

EXPERIMENTAL AND NUMERICAL INVESTIGATION OF TRANSESTERIFICATION
OF VEGETABLE OIL WITH A CONTINUOUS FLOW CAPILLARY REACTOR

by

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ABSTRACT

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Biodiesel, Fatty Acid Methyl Ester (FAME), is a renewable fuel that is a promising alternative to fossil fuels in the future. Biodiesel not only has similar properties to diesel derived from fossil fuel, but it also provides more environmentally friendly due to lower carbon monoxide and sulfur emissions. Biodiesel is composed of methyl esters which can be synthesized from various fatty acid sources with a present of catalyst. Typical feed-stocks include vegetable oils, such as waste cooking oil, animal fats, and even oil from algae. Four primary ways to use vegetable oil as a fuel are direct use, blending with diesel via a co-solvent, using oil produced by thermo cracking (pyrolysis), and using methyl esters made by transesterification/esterification. The transesterification process is the most frequently used methods for making biodiesel because it gives the fuel that has similar or better properties as diesel fuel. However, most biodiesel is still produced using batch reactor technology that is decades old. Improvements in biodiesel quality and economics can be achieved by employing alternate reactor technology for biodiesel synthesis that can reduce reactor size and energy

consumption. Recently, microreactor technology, an important method of process intensification, was widely used to apply in biodiesel to reduce the residence time. In addition, the biodiesel producers typically employ as catalyst to speed the transesterification reaction. The catalysts are usually homogeneous bases but strong acids can work as well.

In this work, the use of capillary reactor technology for the intensification of transesterification was studied. Both homogeneous alkaline and heterogeneous acid catalysis were investigated. Reactions were conducted experimentally in stirred batch and continuous flow capillary reactors. To confirm the intensification process, the titanium micro-reactor was also presented to verify the rapid mass transfer in microscale. Moreover, the batch reactor and capillary reactor are compared to show the effectiveness of biodiesel production in capillary reactor. The results show that, from the homogeneous alkali-catalyst, conversion of vegetable oil greater than 98% could be achieved for significantly lower residence times and energy input compared to the stirred batch reactor case. This enhanced performance was due to the intensification of mass and heat transfer enabled by the use of the capillary reactor. In order to reduce the purifying process, the experiment is investigated the use of a heterogeneous acid catalyst for the transesterification reaction in a capillary reactor. The catalyst will be immobilized in the reactor as a packed bed of micro-particles. The results indicated that high surface area of packed bed reactor gave the 84% oil conversion with a significant reducing in residence time for 1 h. Because of the micro-particles, there was too high pressure drop in the reactor during the experiment. A mathematical model for the multiphase flow in a capillary including transesterification reaction kinetics was developed. The model was solved approximately using a time accurate finite element-based computer code. The predictions made by the model follow the same trends observed in the experiments.

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CHAPTER 1

INTRODUCTION

In recent decades, the leapfrog progress of streamlined science and technology contributed to increase the energy consumption in many sectors. As a result, the energy crisis has become a hot issue seriously discussed worldwide. Engineers and scientists all over the world are working hard to find solutions for this crisis by exploring new disciplines and ways. One of the best possible solutions is alternative energy. In addition, it can generate a significant amount of energy, it is unlimited and at the same time it is environmentally friendly. Biodiesel is one of the best alternative energy to replace the conventional fossil fuel in the future. In 1911, vegetable oils were first used as a fuel of diesel engine invented by Rudolph Diesel[1]. The advantages of vegetable oils as diesel fuel are liquid-nature-protability, heat content (80% of diesel fuel), ready availability, and renewability[2]. However, several chemical properties of vegetable oils and fats among them are the high viscosity and high molecular weight, causing the poor fuel atomization and low volatility leading to incomplete combustion and severe engine deposits. Moreover, there are injector coking and piston ring sticking in the long term of using oils and fats[3]. As the breakthrough, Biodiesel was used in diesel engine because there are many advantages such as high flash point, high cetane number, low viscosity, high lubricity, biodegradability, environmentally friendly due to less carbon monoxide emission, as well as fewer emission profiles compared to conventional fossil fuel [4]. Biodiesel also has similar properties to that of diesel produced from crude oil and can be directly to run existing diesel engines or as a mixture with crude oil diesel [5]. Biodiesel or methyl ester can make from vegetable oils (e.g., soybean, cottonseed, palm, peanut, rapeseed/canola, sunflower, safflower, coconut) or animal fat (tallow) as well as waste cooking oil with alcohol. There are many alcohol used in the biodiesel production such as methanol, ethanol, propanol, butanol, and amyl

alcohol. From these alcohols, the most frequently used materials are methanol and ethanol because they are lower cost and the alkali catalyst is easily dissolved[2].

In the present project, the capillary reactor used is proposed for transesterification of vegetable oil which employs with homogeneous and heterogeneous catalyst. The alkali and acid catalyst are also presented in the experiments. In order to compare the effectiveness of intensive biodiesel synthesis, the comparison of batch, capillary, and micro reactor is indicated by using energy consumption. To illustrate the improvement of the biodiesel production, a numerical finite element model for the transesterification reaction in a slug flow in capillary reactor will be developed and utilized. In the model, the convective and diffusion mass transfer are used in the transesterification reaction.

Chapter 2 contains the background that shows the general methodology in biodiesel synthesis, the effecting variables in biodiesel production, the comparisons of homogeneous and heterogeneous catalysts, the comparisons between alkali and acid catalyst, activity of solid catalysts for biodiesel production in biodiesel production, and characteristics of fluid flow in micro-channel.

Chapter 3 shows the transesterification of vegetable oil with homogeneous alkali catalyst by using the conventional batch reactor. Moreover, the experiments have been intensively investigated the variables affecting in the biodiesel production and the energy consumption is also calculated for batch reactor technology.

Chapter 4 illustrates the improvement of transesterification of vegetable oil with a continuous flow capillary reactor. This work demonstrates the use of capillary reactor for both mixing and intensifying the transesterification reaction. The vegetable oil conversion was observed under various residence times and reaction temperatures. In addition, the results from transesterification in batch reactor and capillary reactor will be also compared. Furthermore, the energy consumption of capillary reactor is computed to compare with batch reactor as well.

Chapter 5 presents the transesterification of vegetable oil in a presence of homogeneous alkali catalyst with titanium micro-reactor. The experimentation shows the effectiveness of residence time reduction by using micro-reactor when compared with capillary and batch reactor at the same condition.

Chapter 6 demonstrates the transesterification of vegetable oil with heterogeneous acid catalyst using TiO_2SO_4 as a catalyst. Moreover, TiO_2SO_4 shows the promising solid acid catalyst in transesterification of vegetable oil with dry methanol using capillary reactor.

Chapter 7 exhibits the development of a numerical finite element model for the transesterification reaction in a slug flow in capillary reactor. In the model, the convective and diffusion mass transfer are used in the transesterification reaction to illustrate the improvement of the biodiesel production.

CHAPTER 2

BACKGROUND

The biodiesel or Fatty Acid Methyl Ester (FAME) which is alternative fuel is one of the promising fuels to replace diesel fuel which will be diminishing in the future. Generally, there are four methods to produce biodiesel which are blending with petro diesel, pyrolysis (thermal cracking), microemulsification (co-solvent blending), and transesterification/esterification. These methods were established to reduce the high viscosity of vegetable oils. The biodiesel can substitute in common diesel engines without operational problems[1]. The transesterification is the most commonly used method for converting oil to biodiesel. The vegetable oils, animal fats, or waste cooking oil are considered to be the reactant in the process with alcohol. The methanol is the preferred alcohol for producing biodiesel because of its low cost. Normally, transesterification employs with catalyst because methanol cannot dissolve in oil. In general, there are three categories of catalysts used for biodiesel production which are alkali, acids, and enzymes. Enzyme catalysts have become more attractive because they do not produce soap. However, they are less used in commercial because they use longer time reaction and are higher operating cost. The others of commonly catalysts using, alkali and acid catalysts are worldwide used for biodiesel production due to low cost of material. Sodium hydroxide and potassium hydroxide were commercially used to be alkali-catalyzed transesterification. The disadvantages of using alkali-catalyzed transesterification are low free fatty acid (FFA) oil requirement, saponification reaction with FFA, and emulsion formation. The acid-catalyzed transesterification/esterification method normally is used for high FFA. The advantage of acid-

catalyzed esterification, it does not make soap in the process but it is slow rate of reaction at low reaction temperature and use high molar ratio between methanol and oil[5].

2.1 The method to make biodiesel from vegetable oils and animal fats [6]

There are four primary ways to make biodiesel, direct use and blending, microemulsion (co-solvent blending), thermo cracking (pyrolysis), and transesterification/esterification.

2.1.1 The direct use and blending with diesel fuel

These methods have been used and studied since the beginning of eighteenth century. The most study concluded that vegetable oil blending with diesel fuel was not suitable for long-term fueling of direct injection diesel engines. Msipa et al.[3] reported that mixture fuel should contain a maximum of 34% unsaturated triacylglycerol in vegetable oil blending with No.2 diesel fuel (DF2) to achieve proper fuel atomization. If the DF2 is mixed with waste vegetable oil for 10%, there will be a loss in 12% of power, slightly increasing in fuel consumption, slightly decreasing in combustion efficiency, the same property in viscosity lubricants. In the long term test, the yielding engine problems are similar to the use of vegetable oils as the fuel. However, there are advantages of the vegetable oil blending with DF2 such as reducing in nitrogen oxides (NO_x), carbon monoxide (CO) and slightly hydrocarbon [6, 7].

2.1.2 Pyrolysis

Pyrolysis is the thermal degradation of vegetable oils by heat in the absence of oxygen, which results in the production of alkanes, alkenes, alkadienes, carboxylic acids, aromatics and small amounts of gaseous products. The chemical compounds of heavy hydrocarbons are similar to the present petroleum refinery product[8].

2.1.3 Microemulsion (co-solvent blends)

Microemulsion (co-solvent blends) is the method that mixing diesel fuel with low-molecular-weight alcohol and ionic or non-ionic amphiphiles for reducing viscosity of vegetable oils. Alcohol such as methanol or ethanol has limited solubility in nonpolar vegetable oil.

Therefore, amphiphilic compound is normally added to increase solubility, and reduce viscosity of oil [9].

2.1.4 Transesterification/esterification

The most commonly used method is transesterification/esterification of vegetable oils and animal fats. The transesterification is the process of exchanging of hydrocarbon group between the oil and alcohol to make biodiesel. Esterification is the process that loses the proton in reaction and gets water in the production. These reactions are often catalyzed by an acid in esterification or base in transesterification[10]. The alkali-catalyst was used in transesterification such as sodium hydroxide or potassium hydroxide. Moreover, sulfuric, hydrochloric, and acetic acid are normally used in the esterification process. The biodiesel product is a heterogeneous mix of fatty acid methyl esters (FAMES) whose composition depends on the oil feedstock. The disadvantages of using alkali-catalyzed transesterification are low FFA oil requirement, saponification, and emulsion formation. The overall transesterification reaction is shown in Figure 1.

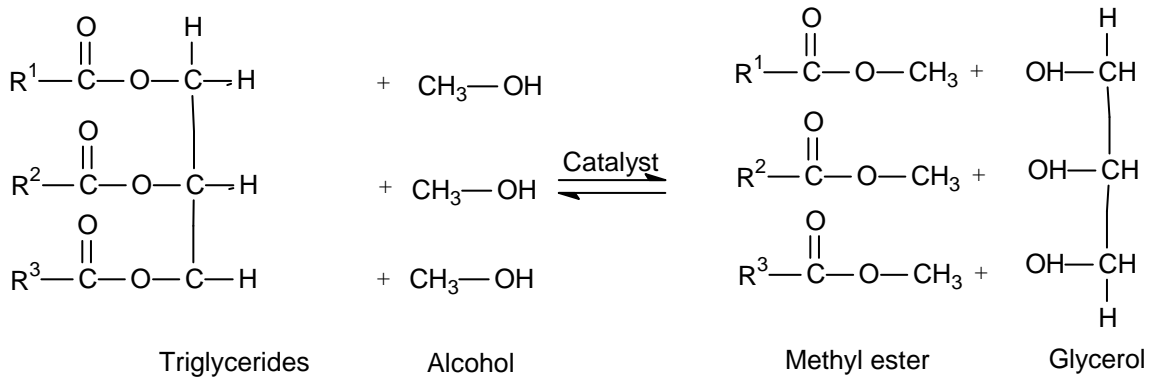


Figure 2.1 Transesterification reaction of oil and alcohol [11]
Where R₁, R₂, R₃ are long chain hydrocarbons (fatty acid chains)

However, the FFA can react with alcohol to form biodiesel by an acid-catalyzed esterification reaction. This reaction is very useful for handling oils or animal fat with high FFA.

The acid-catalyzed esterification does not make soap in the process. However, it is slow rate of reaction at low reaction temperature and use high molar ratio between methanol and oil.

The esterification reaction is shown in Figure 2.

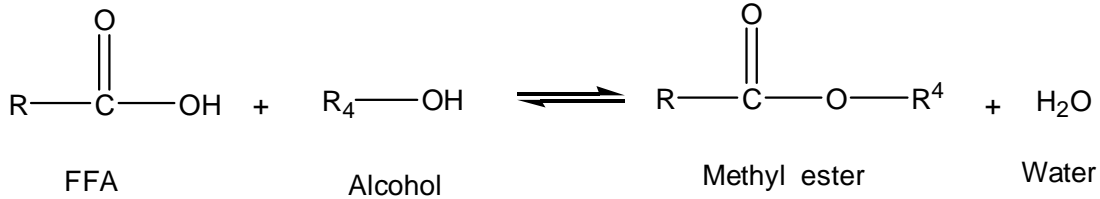


Figure 2.2 Esterification reaction with alcohol [2]
Where R and R⁴ denotes any hydrocarbon chain

2.2 Transesterification and esterification process

2.2.1 Transesterification with conventional batch reactor

At the beginning, biodiesel is produced using conventional batch reactor technology of the transesterification process. It uses the residence times ranging from one hour to several hours. Several aspects including the type of catalyst (alkaline, acid or enzyme), alcohol/vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content have an influence on the course of the transesterification[12]. In the past decades, the effect of mixing on the kinetics of the transesterification of soybean oil with methanol was studied by Nouredini et al[13]. They used the conventional batch reactor to investigate the effect of mixing on the kinetics of the transesterification. They showed that the reaction rate is primarily influenced by the reaction temperature and residence time. In general, with multiple reactions, a high temperature favors the reaction of higher activation energy, and a low temperature favors the reaction of lower activation energy.

