mathrm{dt}} = \mathrm{b.OH.}(\mathrm{k_6.MAG.ROH} - \mathrm{k_{6r}.G.E}) + \mathrm{a.OH.k_{11}.MAG} \qquad (2.19)$$

$$\frac{-\,\mathrm{dROH}}{\mathrm{dt}} = \frac{\mathrm{dE}}{\mathrm{dt}} = \mathrm{b.OH.}(\mathrm{k_2.TAG.ROH} - \mathrm{k_{2r}.DAG.E} + \mathrm{k_4.DAG.ROH} -$$
$$\mathrm{k_{4r}.MAG.E} + \mathrm{k_6.MAG.ROH} - \mathrm{k_{6r}.G.E} - \mathrm{k_8.E}) \qquad (2.20)$$

$$\frac{\mathrm{dOH}}{\mathrm{dt}} = \frac{\mathrm{dA}}{\mathrm{dt}} = \mathrm{b.OH.k_8.E} + \mathrm{a.OH.}(\mathrm{k_9.TAG.} + \mathrm{k_{10}.DAG} + \mathrm{k_{11}.MAG}) \qquad (2.21)$$

$$\frac{\mathrm{dH_2O}}{\mathrm{dt}} = \frac{\mathrm{dFFA}}{\mathrm{dt}} = \mathrm{a.k_{12}.FFA.OH} \qquad (2.22)$$

Where a= [TAG]0 and b= [ROH]0

2.6.3 Other Model

There are various other studies that investigated the transesterification of oil for biodiesel synthesis, under catalytic and non-catalytic conditions. Below is a summary of different kinetic models.

Table 2-1: Summary of different kinetic models

Model	Reactions	Order
Three steps, reversible, alkaline as catalyst	$\text{TG+MeOH} \underset{k-1}{\overset{k1}{\leftrightarrow}} \text{DG+ME}$ $\text{DG+MeOH} \underset{k-2}{\overset{k2}{\leftrightarrow}} \text{MG+ME}$ $\text{MG+MeOH} \underset{k-3}{\overset{k3}{\leftrightarrow}} \text{GL+ME}$	Second order
Three steps, irreversible, no catalyst	$\text{TG+MeOH} \overset{k1}{\rightarrow} \text{DG+ME}$ $\text{DG+MeOH} \overset{k2}{\rightarrow} \text{MG+ME}$ $\text{MG+MeOH} \overset{k3}{\rightarrow} \text{GL+ME}$	First order
One step, reversible, no catalyst	$\text{TG+3MeOH} \underset{k-1}{\overset{k1}{\leftrightarrow}} \text{GL+3ME}$	First order
One step reversible, different base catalysts	$\text{TG+3MeOH} \underset{k-1}{\overset{k1}{\leftrightarrow}} \text{GL+3ME}$	First order, or third order, depends on

2.7 Parameters that influence the transesterification reaction

2.7.1 Reaction temperature

The transesterification reaction is endothermic and according to LE Chateliers principle it will favoured by a high temperature. The reaction can take place at different temperature. In order to increase the rate of reaction, biodiesel production should be performed at a high temperature and pressure (Phan et al., 2008). According to Baroutian et al., (2010) the most desirable range of temperature is between 50˚C to 70˚C. Higher temperatures increase solubility of unwanted materials in the product stream resulting in challenges in separation process. The boiling point of methanol is 64.7˚ C. Thus, the transesterification reaction could be carried out from room temperature up to 65˚C since temperatures higher than this will boil off the alcohol and result in a much lesser yield (Sharma et al., 2008).

Yaakob et al., (2012) stated that the ideal reaction temperature is often near the boiling point of alcohol. Besides, the reaction temperature is also depends on the chemical and physical properties of the type of oil used. Temperature has no detectable effect on the ultimate conversion to ester. However, higher temperatures decrease the time required to reach maximum conversion (Pinto et al., 2005). Transesterification can be conducted at various temperatures ranging from room temperature to the boiling point of the alcohol employed which 68°C in case of methanol so that the reactor does not need to be pressurized. Thus, the usual temperature used during transesterification in most literature is 60-65°C. When the reaction temperature closes or exceeds the boiling point of methanol at 68 °C, the methanol will vaporize and form a large number of bubbles which may inhibit the reaction.