2.2.2 Transesterification with capillary reactor

The residence time to produce biodiesel was the big issue from this method because the residence time to make biodiesel was used from one to several hours in conventional batch reactor. Then, the researchers have been looking for the ways to reduce the residence time for

the reaction process. Unambiguously, resolving the contributions of the reaction kinetics and mass transfer between the phases in such systems is something of a challenge, since mass transfer and homogeneous reaction in one of the liquid phases occur simultaneously and are intimately linked. Nevertheless, a precise determination of the individual effects is essential for reliably predicting the performance of the two-phase liquid-liquid reaction system as a whole under a wide range of conditions [14]. Vortex motions generated by shearing motion within slug flow at larger scales have been long known to enhance mixing within the slug and improve mass transfer rates across interface. Slug flow affords a useful and convenient method of augmenting heat and mass transfer.

In the past few years, the special fluid dynamic characteristics in micro-channel have motivated some research groups to successfully carry out liquid-liquid phase reactions in capillaries with channel diameters less than 1000 μm . By pumping the two immiscible liquids via two separate feed lines and bringing them together in an appropriate mixer (T or Y-type mixer), an alternating flow of the two liquid phases is generated. Since channel walls are very close, resulting Reynolds numbers are small and laminar flow characteristics within the capillaries are obtained. The geometry of the fluid segments depends on the channel diameter, the mixer type, and the flow rates of the liquid phases. An increase in the overall mass transfer rate with decreasing channel diameter is explained by a shortened diffusion pathway at the liquid-liquid phase boundary. This effect is not only caused by an obvious increase in specific surface area, but also by the Taylor flow characteristic of the alternate fluid segments, further enhancing mass transport rates with decreasing channel diameter and increasing the flow rate [15].

The use of alternating slugs of two phases to provide the environment for mass transfer and reaction within the micro-reactor was conducted by Burn et al [16]. The internal circulation, which is stimulated within the slugs by their passage along the channel, is responsible for a large enhancement in the overall mass transfer and reaction rate. They showed the mass transfer performance data by using a glass chip-based reactor in a 380 μm wide channel. In the

experiment, the researchers monitored the extraction of acetic acid from kerosene slugs as they moved along the reactor channel. They conclude that slug flow gave a viable alternative for reacting two phase flow within a micro-channel environment. Circulation within the slugs provided enough enhancements to the mass transfer to make the performance equivalent to diffusion based processes with path lengths less than the channel width. The slug flow provides many enhancements of the reactions with two-phase flow. Kashid et al. [17] studied the effect of wall film and other operating parameters such as the flow velocity and the slug length on internal circulation by CFD simulation. They conclude that, at the low flow velocities and a slug with sufficient length, the flow had no significant effect on circulation time inside the slug. However, with an increase in the flow velocity, the circulation time decreased. The simulations revealed a slight but nevertheless significant effect of the presence of a wall film on the circulation patterns and rates.

Recently, microreactor technology, an important method of process intensification, was widely used to apply in biodiesel to reduce the residence time. Sun et al. [18] applied capillary tube as the micro-channel reactors for the continuous synthesis of the biodiesel. Unrefined rapeseed oil and cottonseed oil were used as the raw materials with methanol and potassium hydroxide used to be a catalyst. The influences of the methanol to oil molar ratios, the residence time, the catalyst concentration, the reaction temperature, and the dimension of the capillary on the production of biodiesel were examined. From the experiments, the micro-channel reactors used for the production of biodiesel were assembled by a stainless steel capillary. They concluded that continuous synthesis of biodiesel was carried out in capillary microreactors and the residence time in the micro-channel reactor was remarkably decreased compared to that needed in bath systems to obtain a high methyl ester yield under the same reaction conditions. The residence times ranged from 3.68 to 19.73 min. A higher methyl ester yield could be obtained and a shorter residence time was needed in a capillary microreactor with a smaller channel size, as a consequence of the larger specific surface area of the capillary with smaller

dimension and intensified mass transfer. Moreover, Guan et al. [19] observed the flow pattern and oil conversion in the microtube under different operating conditions for transesterification. In the experiment, the stainless steel microtubes (inner diameter: 0.4, 0.6, 0.8, and 1.00 mm) were used in various lengths as microreactors. The results indicated that oil conversion was significantly affected by microtube length, microtube diameter, the methanol/oil molar ratio, reaction temperature. They concluded that oil conversion in a microtube reactor increased with the methanol oil molar ratio and with reaction temperature, which significantly affected the flow pattern.

The geometric parameter on the performance of biodiesel producing in microchannel was investigated. Wen et al. [20] studied the zigzag micro-channel reactors to improve the efficiency of homogeneous alkali-catalyzed biodiesel synthesis. They investigated the effects of main geometric parameters on the performances such as hydraulic diameter and number of turns of the micro-channel reactors by the characterization correlation of droplet size distributions by comparing with the conventional bath. The results indicated that, at 240 μ m hydraulic diameter of the micro-channel with 350 turns, the reaction condition at the molar ratio of methanol and oil of 6:1, catalyst amount of 1wt% (based on the soybean oil weight), temperature of 60°C, and the residence time of 28 second gave the yield of biodiesel production up to 97.3%. They concluded that the high reaction efficiency of the zigzag micro-channel reactors is attributed the intensification of the overall volumetric mass transfer by passive mixing at the microscale. This has been approved by the characterization of the droplet size distribution using laser scattering method of this study. Thus, biodiesel synthesis with zigzag micro-channel reactors can be used to design a compact and mini-fuel processing plant for the disturb applications.

2.2.3 Esterification with homogeneous catalyst

When the oils and animal fat have high free fatty acid (FFA) more than 5%, the soap inhibits separation of the glycerol from the methyl ester and contributes to emulsion formation

during the water wash. For these cases, an acid catalyst can be used to esterify the FFA, esterification process. Esterification is the process that uses acid as a catalyst in the reaction of biodiesel producing. There are many acid catalysts used to produce biodiesel such as homogeneous acid catalyst, sulfuric acid, or heterogeneous acid catalyst, Amberlyst. Recently, Marchetti et al.[2] studied the direct esterification reaction of triglycerides to biodiesel and the effects of the variables in the process such as reaction temperature(53-55 °C), amount of catalyst (1.026-5.139% w/w), initial amount of free fatty acid (3.836-27.22% w/w) and the molar ratio alcohol/oil (4.212-10.052). The results from the experiment showed that the sulfuric acid was an attractive alternative to produce biodiesel by direct esterification of a spent oil with high amount of FFA compared with conventional technology using KOH as catalyst. The esterification process indicated that the amount of FFA was reduced from 10.684% w/w to values around 0.54% w/w. Moreover, Zhang et al. [21] studied the pretreatment process for reducing the FFA content of *Zanthoxylum bungeanum* seed oil (ZSO) by means of acid-catalyzed esterification with methanol. They focused on the reaction parameters that effect the conversion of FFA in crude ZSO. They conclude that the optimum condition was selected for the acid-catalyzed esterification, molar ratio of methanol and oil of 24:1, sulfuric acid 2%, temperature 60 °C and reaction time 80 min, which reduced the acid value from 45.51 to less than 2 mg KOH/g.

2.2.4 Esterification with heterogeneous catalyst

According to use the homogeneous acid-catalyzed esterification process, the crude biodiesel have to purify to get rid of water and catalyst by a costly separation of homogeneous catalyst [22]. The esterification by solid catalysts, methacrylic acid, was studied by Shanmugam et al.[23] They concluded that the heteropolyacids showed higher activities than conventional acids. Recently, there is a review of activity of solid catalysts for biodiesel production by Zabeti et al.[24] They reviewed the catalytic activity of several solid base and acid catalyst, particular metal oxides and supported metal oxides. They concluded that solid acid catalysts were able to

do both with transesterification and esterification reactions simultaneously and convert oil with high amount of FFA. However, the reaction rate in the presence of solid base catalysts was faster. The catalyst efficiency depended on several factors such as specific surface area, pore size, pore volume, and active site concentration.

While, the acid catalyzed esterification process has continuously produced biodiesel, the process employ with the water in reaction. Water is the main prohibition in the reaction of esterification process. Kusdiana et al. [25] investigated the effects of water on the esterification of FFA using sulfuric acid as the catalyst. They found that the conversion of oleic acid to methyl oleate was reduced when the water content increased. When the FFA content increased the reaction system, a lower conversion rate was observed due to the increase in the amount of water produced.

The solid catalysts, acidic and basic solids, gave the differences of biodiesel production. Jitputti et al. [26] studied the transesterification in crude palm kernel oil (PKO) and crude coconut oil (CCO) by using ZrO_2 , ZnO , SO_4^{2-}/SnO_2 , SO_4^{2-}/ZrO_2 , KNO_3/KL zeolite, and KNO_3/ZrO_2 . The 6:1 of molar ratio of oil and methanol, 200 °C of reaction temperature, and 350 rpm of mechanical stirrer were used in the experiment. They concluded that ZnO and SO_4^{2-}/ZrO_2 exhibited the highest activity for both PKO and CCO transesterification with methanol. Moreover, in the case of SO_4^{2-}/ZrO_2 , they used 1wt% of acidic catalyst to converse oil and yielded more than 90% of methyl ester in 1 hr. They also showed that SO_4^{2-}/ZrO_2 has a promising to reuse for transesterification. The high porous surface area solid catalyst, sulfated zirconia, was studied by Garcia et al. [27]. They investigated transesterification of soybean oil and esterification of oleic acid by using sulfated zirconia as a catalyst. They concluded that the transesterification yielded 98.6% with the conditions of 120°C, 1 hr., and 5wt% of catalyst. Moreover, the esterification of oleic oil acid was completed after 2 hr. at 92% yield of methyl ester. The solid catalyst with pores and without pores on the surface was investigated to show how water can prohibit the reaction. Park et al. [28] studied the effect of the water produced

during the esterification process by varying the FFA contents of oils by using two kinds of heterogeneous acid catalysts. They used the esterification characteristics of two kinds of heterogeneous acid catalysts, Amberlyst 15 and Amberlyst BD20 in methanol with high free fatty acid (FFA) oils to produce biodiesel. They concluded that the water produced during the esterification process poses a significant problem, as it reduces the activity of the heterogeneous catalyst. In addition, AmberlystBD20, heterogeneous catalyst, showed a good catalytic efficiency for high FFA oils. After reuse, the activity of AmberlystBD20 did not decrease. To overcome the decrease in the esterification rate by water, Park et al. [29] studied oleic and high acid acid oil (HAAO) by esterification with two-step esterification of oleic acid. They used the acid catalyst in methanol with HAAO to run the experiment from the first step. For the second step, the original methanol and catalyst were replaced with fresh methanol and catalyst after experiment ran for 30 minutes. The results indicated that the two-step esterification can reach FAME of over 90% and reduced the time requirement from 4.5 hr. to 1.5 hr. They concluded that the water content in FAME product from esterification severely inhibits the esterification reaction. Moreover, the two-step esterification was promising to reduce reaction time and a good method to remove water during esterification.

2.2.4 Transesterification with superheated methanol

To get rid of the catalyst, Joelianingsih et al. [30] studied the transesterification of vegetable oils with short-chain alcohol for producing biodiesel fuel. They developed the new reactor to produce Fatty Acid Methyl Ester (FAME) by blowing bubbles of superheated methanol vapor in the absence of a catalyst in reactor without stirring at atmospheric pressure. The optimum reaction temperature in the reaction product is 250°C which gives the highest methyl ester content at 95.17%w/w. They conclude that in order to increase process efficiency showed by the value of rate constant, conversion, and the yield of methyl ester the interfacial area of gas-liquid phase should be enlarge. To reduce the temperature of reaction for the supercritical methanol, co-solvent was interested to produce biodiesel. Yin et al. [31] studied

biodiesel synthesis from soybean oil with methanol by using supercritical and subcritical conditions of methanol in high pressure vessel.

2.2.5 Transesterification with co-solvent

In order to decrease the operational temperature at 260°C-350°C and pressure and increase the conversion efficiency of methanol, a novel ideas was presented in which a co-solvent (hexane, carbon dioxide, potassium hydroxide) was add to the reactants. The results indicated that the yield of methyl ester was improved when hexane or CO₂ was added. With hexane or CO₂ as co-solvent in the reaction system, there was a significant increase of methyl esters yield. With optimum reaction temperature of 300°C to reach a 98% yield methyl ester, they conclude that the supercritical methanol method with a co-solvent can improve the product yield. Hexane and condensed CO₂ are excellent solvents for vegetable oil. Furthermore, the CO₂ is a good for environment, is easy to obtain and has good properties in the supercritical conditions. There are many co-solvents that are promising for producing biodiesel. Tan et al. [32] studied non-catalytic supercritical methanol (SCM) reaction by using heptane. They conclude that the non-polar solvent as heptanes was found to have potential to decrease the temperature required in the reaction. The following table is the summarized their work and reported literature.

Table 2.1 Comparison of experiment for the co-solvent

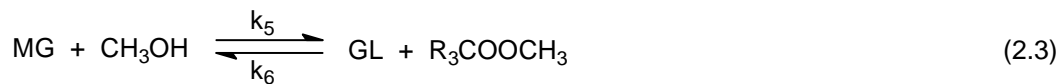
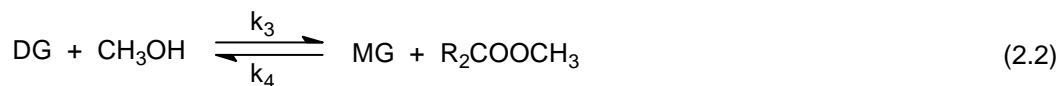
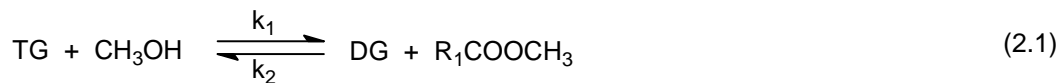
Experimental work	System	Co-solvent	Optimum temperature (°C)	Optimum molar ratio of methanol
Cao et al.[33]	Continuous	Propane	280	0.05
Yin et al.[31]	Batch	Hexane and CO ₂	300	Hexane(0.25wt%) CO ₂ (0.25)
Han et al.[34]	Continuous	CO ₂	280	0.1

Table 2.1 - continued

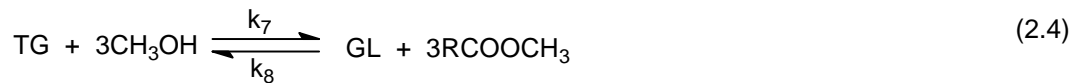
Experimental work	System	Co-solvent	Optimum temperature (°C)	Optimum molar ratio of methanol
Tan et al. [32]	Batch	Heptane	280	0.15-0.20

2.3 Chemical reaction and kinetics

Biodiesel production by transesterification of vegetable oil with methanol (A) consists of a several consecutive, reversible reactions, as shown below. The first step is the conversion of vegetable oil (triglycerides, TG) to diglycerides (DG), which is followed by the conversion of diglycerides to monoglycerides (MG) and finally by the conversion of monoglycerides to glycerides (GL). After the conversion, three mole of methyl ester (ME) are obtained for each triglyceride reacted. The reaction steps are in equation (1) – (3) where k_{1-6} are rate constants[16].