2.7.2 Alcohol to oil ratio

Methanol is a commonly used alcohol for transesterification because of its low price and highly reactive nature (Lang et al., 2001). The stoichiometric ratio required for transesterification is 1:3 moles of vegetable oil to alcohol. However, it has been found that the molar ratio of vegetable oil to alcohol depends on the type of catalyst used for the reaction. For example, the molar ratio of 1:6 moles of soybean oil to methanol has been found to be the most suitable in the case of alkali-catalyzed transesterification because an excess of alcohol is required to drive the reaction (Freedman et al., 1986). For acid-catalyzed transesterification, a 1:30 vegetable oil to alcohol ratio is generally used (Freedman et al., 1984). The alcohol to oil ratio is particularly important in ensuring that the system maintains a two phase system. The transesterification reaction is reversible thus using an excess of reactant which is alcohol can help move the reaction forward. The stoichiometric ratio for transesterification requires 3 moles of alcohol and 1 mole of triglyceride to yield 3 moles of fatty acid alkyl ester and 1 mole of glycerol. However, to achieve better results transesterification will usually carried out with an extra amount of alcohol in order to shift the equilibrium to the desired biodiesel product.

Usual commercial practice is to use excess alcohol. For instance, alcohol to oil ratio of at least 6:1 instead of molar stoichiometric ratio of 3:1. As a result, more biodiesel is formed in a shorter period of time. This also leads in a decrease in residence time and an increase in reactor capacity (Allen et al., 2006). But, the cons is, it does requires the expense of operating cost. Increasing the alcohol to oil ratio beyond the stoichiometric ratio of 3:1 is really advantageous as it enhances the settling process of the products. If a ratio below 7:1 is used, several hours are required for the completion of the settling process.

On the other hand, the settling process takes approximately 30 min for ratios of 7:1 and 8:1 (Phan et al., 2008). Previous study also states that the ratio is subject to the type of catalyst that are to be used. For instance, the optimal ratio for a waste cooking oil feedstock is 4.8 in the presence of NaOH catalyst while it may be up to 250 in the presence of acidic catalysts. El-Sabagh et al., (2011) also stated that when more alcohol to oil molar ratio is used for instance 9:1 or 12:1 the transesterification reaction will shift toward products where the yield of the transesterification reaction increases and viscosity of biodiesel declines (El-Sabagh et al., 2011).

2.7.3 Catalyst weight

The greater in the number of catalysts will increase the reaction speed and thus lead to the increases yield of the biodiesel produced. Large amount of catalyst will further reduce the activation energy so that it increases the number of activated molecules increasing reaction speed. The catalyst functions to accelerate the reaction by reducing activation energy but does not affect the location of equilibrium (Mostapa et al., 2019). In addition, the use of large amounts of alkaline catalysts can neutralize free fatty acids in triglycerides. The optimum concentration of catalyst causes the free fatty acids that react with the catalyst increasing so the number of acidic products becomes lower. The higher number of base catalysts used, the more methyl esters will be formed (Sophie et al., 2018).

The effect of varying the amount of alkali- catalyst was studied by Daniyan et al.,(2015) for palm olein vegetable oil. Production of biodiesel was done with the catalyst (NaOH) in different amounts (wt. %) to the palm olein oil weight. Catalyst amount was varied in the range of 0.6-1.6 wt. % to oil for six different values which are 0.6, 0.8, 1.0, 1.2, 1.4, and 1.6 wt. % of unused oil weight. The study indicates that the excess addition of NaOH increased the yield. The optimum biodiesel yield was achieved using 1.4 wt. % of NaOH to oil, which produced an 88.0% yield of transparent ester. NaOH greater than 1.4 wt. % to oil produced a smaller ester yield, because of the presence of soap and gel formation which prevents ester layer separation (Daniyan et al., 2015).

Vyas et al., (2011) also studied on the effect of variation of amount of catalyst on conversion. Catalyst amount was varied in the range of 0.5% to 2.5% (wt/wt of the oil taken).The result shows that the conversion increased firstly with the increase of catalyst amount from 0.5% to 1.5%. However, with further increase in the catalyst amount from 1.5% to 2.5%, the conversion decreased due to soap formation that will affect the reaction of transesterification (Vyas et al., 2011).

2.8 Integration of sustainability development

The Sustainable Development Goals (SDGs) which also known as Global Goals were adopted by all United Nations Member States in 2015 as a universal call to action in in order to put a stop on poverty, protect the planet as well as to ensure that all people enjoy peace and prosperity by 2030.The SDGs comprise of 17 integrated goals that recognize the action in one area that will affect the outcomes in others. That development must be balance in social, economic and environmental sustainability. The 17 goals are poverty eradication, zero hunger, good health and well-being, quality education, gender equality, clean water and sanitation, affordable and clean energy, decent work and economic growth, industry, innovation and infrastructure, reduce inequality, sustainable cities and communities, responsible consumption and production, climate action, life below water, life on land, peace, justice and strong institutions and partnerships for the goals.

This research is closely related to Goal 7 which is affordable and clean energy. This goal is to ensure access to affordable, reliable sustainable and modern energy for all. The focus is to include access to affordable and reliable energy while increasing the share of renewable energy by 2030. This will leads to the enhancement of regional energy access as well as reducing reliance on conventional diesel. Plus, it will also support the increased in use of renewable resources as feedstocks for a range of industrial processes.