The overall reaction



The general form of the governing set of differential equation characterizing the stepwise reactions involved in the transesterification of triglycerides in equation (2.5) – (2.9)

2.3.1 Reaction rates

$$R_{TG} = \frac{dC_{TG}}{dt} = -k_1 C_{TG} C_A + k_2 C_{DG} C_{ME} \quad (2.5)$$

$$R_{DG} = \frac{dC_{DG}}{dt} = k_1 C_{TG} C_A - k_2 C_{DG} C_{ME} - k_3 C_{DG} C_A + k_4 C_{MG} C_{ME} \quad (2.6)$$

$$R_{MG} = \frac{dC_{MG}}{dt} = k_3 C_{DG} C_A - k_4 C_{MG} C_{ME} - k_5 C_{MG} C_A + k_6 C_{GL} C_{ME} \quad (2.7)$$

$$R_{ME} = \frac{dC_{ME}}{dt} = k_1 C_{TG} C_A - k_2 C_{DG} C_{ME} + k_3 C_{DG} C_A - k_4 C_{MG} C_{ME} + k_5 C_{MG} C_A - k_6 C_{GL} C_{ME} \quad (2.8)$$

$$R_{GL} = \frac{dC_{GL}}{dt} = -k_5 C_{MG} C_A + k_6 C_{GL} C_{ME} \quad (2.9)$$

Where C denotes the concentration of substances

The rate constant or energy of activation (k) is the function of temperature and derived from the Arrhenius equation[16]which shown below

$$k(T) = A e^{-E_a/RT} \quad (2.10)$$

Where A is the Arrhenius pre-factor [1st order : s⁻¹]

E_a is the activation energy of reaction [kJ/mole]

Taking the natural log of Arrhenius equation,

$$\ln(k) = -\frac{E_a}{RT} + \ln(A) \quad (2.11)$$

This equation is linear with respect to 1/T. If k is determined for varying temperatures, the plot of ln(k) vs. 1/T should produce the straight line of slope -E_a/R.

This section includes the development of all theoretical elements that are required to build a simulation model for producing biodiesel using Finite Element Method (FEM) with COMSOL on Matlab. The following assumptions are for all simulations considering:

1. Front and back interface of each slug are the same: periodical boundary condition
2. The slug size is the same for all velocities
3. The problem is considered axis symmetric in three dimension
4. The fluid in each slug is consider to be the Newtonian fluid, incompressible, and isothermal

The following incompressible and steady Navier-Stokes equations are solved for velocity (v):

$$(\vec{v} \cdot \nabla) \vec{v} + \frac{\Delta p}{\rho} + \frac{\mu}{\rho} \nabla^2 \vec{v} = 0 \quad (2.12)$$

We assume the steady state, no body force and axisymmetric in three dimensions. To reduce the residence time of biodiesel production, the micro scales are opening up new avenues for the development of compact devices for functions ranging from reactions to extraction and separation. Much of the initial work in this field has concentrated on the development of system using single phase flow with mass transfer. There are two mechanisms by mass transfer which are convection within the slug and diffusion between two slugs. The convection is due to the circulations within each slug because of the shearing between slug axis and capillary wall while the diffusion is because of concentration gradient between consecutive slugs. The first phenomena depends on physical properties of fluids, slug geometry and flow velocity while the latter is depending on the interfacial area available for transfer and concentration gradient between slugs[35].

The following equation is the mass convection-diffusion equation for the capillary reactor in biodiesel production.

$$\frac{\partial C_i}{\partial t} + \vec{v} \cdot \nabla C_i - D_i \nabla^2 C_i - R_i = 0 \quad (2.13)$$

Where C_i is the concentration of reactant i

\vec{v} is velocity field solved from eq.(11)

D_i is the diffusion coefficient of species i

R_i is the reaction rate equation i from eq. (4)-(8)

The diffusion coefficient

$$D = \frac{k_B T}{6\pi\eta R} \quad (2.14)$$

Where k_B is Boltmann Constant = $1.3806503 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$

T is temperature [K]

η is dynamic viscosity [$\text{N} \cdot \text{m}^{-2} \cdot \text{s}$]

R is radius molecule [m]

CHAPTER 3

TRANSESTERIFICATION OF VEGETABLE OIL WITH A CONVENTIONAL BATCH REACTOR

3.1 Introduction

It is well known that the biodiesel is made from vegetable oils or animal fats with alcohol. The transesterification is worldwide used to convert oil to biodiesel or methyl ester. This process mostly produces biodiesel from oils/fats with alcohol by using alkali catalyst. There are some advantages of transesterification such as low temperature reaction requirement, faster rate reaction as compared to acid catalysts. However, there are some disadvantages of alkali-catalyzed transesterification such as low Free Fatty Acid (FFA) oil requirement, low water content in reactants requirement, saponification, and emulsion formation. Normally, biodiesel is produced using conventional batch reactor technology. The transesterification process uses the residence times ranging from one hour to several hours. Several aspects including the type of catalyst (alkaline, acid or enzyme), alcohol to vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content have an influence on the course of the transesterification[12]. To understand the biodiesel reaction rate, Freedman et al. determined the rate constants with variation of molar ratio of oil and methanol, reaction temperature, and type and amount of catalyst using conventional batch reactor. They also investigated the energy of activation for forward and reverse reaction. Moreover, Nouredini et al.[13] studied the effect of mixing on the kinetics of the transesterification of soybean oil with methanol in conventional batch reactor. They reported that variations in mixing intensity appeared to effect the reaction parallel to the variations in temperature. Recently, SaKai et al.[36] also investigated an economic feasibility study of the conventional batch reactor with homogeneous and heterogeneous alkali catalysts. They indicated that the manufacturing costs

that involved in the heterogeneous catalyst process were lower than in the homogeneous catalyst process with various reasons of heterogeneous catalyst properties.

In a present study, the experiment has been intensively investigated in order to understand the variables affecting the transesterification process by using the conventional batch reactor. The reaction temperature, residence time, and mixing intensities as the variables affecting have been studied while molar ratio of oil to methanol, and concentration of catalyst (Potassium hydroxide, KOH) have been kept constant.

3.2 Materials and Equipment

Food grade soybean oil purchased from a local grocery store was used for the vegetable oil feedstock. The free fatty acid (FFA) content of the oil determined according to AOCS method #Ca 5a-40(15) was determined to be 0.08%. The methanol and potassium hydroxide (KOH) were reagent grade (Sigma-Aldrich).

3.3 Experiment Procedure

Vegetable oil and methanol were prepared for the production of biodiesel in a 500 ml of flask, conventional batch reactor. A 6.38 wt% solution KOH in methanol was prepared under nitrogen to avoid water contamination. A 7.5 molar ration of methanol to oil and the 1.77 wt% KOH to oil weight ratio were used in the study.

Three different mixing intensities were used to investigate reaction effect in three differences of rotational speed. The rotational speeds were set at 50, 75, and 100 rpm. The mixing intensity also can be represented by Reynolds number (N_{Re}) and can be written by following equation[13].

$$N_{Re} = \frac{nD_{ap}^2}{\mu} \quad (3.1)$$

Where n is the angular speed (rad/s)

D_a is the diameter of propeller (m)

ρ is the density of oil (kg/m^3)

μ is the viscosity of oil ($\text{N}\cdot\text{m}^{-2}\cdot\text{s}$)

The following table is the conversion of rotational speed to Reynolds number.

Table 3.1 The rotational speed and Reynolds number

Rotational speed (rpm)	Reynolds number	
	30 °C	50 °C
0	0.00	0.00
50	81.45	148.94
75	122.18	223.42
100	162.91	297.89

To examine the temperature dependency of reaction, the 30°C and 50°C were studied with a constant molar ratio of methanol to oil and 0.9 M concentration of KOH. All reactions were carried out at atmospheric pressure.

The 500 ml flash reactor was used with mechanical stirrer by varying the rotational speed. The assembled reactor was placed in the constant temperature water bath and heated to the desired temperature. Heating was provided by a 500 watt immersion heater with a thermostat. Since water bath was heated to the reaction temperature, oil and methanol was following added in the reactor. The reactor was sealed during the experiment to prevent the methanol leakage and the moisture from environment. The timing reaction was recorded as soon as the mechanical stirrer starting (model IKA EUROSTAR power control-visc, IKA)

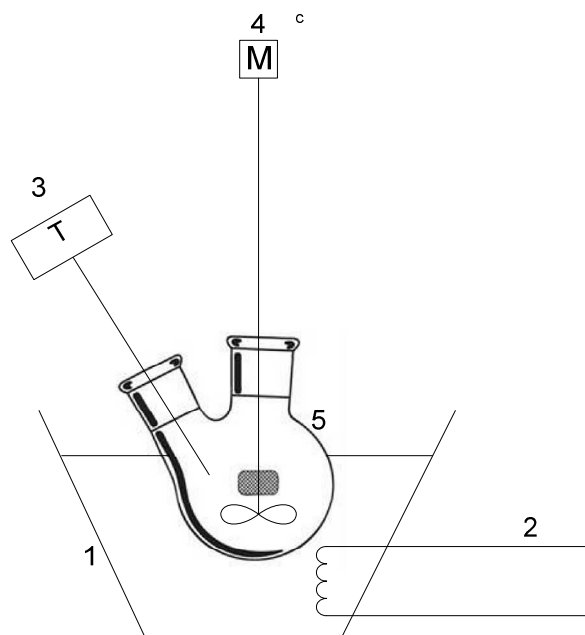


Figure 3.1 Experimental schematic of transesterification of vegetable oil with a conventional batch reactor (1)Water bath, (2)Heater, (3)Thermocouple,(4)The mechanical stirrer,(5)Conventional bath reactor

3.4 Chemical Analysis

The FAME product samples were centrifuged for 15 minutes and then dried under -80 kPa vacuum at 50°C for 20 minutes. The samples were prepared and tested according to the ASTM 6584 test procedure for quantifying free and bound glycerin[37]. A gas chromatograph (GC) equipped with flame ionization detector (SRI 8610C) was used. We verified accuracy of the testing procedure by testing a commercial B-100 biodiesel sample. This same sample was sent to an external lab for an independent ASTM 6584 test. Both test results were in agreement.

3.5 Results and discussion

The alkali-catalyzed transesterification of vegetable oil with different rotational speed and reaction temperature, and residence time were investigated in the experiment. The 7.5 of molar ratio of methanol to oil and the 1.77wt% KOH to oil weight ratio were kept constant in the study.

3.5.1 The Effect of residence time on conversion

The figure 3.2 shows effect of conversion of monoglycerides, diglycerides and triglycerides. As the results, at the beginning, the conversion rate is slow, the following rate is a sudden surge, and the final rate is slow when it goes through nearly equilibrium. The results indicate that the conversion of oil is dependency of residence time.

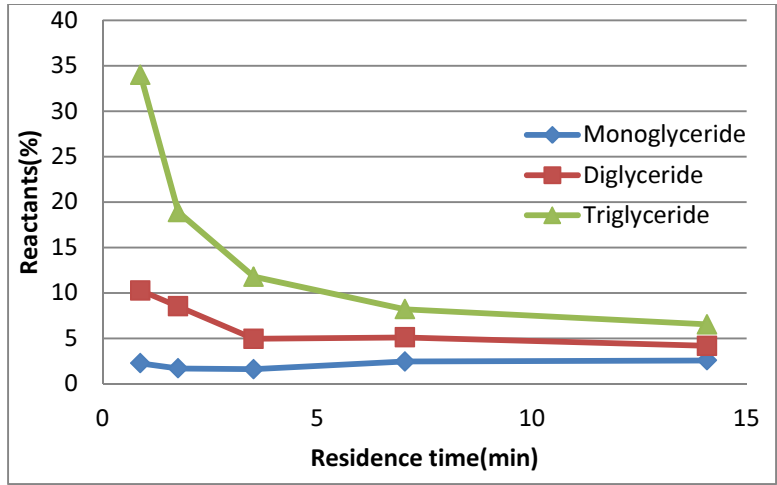


Figure 3.2 The conversion of monoglycerides, diglycerides and triglycerides versus residence time at 100 rpm and 50°C

3.5.2 The effects of oil conversion on temperature

Figure 3.3 and Figure 3.4 show the effects of temperature on oil conversion at 75 rpm and 100 rpm, respectively. The results demonstrate that rate of reaction depended on reaction temperature and the trend of both graphs is the same as seen in the Figure 3.3 and 3.4 at two different mixing intensities. The time for the mass transfer region is shortened as temperature is increased. In the reaction, a higher temperature always favors higher activation energy of reaction. On the other hands, a lower temperature always gives lower activation energy of reaction. The results concluded that temperature had influential effect on the oil conversion.

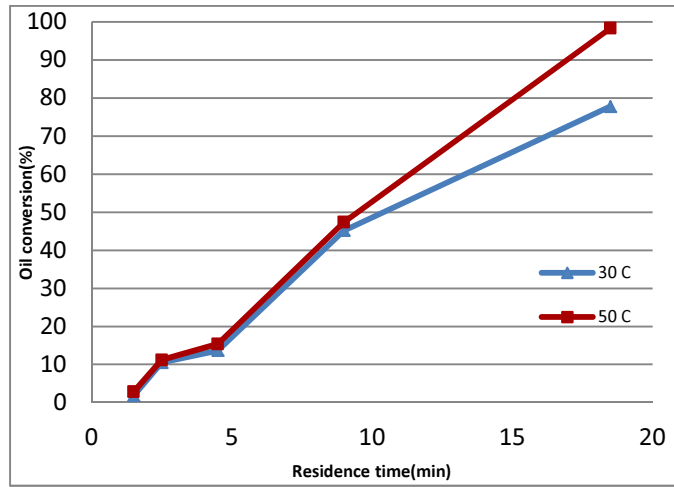


Figure 3.3 The effects of temperature on oil conversion at 100 rpm

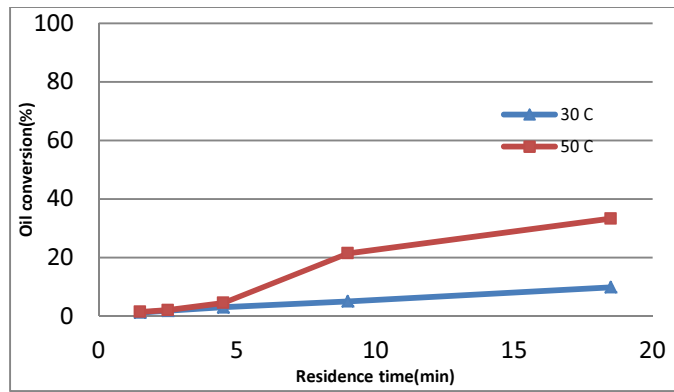


Figure 3.4 The effects of temperature on oil conversion at 75 rpm

3.5.3 The effect of conversion on the mixing intensity

The temperature has obviously effect on oil conversion. To illustrate, the higher reaction temperature favors the higher oil conversion. This section demonstrated the results from the variable mixing intensities. Four different mixing intensities, 50 rpm, 75 rpm, 100 rpm, and zero rpm, were applied to examine the effect of oil conversion. The Reynolds numbers has been shown in the Table 3.1.

The figure 3.5 shows the effects of various mixing intensities on the oil conversion at 50°C. The results present that, at the beginning, there are two-phase of the reactants. The reaction is diffusion-controlled and a slow rate of reaction is the effect of poor diffusion between two phases. The following stage is the increase of reaction rate because of the single-phase reactants appeared. As the expected results, the highest Reynolds number, 100 rpm, indicates the highest oil conversion. Then, the higher Reynolds number has more energy to mix the reactants to achieve the final state of reaction. The results indicated that the residence time was decreased when the mixing intensity was increased. Furthermore, the mixing intensity where high vigorous agitation was used to enhance mixing of reactants was significant effects on the rate of oil conversion.

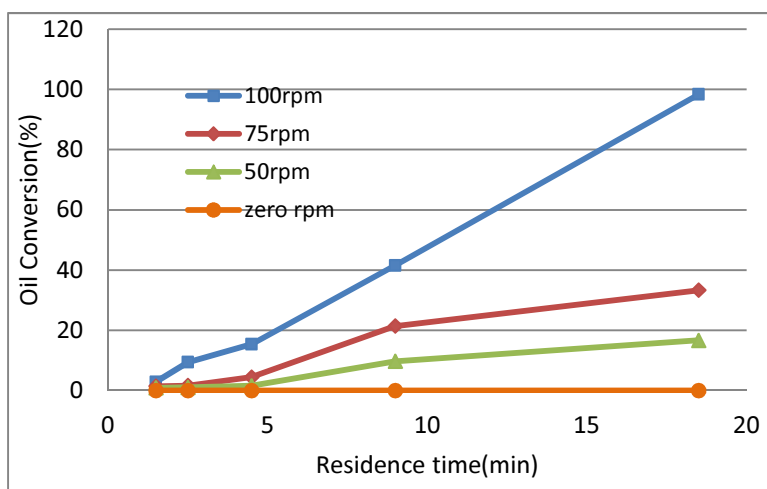


Figure 3.5 The effects of mixing intensity on oil conversion at 50°C.

3.5.4 The power and energy consumption

The power and energy consumption were determined to compare with the capillary reactor. They were calculated using equation (3.1) and (3.2). In the experiment, the mechanical stirrer was used for batch reactor to be an agitator and torque measurement. The mass flow rate of methyl ester was assumed that the reaction was perfectly conversion at 100%. In theoretically, one molecule of oil always gives 3 molecules of methyl ester.

From the experimental setting, the mixing intensity was used at 100 rpm to observe the torque measurement because a 100 rpm gave the highest oil conversion and almost the same oil conversion as capillary reactor. As the results, the power and energy were 0.08763 watt and 0.29851 J·g⁻¹. The residence time used for 98% oil conversion was 18.5 minutes. The results are summarized in Table 3.1.

The power from batch reactor:

$$\text{Power} = T \cdot \omega \quad (3.2)$$

where

T is torque [N·m]

ω is the angular velocity [rad/s]

Energy consumption per gram biodiesel is defined as following equation.

$$\text{Energy consumption} = \frac{\text{Power}}{\dot{m}_{ME}} = \frac{\text{Power}}{\rho_{ME} Q_{ME}} \quad (3.3)$$

where \dot{m}_{ME} is the mass flow rate of methyl ester [g/s]

ρ is the density [g/m³]

Q is the flow rate [m³/s]

MW is molecular weight [g/mole]

The mass flow rate of methyl ester for Batch reactor:

$$\frac{m}{\text{time}} = \frac{3 \cdot m_{oil} \cdot \frac{MW_{ME}}{MW_{oil}}}{\text{time(sec)}} \quad (3.4)$$

Table 3.2 The power and energy consumption of batch reactor

Name	Reaction mode	Residence time (min)	Yield (%)	Torque (N.m)	Power(watt)	Energy(Jg ⁻¹)
Batch reactor	Batch	18.5	98.3284	0.8368e-2	0.08763	0.29851

3.6 Conclusion

The alkali-catalyzed transesterification of vegetable oil with conventional batch reactor technology was studied by a constant of 7.5:1 molar ratio of methanol to oil and 6.38% wt. of KOH solution in methanol. The volumetric ratio of oil and methanol was 3.2:1. The reaction required the higher mixing intensity and higher temperature to achieve the shorten residence time. At 100 rpm, there was 98% oil conversion using 0.29851 J.g⁻¹ of energy consumption. The power and energy were calculated by using 100 rpm for mixing intensity presented to use for comparison in next chapter. In the conclusion, the mixing intensity, reaction temperature, and residence time is significant variables on the oil conversion in batch reactor technology.

CHAPTER 4
TRANSESTERIFICATION OF VEGETABLE OIL WITH A CONTINUOUS FLOW
CAPILLARY REACTOR

4.1 Introduction

Nowadays, many countries around the world are facing an energy crisis. The price of oil has been continuously increasing while the demand is nowhere near being satisfied. Therefore, many governments, educational institutes and research laboratories have been looking to reduce the oil consumption and find alternative fuel sources. In addition, not only should a good source of energy be substituted for oil, but also it should be environmentally friendly.

Recently, renewable energy has been a major area of study which has received a lot of attention from researchers and industries around the world. Various types of renewable energy including biofuels, solar, hydro power, geothermal, and biomass, can generate a significant amount of energy and protect the environment at the same time.

Biodiesel is an alternative fuel for diesel engines that is produced by the alkali-catalyzed reaction of a vegetable oil or animal fat with an alcohol such as methanol. It is a renewable fuel with a better quality of exhaust gas emissions (zero net CO₂ production). For these reasons, biodiesel has become more attractive as an alternative fuel source for the future. Additionally, biodiesel is superior to fossil diesel fuel in terms of cetane number, flash point, and lubricity characteristics, without any significant difference in heat of combustion between these fuels [38, 39].

Normally, biodiesel is produced using conventional batch reactor technology. The transesterification process uses the residence times ranging from one hour to several hours. Several aspects including the type of catalyst (alkaline, acid or enzyme), alcohol/vegetable oil

molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content have an influence on the course of the transesterification[12].

In the past few years, the special fluid dynamic characteristics in micro-channels have motivated some research groups to successfully carry out liquid-liquid phase reactions in capillaries with channel diameter less than 1000 μm . By pumping the two immiscible liquids via two separate feed lines and bringing them together in an appropriate mixer (T or Y-type mixer), an alternating flow of the two liquid phases is generated. Since channel walls are very close, resulting Reynolds numbers are small and laminar flow characteristics within the capillaries are obtained. The geometry of the fluid segments depends on the channel diameter, the mixer type, and the flow rates of the liquid phases. An increase in the overall mass transfer rate with decreasing channel diameter was explained by a shortened diffusion pathway at the liquid-liquid phase boundary. This effect is not only caused by an obvious increase in specific surface area, but also by the Taylor flow characteristic of the alternate fluid segments, further enhancing mass transport rates with decreasing channel diameter and increasing the flow rate [15].

Moreover, Wen et al.[20] observed that the high reaction efficiency of the micro-channel reactor is attributed to the intensification of overall volumetric mass transfer by passive mixing at the micro-scale. The residence time was decreased when using a capillary micro-reactor with a 250 micron diameter, a KOH concentration 1.0%, and a methanol to oil molar ratio of 6:1 at a reaction temperature of 60°C [18]. This report provided another data for micro-channel. The segmented flow was converted to a quasi-homogeneous phase due to intense aggregation of fine droplets in the exit region of the micro-tube. When the methanol/oil molar ratio was 23.9 at 60 °C in the micro-channel with an inner diameter of 0.8 mm, the oil conversion reached 100% within a residence time of 100 s, corresponding to a micro-tube length of 300 mm, where the segmented flow just converted to the quasi-homogeneous phase [40]. However, in these studies, the reactants were premixed before being directed into the micro-channel reactor. It was thought insufficient mixing could be accomplished at the micro-scale.

According to the results from chapter 3, the conventional batch reactor was showed that the mixing intensity and temperature had a significant effect on the residence time and oil conversion. To illustrate, the higher temperature favors the higher oil conversion and, similarly, the higher mixing intensity gives the higher oil conversion.

In this chapter, a capillary reactor had been used in order to improve the efficiency of transesterification of vegetable oil with methanol. This work demonstrates the use of capillary reactor for both mixing and intensifying the transesterification reaction. The vegetable oil conversion was observed under various residence times and reaction temperatures. Finally, the power and energy consumption per unit mass was also calculated to compare with the batch reactor and show the improvement of capillary reactor in biodiesel synthesis.

4.2 Materials

Food grade soybean oil purchased from a local grocery store was used for the vegetable oil feedstock. The free fatty acid (FFA) content of the oil determined according to AOCS method #Ca 5a-40(15) was determined to be 0.08%. The methanol and potassium hydroxide (KOH) were reagent grade (Sigma-Aldrich).

4.3 Experiment and Procedure

Vegetable oil and methanol were prepared for the production of biodiesel in a capillary reactor. A 6.38 wt% solution KOH in methanol was prepared under nitrogen to avoid water contamination. The Teflon (PTFE) capillary reactor used for the experiment was purchased from Upchurch Scientific. The capillary tube had an inner diameter of 500 μm and a length of 1.52 m. The Teflon material is chemically resistant to the reactants and products and is optically clear, thus allowing the flow patterns to be observed.

The capillary tube was connected to a Y-type micro-mixer (Upchurch Scientific) with 0.5 mm thru holes. Syringes were connected to the inlet ports of the micro-mixer via 1.0 mm diameter PTFE tubing (Upchurch Scientific). The pressure gage was settled between outlet of micro-mixer and inlet of capillary reactor to measure the pressure drop from capillary reactor.

The syringes were placed in an infusion syringe pump (model KDS200, KD Scientific). The reactor was placed in a stirred water bath. Heating was provided by a 500.0W immersion heater with a thermostat. The experimental schematic is illustrated in Figure 4.1.

The outlet of the capillary reactor was placed in a 11.0 mL glass vial. This collection vial contained 8.0 mL of a water and HCl mixture with pH of 1.4. This served to quench the reaction after the remaining reactants had left the reactor. The products in the collection vial gravity separated with the FAME/oil phase on top and glycerol/water phase on the bottom. Approximately 2.0 mL of product was collected for each run.

A 30.0 mL syringe was used for the oil and a 5.0 mL syringe was used for the methanol solution. This resulted in a constant 3.24:1 volume flow rate ratio of oil to methanol. In addition, the molar ratio of oil to methanol was 1:7.55 and the KOH to oil weight ratio was 1.77 wt%.

The flow rate of the oil was controlled by the syringe pump and was varied from 1.0 mL/hr to 16.0 mL/hr. The bath temperature was held at either 30°C or 50°C.

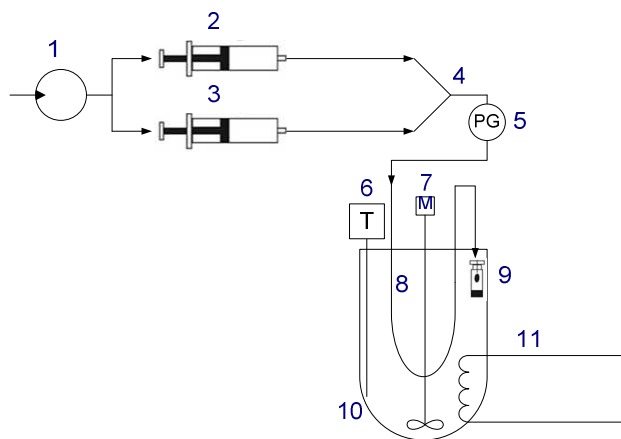


Figure 4.1 Schematic diagram of transesterification of biodiesel system in capillary reactor with (1)pump, (2)oil syringe (30mL), (3)methanol syringe (5mL), (4) Y-type micromixer, (5) pressure gage, (6) temperature control monitor, (7) magnetic stirring, (8) capillary reactor, (9) collection vial, (10) water bath, and (11) immersion heater

4.4 Chemical Analysis

The FAME product samples were centrifuged for 15 minutes and then dried under -80 kPa vacuum at 50°C for 20 minutes. The samples were prepared and tested according to the ASTM 6584 test procedure for quantifying free and bound glycerin[37]. A gas chromatograph (GC) equipped with flame ionization detector (SRI 8610C) was used. We verified accuracy of the testing procedure by testing a commercial B-100 biodiesel sample. This same sample was sent to an external lab for an independent ASTM 6584 test. Both test results were in agreement.

4.5 Results and Discussion

Accordingly, the conventional batch reactor was showed that the mixing intensity and temperature had a significant effect on the residence time and oil conversion. In this section we detail the results of the experimental testing using capillary reactor for transesterification of vegetable oil. We also found that the flow rate and the temperature had a significant effect on the rate of conversion of oil to FAMEs. In addition, the rates of conversion were significantly faster than the stirred batch reactors. These results are described below.

4.5.1 Effect of residence time on conversion

The residence time, which depends on the flow rate, is found to range from 1 minute to 18 minutes. Figure 4.2 shows the amount of oil by percent weight verses residence time. As we expected, the mass of the oil in the sample is decreasing with increased residence time. The triglycerides (TG) dominate the oil mass until residence time of 15 minutes. This is consistent with the three-stage nature of the transesterification reaction. In addition, the transesterification reaction dramatic decreases the amount of TG, diglycerides (DG), and monoglycerides (MG) at the beginning and they slightly decrease after residence time at 10 min. This is consistent with rapid mass transfer that occurs during the first five minutes in the reactor.

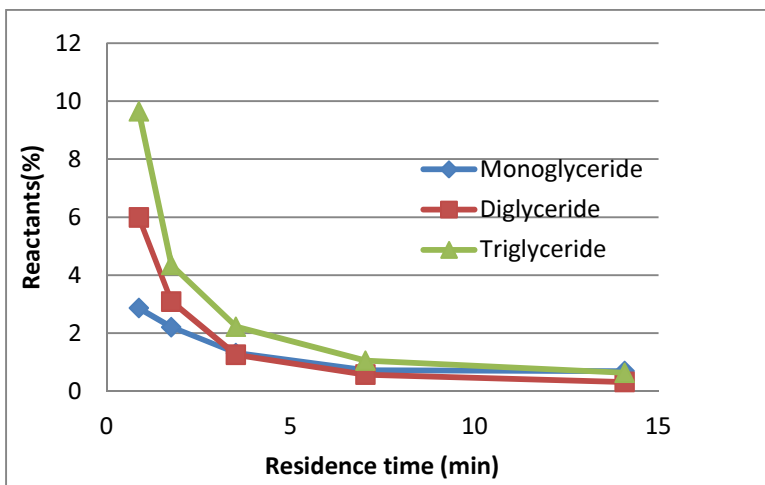


Figure 4.2 Oil components during the transesterification at 50°C.

Figure 4.3 shows the percentage conversion of oil to FAMEs versus flow rate at 50°C. We see that the conversion decreases from 98% to 83% when the flow rate increases from 1.3 ml/h to 21 ml/h. This underlines the significant effect of the flow rate on the conversion of oil to FAMEs.

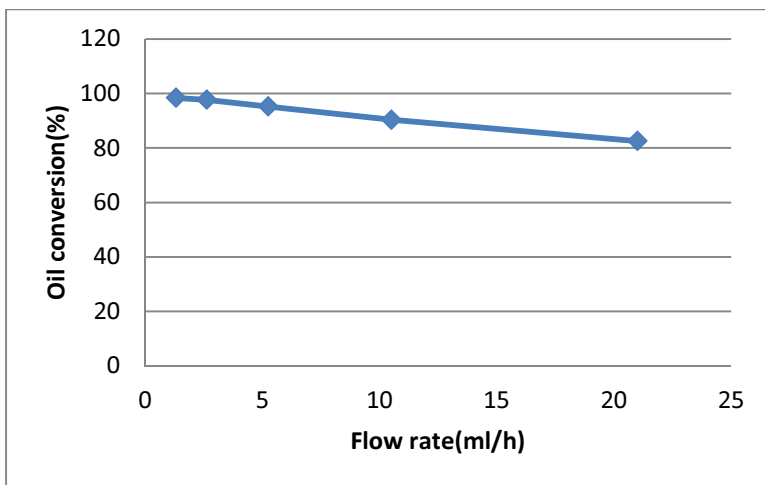


Figure 4.3 Oil conversion verses flow rate at 50 °C

Figure 4.4 shows the effect of residence time on the conversion of oil at 50 °C. We see that the oil conversions are increased from 83% to 98% when the residence times are increased from 1 min to 14 min. A conversion of 90% is achieved in 2 minutes. Furthermore, the increase of residence time corresponds to the decrease in flow rate of the reactants.

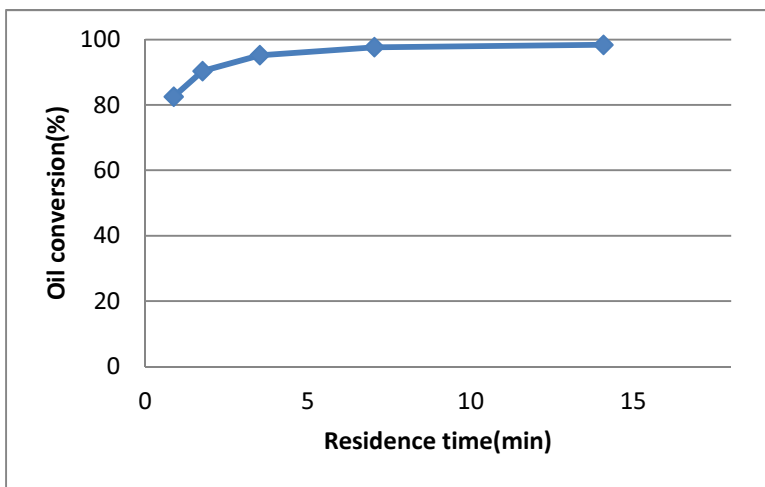


Figure 4.4 Effect of the residence time on conversion at 50°C

4.5.2 Effect of temperature on conversion

Our results show temperature also influences the oil conversion to FAMEs in the capillary reactor. In Figure 4.5, the influence of temperature on the conversion of oil to FAMEs is evident. We see that for a particular residence time, the conversion increases as temperature goes up. For example, when the temperatures are changed from 30 °C to 50 °C, the yield is increased from 86% to 98% at a residence time of 14 min, an increase of 14%. For a residence time of 1 minute there is a 53% increase in oil conversion for 50°C compared to 30 °C.

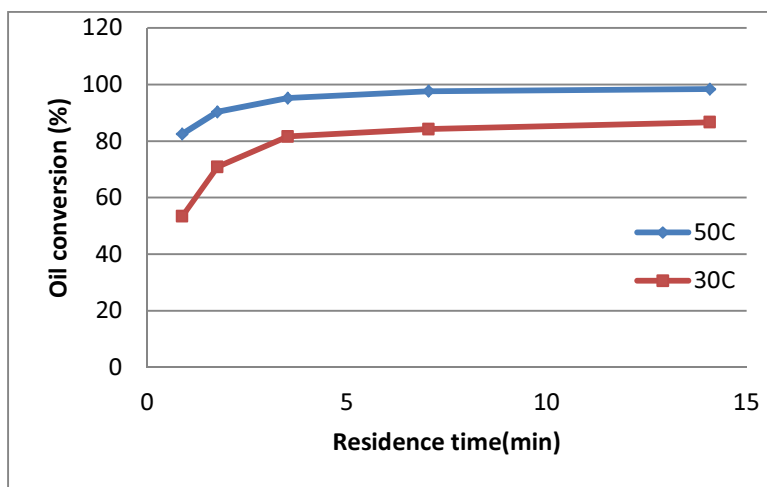


Figure 4.5 Effect of temperature on conversion

4.5.3 The power and energy consumption

In order to compare the improvement of capillary reactor, the energy consumption was determined using equation (4.1). Moreover, the power from the capillary reactor was calculated by using equation (4.2). In addition, the mass flow rate of methyl ester was also calculated from equation (4.3). The reaction was assumed that it was perfectly conversion to 100%, in theoretically, which one molecule of oil gives three molecules of biodiesel. It was clearly showed that the power and the energy consumption using capillary reactor were $4.0833e-7$ watt and $0.001629 \text{ J}\cdot\text{g}^{-1}$ at volume flow rate of $1 \text{ ml}\cdot\text{hr}^{-1}$. Therefore, the results are summarized in Table 4.1.

Energy consumption per gram biodiesel is defined as following equation.

$$\text{Energy consumption} = \frac{\text{Power}}{m_{\text{ME}}} = \frac{\text{Power}}{\rho_{\text{ME}} Q_{\text{ME}}} \quad (4.1)$$

Where m_{ME} is the mass flow rate of methyl ester [g/s]

ρ is the density [g/m^3]

The power for capillary reactor:

$$\text{Power} = Q \Delta P \quad (4.2)$$

Where Q is the flow rate [m^3/s]

ΔP is the pressure drop [kPa]

The mass flow rate of methyl ester for Capillary reactor:

$$m_{ME} = 3 \cdot \rho_{oil} \cdot Q_{oil} \cdot \frac{MW_{ME}}{MW_{oil}} \quad (4.3)$$

Where MW is molecular weight [g/mole]

Q is the flow rate [ml/s]

Table 4.1 The power and energy consumption of capillary reactor

Name	Reaction mode	Re	Yield (%)	Pressure drop (kPa)	Power(watt)	Energy(Jg^{-1})
Capillary reactor	Continuous	0.00361	98.3550	1.47	4.0833e-7	0.001629

4.6 Reynolds Number and Flow Rate

In this section we consider the role of the Reynolds number on the performance of the capillary reactor. We define the Reynolds number as follows[13]:

$$Re = \frac{4Q}{\pi \nu D} \quad (4.4)$$

where

Q is the oil volume flow rate,

μ is the oil kinematic viscosity, and D is the tube diameter.

Table 1 shows the Reynolds number based on flow rate and temperature. The data indicates the flow is entirely laminar for all cases that we have investigated. This is very interesting as the data suggests rapid mass transfer is occurring in the absence of turbulent mixing. This is in direct contrast to convection reactor technology where high turbulent flows are used to enhance mixing of reactants.

Table 4.2 The flow rate and the Reynolds number

Flow rate (ml/h)	Reynolds number	
	30°C	50°C
1.3	$1.97 \cdot 10^{-3}$	$3.61 \cdot 10^{-3}$
2.6	$3.96 \cdot 10^{-3}$	$7.23 \cdot 10^{-3}$
5.2	$7.91 \cdot 10^{-3}$	$1.45 \cdot 10^{-2}$
10.5	$1.58 \cdot 10^{-2}$	$2.89 \cdot 10^{-2}$
21.0	$3.16 \cdot 10^{-2}$	$5.89 \cdot 10^{-2}$

For comparison, we did the transesterification of soybean oil in a conventional stirred batch reactor for various mixing intensities or different Reynolds numbers. According to previous chapter, for a Reynolds number of 298 at 50°C reaction temperature, a residence time of 14 minutes was required to reach a conversion of 98%. In our case, the capillary reactor achieves the same level with a Reynolds number of zero at the same temperature. Here we can clearly see the advantage of the capillary reactor. The lower peak velocities lead to shorter reactors and lower pressure drops compared to conventional plug flow reactors with static mixers. This translates into savings in capital and operating costs for continuous flow production of biodiesel.

4.7 Flow Pattern

It is known that oil and methanol are immiscible fluids. Due to the high interfacial forces between the two phases, the oil phase and the methanol phase separated from each other. In a micro-channel, this results in a slug flow pattern[16].

We observed the pattern of reactant flow within the capillary. Figure 6 shows a photo of the segmented flow pattern. Here we can see spherical droplets of methanol bounded by longer slugs of oil. We note that this phenomenon is the same as that of acetic and aqueous KOH in a capillary reactor report by Burns et al.[11]. In that study, the intensification of the mass transfer

was achieved through the use of a microchannel reactor. This intensification is due to the large surface area to volume ratio provided by the micro-channel.

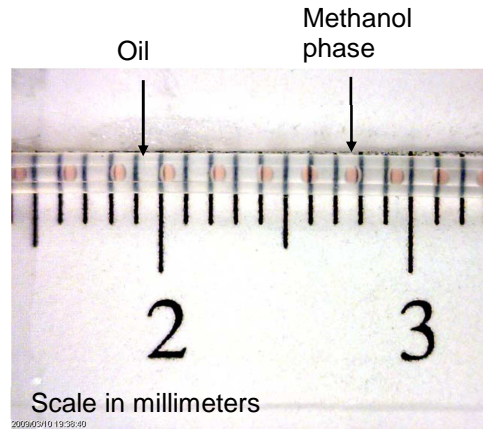


Figure 4.6 Flow pattern formed by flow of oil and methanol

The surface area to volume ratio for the oil slug in the capillary tube is a nonlinear function of the tube diameter. For our case, this ratio is estimated by the formula:

$$\frac{SA}{V} = \frac{4.625}{D} \quad (4.5)$$

where SA is the slug surface area and V is the slug volume. The variation of surface area to volume verse diameter is shown in Figure 7. Here we see the rapid increase for diameters less than 1.0 mm.

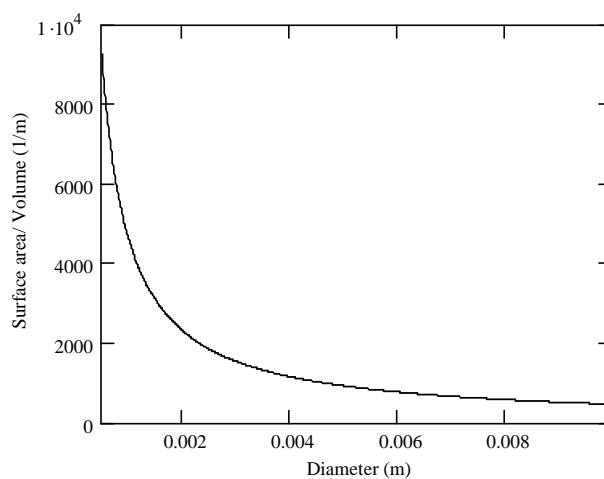


Figure 4.7 Surface area to volume verses diameter

Although there is no convective mixing in the capillary due to turbulent flow, the large surface area to volume ratio allows for rapid mass transfer by diffusion on the microscale. Thus, this explains why the rapid mass transfer is possible, even for slow moving flows with Reynolds number less than 1.0.

4.8 Comparison of Transesterification between Batch Reactor and Capillary Reactor

The batch reactor is the normally used to produce the biodiesel or methyl ester. This method used the time for production for 1 hour to several hours with vigorous stirrer. Recently, the micro-channel was used for the application in biodiesel production because of lower pressure drop, less time reaction, and self-mixing.

The results from chapter 3 and this chapter were compared to show the effectiveness of capillary reactor in biodiesel production. The experiments were conducted at the same conditions to compare the results. For capillary reactor, at the Reynolds number of 0.00361, this value is nearly zero and we assume that the Reynolds number of capillary reactor is zero. From zero Reynolds number, the experiment from batch reactor was conducted with no mechanical stirrer to make zero Reynolds number. The results are discussed in the following section.

4.8.1 Comparison of batch and capillary reactor on effect of conversion

In this section, the following data are presented batch reactor and capillary reactor. The 3.24 volume ratio of oil and methanol, 7.5 of molar ratio of methanol to oil, 1.77wt% of KOH in oil, and the same Reynolds number were kept constant. From the experiment, we detail the results of the experimental testing. We found that the residence time and type of reactor had a significant effect on the rate of conversion of oil to FAMEs. These results are detailed below.

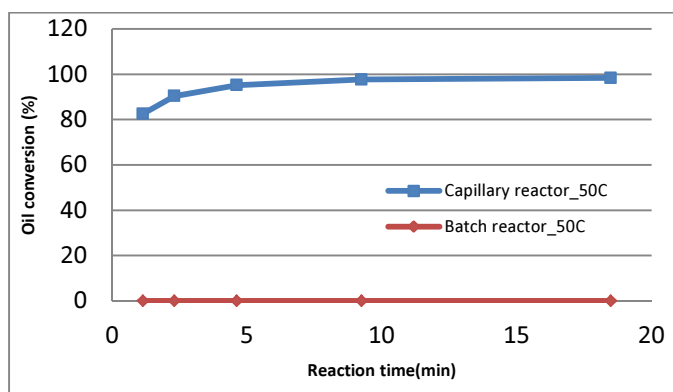


Figure 4.8 Effect of the residence time on conversion from batch reactor and capillary reactor at 50°C

Figure 4.8 shows the effect of residence time on oil conversion at 50°C from batch reactor and capillary reactor. The results at the same Reynolds number show that the percent of oil conversion from capillary reactor and batch reactor are 98% and 0%, respectively. In the same time of reaction, capillary reactor gives the percent of oil conversion much higher than batch reactor at the same condition because of the effect of slug flow in capillary reactor. Moreover, because the convective and diffusion mass transfer for the slug flow in capillary reactor do the role of reaction intensification, the capillary reactor can improve the efficiency of transesterification of vegetable oil with methanol than batch reactor. This is very interesting as the data suggests rapid mass transfer is occurring in the absence of turbulent mixing in capillary reactor. This is indirect contrast to convection reactor technology where higher flows are used to enhance mixing of reactants.

4.8.2 Comparison between batch and capillary reactor on energy consumption

The comparison between capillary and batch reactor were conducted to evaluate the improvement by using energy consumption when the residence time and percent of oil conversion were kept the same. The conditions were demonstrated at temperature 50°C, the 3.24 volume ratio of oil and methanol, 7.5 of molar ratio of methanol to oil, 1.77wt% of KOH in oil. Moreover, the Reynolds number was used at 0.00361 for capillary reactor and 297.89 for batch reactor. The 90% of oil can be converted to biodiesel in 2 minute using capillary reactor while 11% of oil conversion is appeared in batch reactor at the same residence time. After reaction for 14 minutes, the oil conversion for batch and capillary reactor achieved to 98% as shown in Figure 4.9. The results clearly illustrated that capillary reactor can get more oil conversion rate than batch reactor in the short time.

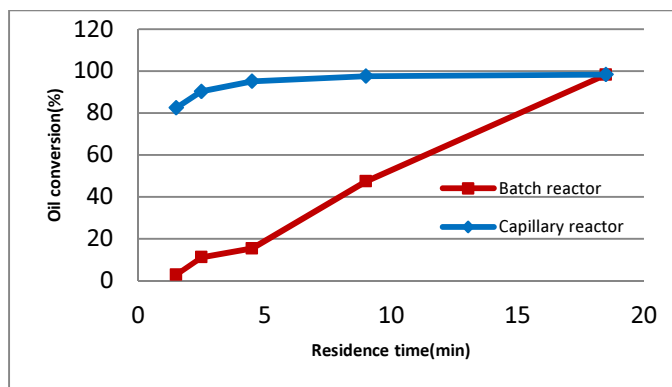


Figure 4.9 The effect of oil conversion on different reactor

The oil conversion and residence time were introduced to compare the intensive effectiveness of capillary and batch reactor. This section shows the calculation of energy consumption for capillary and batch reactor using pressure drop and mass flow rate of methyl ester. To clarify, the pressure drop was measured via the pressure gage and power from the capillary reactor was calculated by using equation (4.3). The results are summarized in Table 4.2. Energy consumption per gram biodiesel is defined as following equation.

$$\text{Energy consumption} = \frac{\text{Power}}{m_{ME}} = \frac{\text{Power}}{\rho_{ME} Q_{ME}} \quad (4.6)$$

The mass flow rate of methyl ester for Capillary reactor:

$$m_{ME} = 3 \cdot \rho_{oil} \cdot Q_{oil} \cdot \frac{MW_{ME}}{MW_{oil}} \quad (4.7)$$

The power for capillary reactor:

$$\text{Power} = Q \Delta P \quad (4.8)$$

Where m_{ME} is the mass flow rate of methyl ester [g/s]

ρ is the density [g/m³]

Q is the flow rate [m³/s]

MW is molecular weight [g/mole]

ω is the angular velocity [rad/s]

The table 4.2 exhibits the power and energy consumption of capillary and batch reactor. At the same residence time, the capillary and batch reactor give the same oil conversion within different Reynolds number. The results clearly indicate that the capillary reactor shows the small energy consumption per unit gram of biodiesel of 0.001629 Jg⁻¹, merely 0.55% of batch reactor. It is evident that capillary reactor uses less power than batch reactor. This obviously presents that the energy consumption can be remarkably decreased by using the capillary reactor.

Table 4.3 Comparison of energy consumption

Name	Reaction mode	Yield (%)	Power(watt)	Energy(Jg ⁻¹)
Capillary reactor	Continuous	98.3550	4.0833e-7	0.001629
Batch reactor	Batch	98.3284	0.0876	0.298673

4.9 Conclusion

The transesterification of vegetable oil was demonstrated using a capillary reactor to compare with the conventional batch reactor. Dependence of oil conversion on reaction temperature and residence time was verified using capillary reactor. It was found that not only

the residence time in capillary reactor was significantly decreased but the conversion of oil was also high. These results were achieved with laminar flow conditions and moderate temperatures. The Reynolds number of capillary reactor was much less than conventional batch reactors for the same level of oil conversion. The reaction temperature was increased to achieve higher level of conversion. A slug flow pattern was observed and suggested to be the main factor that contributes to the rapid mass transfer within the capillary. In addition, the slug flow in capillary reactor contributes the effectiveness of biodiesel production by giving the higher oil conversion and shorter reaction time compared with batch reactor at the same Reynolds number, Reynolds number of zero. At the same residence time, the capillary reactor showed the high performance in reduction of power and energy consumption per unit gram. In conclusion, the capillary reactor has significant effectiveness than conventional batch reactor on oil conversion, residence time, power, and energy consumption.

CHAPTER 5

TRANSESTERIFICATION OF VEGETABLE OIL WITH A CONTINUOUS FLOW

TITANIUM MICROREACTOR

5.1 Introduction

Due to the depleting reserves of fossil fuel and the increasing price of oil and demand, many educational institutes and research laboratories have been looking for alternative fuel sources to reduce the fossil fuel consumption. In addition, not only should a good source of energy be substituted for oil, but also it should be environmentally friendly.

Biodiesel is an environmentally alternative fuel for petrodiesel engines that is produced by the alkali-catalyzed reaction of a vegetable oil or animal fat with an alcohol such as methanol. Biodiesel provides several of important advantages over fossil fuel. These benefits consist of inherent lubricity low toxicity, derivation from a renewable and domestic feedstock, superior flash point and biodegradability, negligible sulfur content, and lower exhaust emissions. Important disadvantages of biodiesel include high feedstock cost, inferior storage and oxidative stability, lower volumetric energy content, and inferior low-temperature operability[1]. Additionally, biodiesel is superior to fossil diesel fuel in terms of cetane number, flash point, and lubricity characteristics, without any significant difference in heat of combustion between these fuels [38, 39]. For these reasons, biodiesel has become more attractive as an alternative fuel source for the future.

Generally, biodiesel, transesterification process, is produced using conventional batch reactor technology. The transesterification process uses the residence times ranging from one hour to several hours. Several aspects including the type of catalyst (alkaline, acid or enzyme),

alcohol/vegetable oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content have an influence on the course of the transesterification[12].

The over past two decades, microreactors, the microfluidics, have remarkably enhanced for many disciplines such as portable energy devices, intensification of heat and mass transfer, reaction kinetics and mechanism studies [5]. They have significantly influenced for fast and effective mixing [6]. Since channel walls are very close, resulting Reynolds numbers are small and laminar flow characteristics within the capillaries are obtained. The liquid-liquid slug flow capillary micro-reactor has been played the important role to be useful instrument for the enhance heat and mass transfer limited reactions [7]. The shear between the wall surface and the slug axis produce the internal circulations. These circulations renew the interface and enhance the diffusive penetration and consequently, increase the observed reaction rates [8]. Since the micro-channel has been worldwide used for a number of applications, Guan et al.[41] studied two-phase behavior in microtube reactors during biodiesel production from waste cooking oil (WCO) to understand and investigate the characteristic of flow pattern. Moreover, they also examined the relationship between flow pattern and biodiesel yield. The results showed that the flow patterns using WCO were changed from liquid-liquid slug flow at the inlet region to a parallel flow at the middle region, and then to a homogeneous liquid flow at the outlet region as the reaction preceded.

However, there are technological challenges facing biodiesel production via transesterification such as residence time, high operating cost and energy consumption, and low product efficiency [9]. In order to enhance the efficiency of biodiesel synthesis and reduce the operating cost, there are numerous research developments for biodiesel production. The capillary reactor is applied to intensification process to reduce the residence time, size of reactor, operating cost as well. To illustrate, Wen et al.[10] observed that the high reaction efficiency of the micro-channel reactor is attributed to the intensification of overall volumetric

mass transfer by passive mixing at the micro-scale. The residence time was obviously decreased when using a capillary micro-reactor with a 250 micron diameter, a KOH concentration 1.0%, and a methanol to oil molar ratio of 6:1 at a reaction temperature of 60°C [11]. This report provided another data for micro-channel. The segmented flow was converted to a quasi-homogeneous phase due to intense aggregation of fine droplets in the exit region of the microtube. When the methanol/oil molar ratio was 23.9 at 60 °C in the micro-channel with an inner diameter of 0.8 mm, the oil conversion reached 100% within a residence time of 100 s, corresponding to a micro-tube length of 300 mm, where the segmented flow just converted to the quasi-homogeneous phase [12]. Moreover, Fu et al.[53] presented that the channel geometry has an effect of chemical reaction in micro-channel via the experiment and theoretical investigation. They indicated that the simple diverging cross-section can be used to develop the microfluidic devices, which is micro-channel reactor. According to self-mixing in micro-channel, Yu et al.[1] presented the intensification of biodiesel synthesis by using metal foam reactors to help mixing the reactants, reduce the operating cost by applying an intensification mixing process and reducing the residence time. They also compared the energy consumption from metal foam, zigzag micro-channel, and conventional batch reactor. The results indicated that the metal foam reactor was more effective than zigzag micro-channel, and conventional batch reactor.

In this experiment, a stack of 13 layers of titanium microreactor attached to a Y-type micromixer has been used in order to improve the efficiency of transesterification of vegetable oil with methanol. This work presents the use of titanium micro-channels for both mixing and intensifying the transesterification reaction and the demonstration of the influence of residence time on the biodiesel production. The vegetable oil conversion was observed under various residence times at 50°C, 1:7.55 molar ratio of oil to methanol, and 1.77 wt% KOH of oil

5.2 Materials

5.2.1 Chemicals

Food grade soybean oil purchased from a local grocery store was used for the vegetable oil feedstock. The free fatty acid (FFA) content of the oil determined according to AOCS method #Ca 5a-40(15) was determined to be 0.08%. The methanol and potassium hydroxide (KOH) were reagent grade (Sigma-Aldrich).

5.2.2 Fabrication of titanium micro-channel reactors

The micro-channel reactors were made of titanium plate and they were patterned on titanium by laser cutting. The pattern of micro-channel is rectangular with the 0.6 mm width, 0.1 mm depth, and 42.67 mm length as shown in Fig. 5.1. The cover sheet has two holes, which act as the flow paths. The thirteen layers of titanium reactors were packed by diffusion bonding. Bonding process was carried out at 700 °C with 15°C/min and hold for 150 min under 53.62 Pa pressure in vacuum of 500×10^{-5} Pa using diffusion welding furnace. After the diffusion bonding, the reactors were cooled to room temperature and no heat treatment was applied.

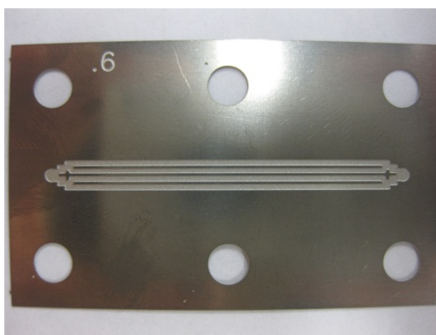


Figure 5.1 The titanium micro-reactor

5.3 Experiment Procedure

Vegetable oil and methanol were prepared for the production of biodiesel in a capillary reactor. A 6.38 wt% solution KOH in methanol was prepared under nitrogen to avoid water contamination. The reactors had an inner dimension of 0.6 mm width, 0.1 mm depth and a

length of 42.67 mm. In addition, a 30.0 mL syringe was used for the oil and a 5.0 mL syringe was used for the methanol solution. This resulted in a constant 3.24:1 volume flow rate ratio of oil to methanol. Moreover, the molar ratio of oil to methanol was 1:7.55 and the KOH to oil weight ratio was 1.77 wt%. Additionally, the flow rate of the oil was controlled by the syringe pump and was varied from 1.0 ml·hr⁻¹ to 16.0 ml·hr⁻¹. The bath temperature was kept constant at 50°C.

The experiment was set by using an infusion syringe pump (model KDS200, KD Scientific) to control the flow rate. A 30 ml oil syringe and 5 ml methanol syringe were connected after pump. Oil and methanol were consistently mixed by using a Y-type micromixer (Upchurch Scientific) with a 0.5 mm diameter. Furthermore, the mixture was measured the pressure drop by placing the pressure gage between micromixer and the inlet of titanium microreactor. The reaction was continuously occurred at the titanium reactor. Additionally, the reactor was placed in the constant heating bath using a 1000 watt hotplate/stirrer (model VMS-C7, VWR). The experiment schematic is illustrated in Figure 5.1.

The outlet of the reactor was placed in a 11.0 mL glass vial. This collection vial contained 8.0 mL of a water and HCl mixture with pH of 1.4. This serves to quench the reaction after the remaining reactants have left the reactor. The products in the collection vial gravity separated with the FAME/oil phase on top and glycerol/water phase on the bottom. Approximately 2.0 mL of product was collected for each run.

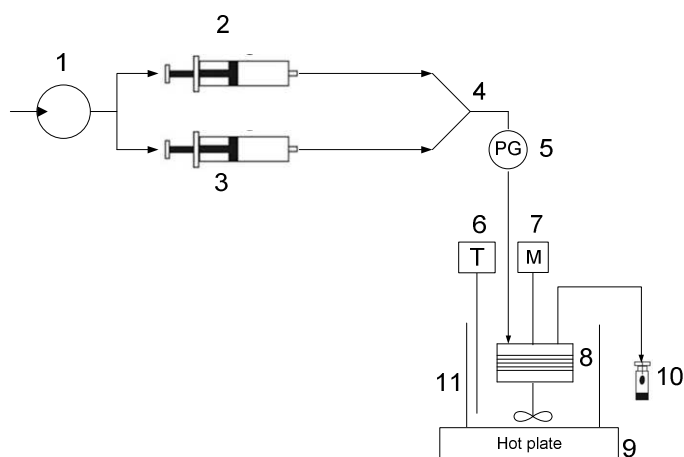


Figure 5.2 Schematic diagram of transesterification of biodiesel system in micro-reactor with (1)pump, (2)oil syringe (30mL), (3)methanol syringe (5mL), (4) Y-type micromixer, (5) pressure gage, (6) temperature control monitor, (7) magnetic stirring, (8) titanium reactor, (9) Hot plate (10) collection vial, and (11) water bath

5.4 Chemical Analysis

The FAME product samples were centrifuged for 15 minutes and then dried under -80 kPa vacuum at 50°C for 20 minutes. The samples were prepared and tested according to the ASTM 6584 test procedure for quantifying free and bound glycerin[37]. A gas chromatograph (GC) equipped with flame ionization detector (SRI 8610C) was used. We verified accuracy of the testing procedure by testing a commercial B-100 biodiesel sample. This same sample was sent to an external lab for an independent ASTM 6584 test. Both test results were in agreement.

5.5 Results and Discussion

From chapter 4, the capillary reactor was introduced and it showed improvement in biodiesel synthesis. The results illustrated that the flow rate and the temperature had a significant effect on the rate of conversion of oil to FAMEs. This section will investigate the influence of titanium micro-reactor on temperature and residence time. According to the results from previous chapter, the higher temperature favors the higher oil conversion. Consequently, the experiment in this chapter will be conducted only at high temperature, 50°C, for reaction temperature with various residence times. In order to understand the relationship between

residence time and diameter of reactor, the results from chapter 4 will be compared with results in this chapter. Finally, we compare the results of the experimental testing and the calculated energy consumption from the stirred batch, capillary reactor, and titanium micro-reactor to show the improvement of biodiesel production. These results are detailed below.

5.5.1 Effect of residence time on conversion

The residence time, which depends on the flow rate, was clearly found to range from 30 second to 8 minutes. Figure 5.3 presents the amount of oil by percent weight verses residence time. As expected, the mass of the oil in the sample is reduced with increased residence time. The triglycerides (TG) dominate the oil mass until residence time of 4 minutes. This is consistent with the three-stage nature of the transesterification reaction. Diglyceride (DG), and monoglyceride (MG) are intermediates [52]. In addition, the transesterification reaction rapidly decreases the amount of TG, DG, and MG at the beginning and they slightly decreased after residence time at 4 min. It is obviously with rapid mass transfer that occurs during the first four minutes in the reactor.

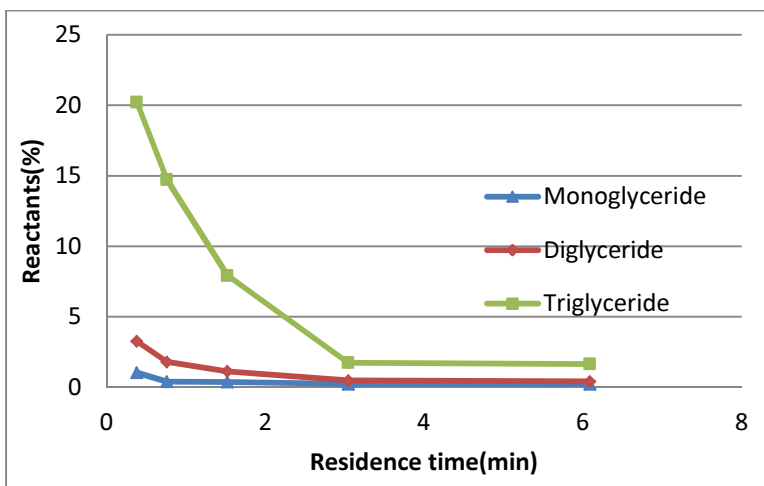


Figure 5.3 Oil components during the transesterification at 50°C.

5.5.2 The effect of oil conversion on flow rate

Figure 5.4 illustrates the relationship between oil conversion and flow rate of oil at 50°C. The results demonstrate as expected. The conversion decreases from 98% to 75% when the flow rate increases from 1.3 ml·h⁻¹ to 21.0 ml·h⁻¹. This underlines the significant effect of the flow rate on the conversion of oil to FAMEs.

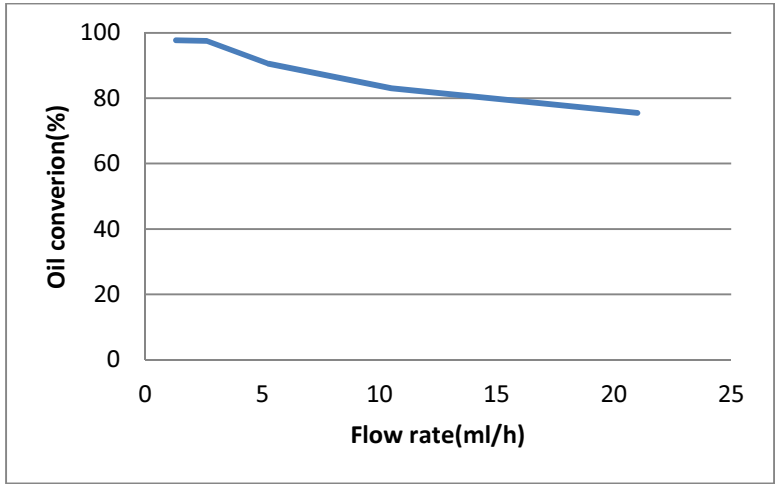


Figure 5.4 Oil conversion verses flow rate at 50 °C

5.5.3 The effect of oil conversion on residence time

Figure 5.5 indicates the effect of residence time on the conversion of oil at 50 °C. The results evidently depict that the oil conversion increased from 75% to 98% when the residence time increased from 30 second to 6 minutes. From the graph, the oil conversion gets 90% by using 2 minutes for the reaction time. Furthermore, the increase of residence time corresponds to the decrease in flow rate of the oil.

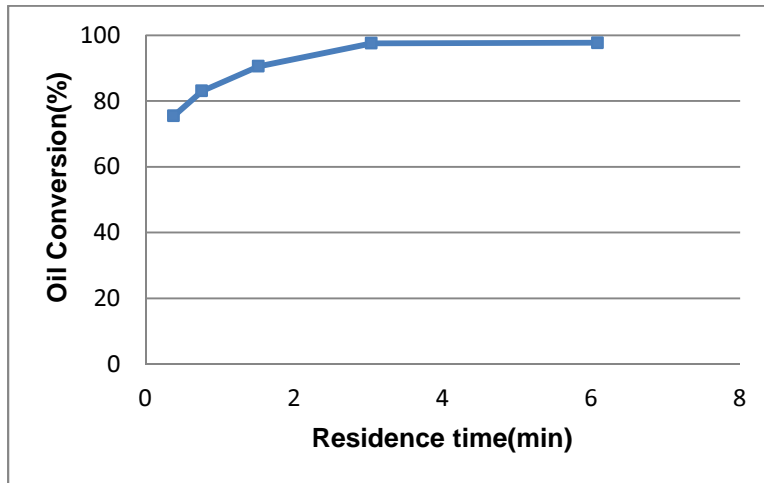


Figure 5.5 Effect of oil conversion on residence time at 50°C

5.5.4 The comparison of oil conversion for titanium micro-reactor, capillary, and batch reactor

The figure 5.6 compares the oil conversion among titanium microreactor, capillary reactor, and batch reactor at 50°C. The results clearly show that titanium reactor gives the highest efficiency on oil conversion when compare with capillary and batch reactor, respectively. The graph presents the dramatic trend that batch reactor needs much longer time to produce the same amount of FAMEs when compare with the titanium reactor. From the outcomes, the percentages of oil conversion from titanium reactor and capillary reactor are almost the same. However, the titanium reactor used only 8 minutes to get the same percentage of oil conversion on capillary reactor. From the results, the smaller dimension showed the 50% shorter residence time than bigger dimension. Then, titanium reactor uses less residence time than capillary reactor because the titanium reactor has dimension of reactor much smaller than capillary reactor. Consequencely, the titanium reactor has higher mass transfer, diffusion, rate than capillary reactor and batch reactor. Furthermore, the dimension of reactor has significant effect on the residence time of biodiesel production.

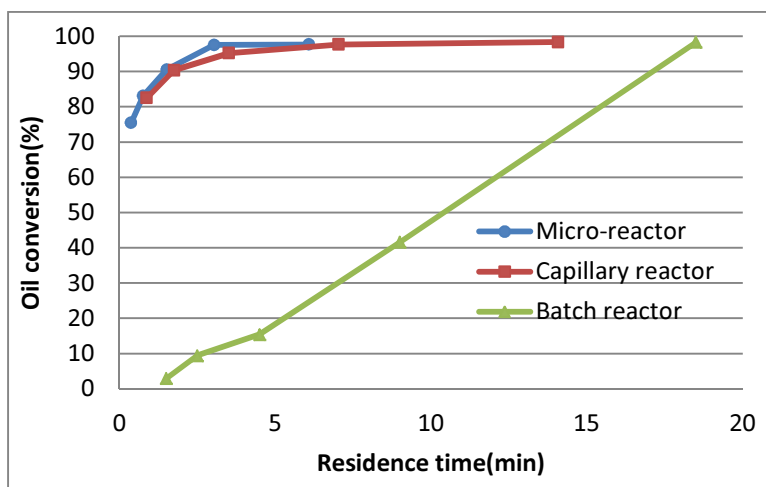


Figure 5.6 Comparison of titanium, capillary, and batch reactor

Table 5.1 The flow rate and the Reynolds number

Flow rate (ml/h)	Reynolds number at 50°C	
	Titanium reactor	Capillary reactor
1.3	$6.12 \cdot 10^{-3}$	$3.61 \cdot 10^{-3}$
2.6	$1.22 \cdot 10^{-2}$	$7.23 \cdot 10^{-3}$
5.2	$2.45 \cdot 10^{-2}$	$1.45 \cdot 10^{-2}$
10.5	$4.90 \cdot 10^{-2}$	$2.89 \cdot 10^{-2}$
21.0	$9.80 \cdot 10^{-2}$	$5.89 \cdot 10^{-2}$

From the table 5.1, we can clearly see the advantage of the microfluidics. The higher dimension gives the shorter residence time. However, the smaller dimension has higher Reynolds number but it is still be in the laminar flow pattern.

The lower peak velocities and shorter residence times lead to shorter reactors and lower pressure drops compared to conventional plug flow reactors with static mixers. This translates into savings in capital and operating costs for continuous flow production of biodiesel.

5.5.5 The summary of energy consumption and power for titanium micro-reactor, capillary, and batch reactor

The table 5.2 presents the power and energy consumption per unit mass of titanium micro-reactor, capillary and batch reactor. At the same residence time, the micro-reactor, capillary and batch reactor give the same oil conversion within different Reynolds number. The results clearly indicate that the capillary reactor shows the small energy consumption per unit gram of biodiesel of 0.001629 Jg^{-1} , merely 0.55% of batch reactor. It is evident that capillary reactor uses less power than batch reactor. This obviously presents that the energy consumption can be remarkably decreased by using the capillary reactor.

Table 5.2 Comparison of energy consumption

Name	Reaction mode	Yield (%)	Power(watt)	Energy(Jg^{-1})
Micro-reactor	Continuous	97.68	$5.1328\text{e-}7$	0.002500
Capillary reactor	Continuous	98.3550	$4.0833\text{e-}7$	0.001629
Batch reactor	Batch	98.3284	0.0876	0.298673

5.6 Conclusion

The transesterification of vegetable oil was demonstrated using a microreactor made by titanium. The dimension of titanium reactor was smaller when compared with capillary reactor for 40% and it gave the shorter residence time for 60%. Dependence of oil conversion on reaction was verified using microreactor. The required residence times are much less than capillary and batch reactors for same level of conversion. The results illustrated that the smaller dimension gave the lower residence time because the small dimension had higher mass transfer rate.

CHAPTER 6
TRANSESTERIFICATION OF VEGETABLE OIL WITH ACID CATALYST IN
CAPILLARY REACTOR

6.1 Introduction

Heterogeneous and homogeneous catalysts are normally performed via transesterification reaction of vegetable oils to produce biodiesel. Due to the numerous advantage of solid catalyst, the heterogeneous catalysts are promising for making biodiesel because they are environmentally friendly, reusable, and regenerated catalysts. However, high molar ratio of alcohol to oil, high amount of catalyst, high pressure and high temperature are required in the heterogeneous catalysts for the biodiesel reaction. Moreover, one of the major disadvantages of homogeneous catalysts is that they cannot be reused or regenerated and the separation of catalyst from products, it is difficult and requires more equipment which could lead to the higher production costs[42]. Because of separation issue, Zabeti et al. [24] reviewed the catalytic activity of several solid base and acid catalysts, particularly metal oxide and supported metal oxide for biodiesel production. In order to reduce the process of production, solid acid catalysts were able to do transesterification and esterification simultaneously and convert oil with high free fatty acid. For the metal oxides, magnesium oxide, calcium oxide, and strontium oxide were used to be the alkali earth metal oxides and zirconium oxide titanium oxide, and zinc oxide were used to be the transition metal oxides. For the catalyst supporters, the studies showed that alumina, silica, zinc oxide, and zirconium have been used in biodiesel production. Moreover, the sulfated TiO₂ and ZrO₂ also showed strong acidity for the supporter[43]. Because of various of heterogeneous catalyst benefits, Nawaratna et al. [44] studied the transesterification of soybean oil using isopropanol as alcohol with the presence of titanium isopropoxide as a catalyst. They were interested in the varying degrees of polymerization with

different temperature and residence time. The results indicated that the highest yield of methyl ester was obtained 41.56% at 200°C with 1%(w/w) of the monomeric form of the catalyst after 3 h. They concluded that reaction temperature and residence time were the significant effects on the behavior of the dimeric and higher forms. Serio et al. [45] used 2wt% of $\text{VOPO}_4 \cdot \text{H}_2\text{O}$ to be a solid acid catalyst in the transesterification of soybean oil at 150°C reaction temperature, 1:1 molar ratio of alcohol to oil, and the reaction reached to the 80% of oil conversion. Jitputti et al. [26] used 3wt% of ZnO as a solid acid catalyst in the transesterification of palm kernel and coconut oil at 300°C, 6:1 molar ration of alcohol to oil and conversion reached to 86% and 78%, respectively. They also used 1wt% of $\text{ZrO}_2/\text{SO}_4^{2-}$ as a solid acid catalyst in the transesterification of palm kernel and coconut oil at 200°C, 12:1 molar ration of alcohol to oil and conversion reached to 90% and 86%, respectively. The Titanium has been attractive for a promising solid acid catalyst, He et al. [43] used 2 wt% of $\text{TiO}_2/\text{SO}_4^{2-}$ as a solid acid catalyst in the transesterification of cottonseed oil at 230°C, 12:1 molar ration of alcohol to oil and conversion reached to 90%. Kaita et al.[46] used 10 g of $\text{Al}_2\text{O}_3/\text{PO}_4^{3-}$ as a solid acid catalyst in the transesterification of palm kernel oil at 200°C, 5:1 molar ration of alcohol to oil and conversion reached to 69%. Delfort et al. [47] used 6wt% of $\text{Al}_2\text{O}_3/\text{TiO}_2/\text{ZnO}$ as a solid acid catalyst in the transesterification of colaza oil at 200°C, 1:1 molar ration of alcohol to oil and conversion reached to 94%. Because of the stability of titanium, Wen et al.[48] studied the mixed oxides of $\text{TiO}_2\text{-MgO}$ by sol-gel method to produce biodiesel from waste cooking oil with a batch reactor. They used conditions at 160°C with 50 of methanol and oil molar ratio for 6h. The results showed that $\text{TiO}_2\text{-MgO}$ had a promising to synthesize the biodiesel in the large scale. Moreover, the activity of catalyst was also good when reused and regenerated. The large particle size of a solid acid catalyst was produced by Peng et al.[49] They used $\text{SO}_4^{2-}/\text{TiO}_2\text{-SiO}_2$ for transesterification of oil with high FFAs in batch reactor. The results indicated that the catalyst had a good stability and could be reused. The esterification with a present of solid super acid was studied by Li et al.[50] They investigated the compound of $\text{SO}_4^{2-}/\text{ZrO}_2\text{-TiO}_2$ with

lanthanum as a catalyst. The conditions were prepared by 5 wt.% of catalyst at 60°C with 5 h for residence time. The results indicated that the yield reached above 95% and catalyst could be recycled without treatment

This chapter was aimed to evaluate the promising of the solid acid catalyst, $\text{TiO}_2/\text{SO}_4^{-2}$, in transesterification of vegetable oil with dry methanol using 1:24 molar ratio of oil and methanol at 200°C.

6.2 Materials

Food grade soybean oil purchased from a local grocery store was used for the vegetable oil feedstock. The free fatty acid (FFA) content of the oil determined according to AOCS method #Ca 5a-40(15) was determined to be 0.08%. The dry methanol was reagent grade (Sigma-Aldrich). Moreover, TiOSO_4 was used as a solid catalysts and dry in the oven at 50-55°C for 2 days to get rid of the water. The Teflon (PTFE) capillary reactor used for the experiment was purchased from Upchurch Scientific. The Teflon material is chemically resistant to the reactants and products and is optically clear, thus allowing the flow patterns to be observed.

6.2.1 Catalyst preparation

The Titanium dioxide sulfate ($\text{TiO}_2/\text{SO}_4^{-2}$) was prepared by using Titanium dioxide (TiO_2) and sulfuric acid (H_2SO_4). The preparation started with diluting 20 ml of titanium tetrachloride (TiCl_4) in 1000 ml of water bath at 0°C with fast agitation. After we got the TiOCl_4 solution, the aqueous ammonia (18 wt%) was used to be a precipitating agent. The aqueous ammonia was added into the TiOCl_4 until ph 7. The mixture consisted of precipitation of TiO_2 and Cl^- solution in water. The TiO_2 particle was washed with water and filtered. The TiO_2 particle was dried to prepare the sulfate step. The sulfated titanium dioxide was prepared using dried titanium particles by impregnation with a 0.5 mol/L of H_2SO_4 for 24 hour [43]. After filtered, the $\text{TiO}_2/\text{SO}_4^{-2}$ was dried and calcined at 450°C for 4 hours [54].

The particle size of $\text{TiO}_2/\text{SO}_4^{-2}$ can measure by using Powder X-ray Diffusion (XRD) measurements. The powder X-ray Diffraction (XRD) measurements were performed on a XRD D500 Kristalloflex810, Siemens, with $\text{Cu } k\alpha$ 1.54 Angstroms a radiation range 15-70° (2θ) at 40kV and 30mA, and a scan speed of 0.02°/sec

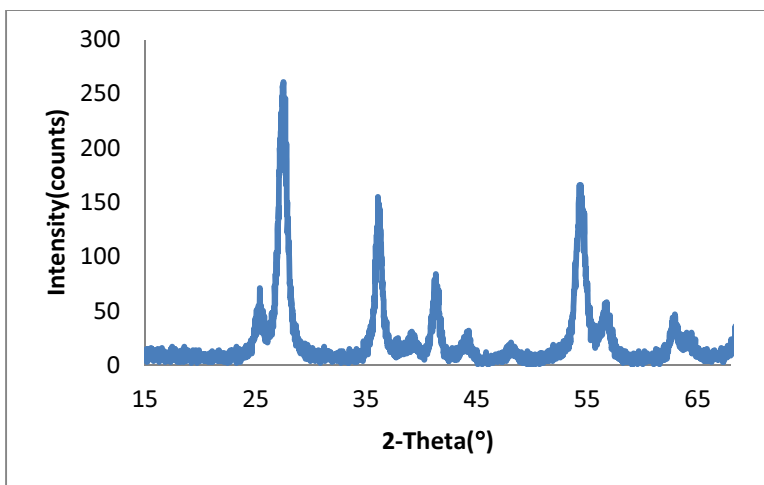


Figure 6.1 The XRD pattern of $\text{TiO}_2/\text{SO}_4^{-2}$

6.3 Experiment Procedure

Vegetable oil and dry methanol were prepared for the production of biodiesel in a capillary reactor. $\text{TiO}_2/\text{SO}_4^{-2}$ was used as a solid catalyst and placed in the PTFE capillary reactor. The capillary tube had an inner diameter of 1mm and a length of 0.30 m.

The capillary tube was connected to a Y-type micromixer (Upchurch Scientific) with 0.5 mm thru holes. Syringes were connected to the inlet ports of the micromixer via 1.0 mm diameter PTFE tubing (Upchurch Scientific). The syringes were placed in an infusion syringe pump (model KDS200, KD Scientific). The pressure gage was set in between the outlet of micromixer and inlet of capillary reactor. The reactor was placed in a stirred water bath. Heating was provided by a 500.0W immersion heater with a thermostat. The experimental schematic is illustrated in Figure 6.1.

The outlet of the capillary reactor was placed in a 11.0 mL glass vial. The products in the collection vial gravity separated with the FAME/oil phase on top and glycerol/water phase on the bottom. Approximately 2.0 mL of product was collected for each run.

A 5.0 mL syringe was used for the oil and dry methanol. This resulted in a constant 1:1 volume flow rate ratio of oil to methanol. In addition, the molar ratio of oil to methanol was 1:24.

The

The flow rate of oil and methanol were controlled by the syringe pump and were fixed at 0.25 ml/h for this experiment. The bath temperature was held at 200°C.

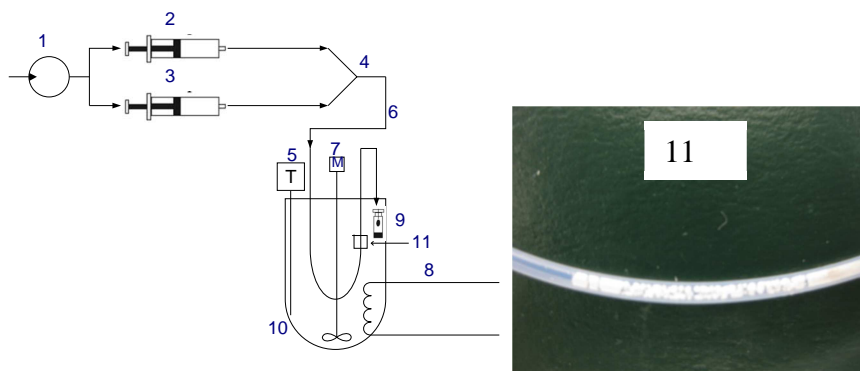


Figure 6.2 Schematic diagram of transesterification of biodiesel system with acid catalyst in capillary reactor with (1)pump, (2)oil syringe (30mL), (3)methanol syringe 95mL), (4) Y-type micromixer, (5) temperature control monitor, (6) capillary reactor, (7) magnetic stirring, (8) immersion heater (9) collection vial, (10) oil bath, and (11) $\text{TiO}_2/\text{SO}_4^{2-}$ in capillary reactor

6.4 Chemical Analysis

The FAME product samples were centrifuged for 15 minutes and then dried under -80 kPa vacuum at 50°C for 20 minutes. The samples were prepared and tested according to the ASTM 6584 test procedure for quantifying free and bound glycerin[37]. A gas chromatograph (GC) equipped with flame ionization detector (SRI 8610C) was used. We verified accuracy of the testing procedure by testing a commercial B-100 biodiesel sample. This same sample was sent to an external lab for an independent ASTM 6584 test. Both test results were in agreement.

6.5 Results and Discussion

The experiment was performed with oil/methanol molar ratio of 1:24, 200°C reaction temperature, 48.16 wt% of the catalyst (based on weight of the vegetable oil) for the transesterification of vegetable oil with dry methanol by using $\text{TiO}_2/\text{SO}_4^{-2}$ as a solid acid catalyst.

6.5.1 The effect of oil conversion on residence time

The figure 6.2 shows the relationship between oil conversion and residence time. It is very interesting that, at 200°C, methanol is evaporated and moves very fast by itself. Unfortunately, the results indicate that the average oil conversion is 84% at residence time 1 h. Furthermore, the experiment cannot run more than 9 h because the pressure in reactor is very high and catalyst plugs the reactor. The pressure drop will be talked in the following section.

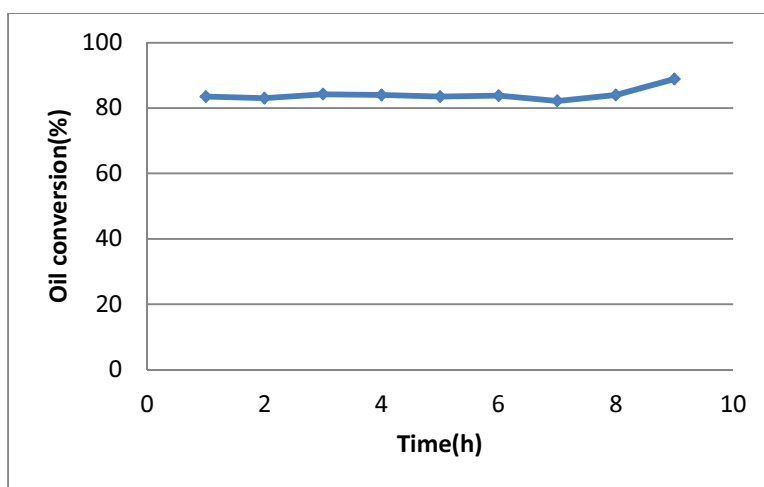


Figure 6.3 The effect of oil conversion on residence time at 200°C

6.5.2 The effect of pressure on residence time

The figure 6.4 presents the relationship between the pressure drop and time. The experiment was conducted using capillary reactor with $\text{TiO}_2/\text{SO}_4^{-2}$ as a catalyst at an average particle size of 22.6 μm . The graph shows the effect of pressure drop on residence time. As we expected, the pressure drop gradually increase with the increasing residence time. The results clearly indicate that the pressure drop is going up due to the packed titanium in reactor.

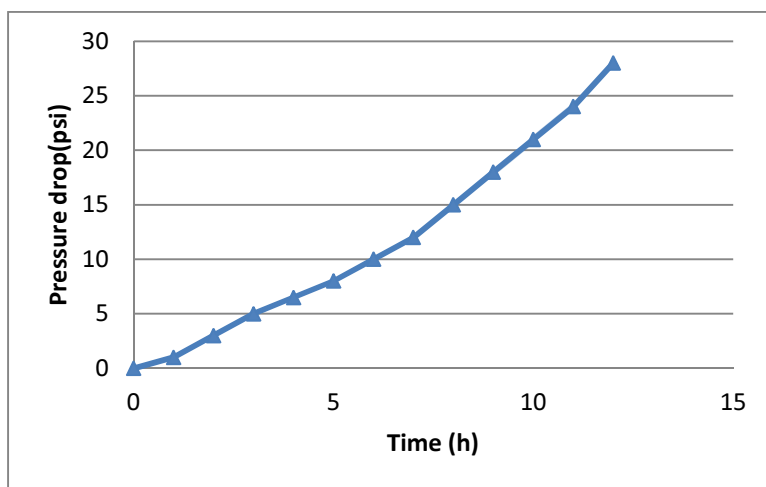


Figure 6.4 the effect of pressure drop on residence time.

6.6 Conclusion

This project proposes the experiment and numerical investigation of transesterification of vegetable oil with capillary reactor by studying homogeneous and heterogeneous catalyst. In addition, the capillary reactor technology can reduce the reaction time for biodiesel production, improve the efficiency of transesterification, and use the absence of turbulent mixing. With a homogeneous catalyst, potassium hydroxide used applied a basic catalyst in capillary reactor. For the heterogeneous catalyst, the project is focused on transesterification process with solid acid catalyst using $\text{TiO}_2/\text{SO}_4^{-2}$. There is a promising solid acid catalysts such as no soap, no more washing step, and no separation, as well as esterification of the free fatty acid in vegetable oil simultaneously. The project shows improvement of biodiesel production by using slug flow in capillary reactor. Finally, the simulation model using finite element method for the slug flow in capillary reactor of transesterification will be investigated for the new modeling in capillary reactor. In the model, the convective and diffusion mass transfer are used in the transesterification reaction to illustrate the improvement of the biodiesel production.

CHAPTER 7

NUMERICAL INVESTIGATION OF BIODIESEL PRODUCTION CAPILLARY MICROREACTOR

7.1 Introduction

The over past two decades, microreactors, the microfluidics, have remarkably enhanced for many disciplines such as portable energy devices, intensification of heat and mass transfer, high volume/surface ratio, short diffusion distance fast, and efficient heat dissipation, reaction kinetics and mechanism studies [47],[51]. The advantages of microreactor also include reduce time and energy in the reaction. According to the enhancement of microfluidics, the characteristic of flow pattern in microreactor has been studied by Kashid et al. [49,50]. They investigated slug flow in capillary reactor by using computational fluid dynamics (CFD) to predict the internal circulation and slug flow generation. Liquid-liquid slug-flow reactor has been occurred by mass transfer process. The convection with in slug and diffusion between slugs are the mass transfer process. To illustrate, the convection process due to the internal circulations within each slug because the shear force acts among the slug axis and capillary wall. Moreover, the diffusion process happens when there are the concentration gradients between two consecutive slugs [35]. Then, the slug flows have significantly influenced for fast and effective mixing [48]. Since channel walls are very close, resulting Reynolds numbers are small and laminar flow characteristics within the capillaries are obtained. In order to reduce the residence time for biodiesel production, microreactor technology was widely used to apply in biodiesel. Recently, Wen et al.[20]observed that the high reaction efficiency of the microchannel reactor is attributed to the intensification of overall volumetric mass transfer by passive mixing at the microscale. Moreover, Guan et al. [41] showed the continuous biodiesel process that the residence time was decreased when using a capillary microreactor within a residence time of

100 s. Since the microreactors have been successfully to reduce the residence time to produce biodiesel. The slug flow capillary microreactor has been studied to understand the mechanism of convection and diffusion. Because of high heat transfer in microreactor, Pohar et al.[51] studied the heat transfer of aqueous flows in microreactor. They compared the results between the mathematical modeling in a three-dimension and experimental data for laminar flow at steady state. The results showed that both are perfectly agreement. The characteristic of flow was observed to understand the reaction of the process. Guan et al.[52] studied the flow patterns, slug flow, of transesterification of oil in microtube. Furthermore, Carucci et al.[53] predicted the flow characteristics for microchannels by using a two-dimensional finite element model and computational fluid dynamics (CFD) simulations. Moreover, the reaction rate constants of biodiesel provided the speed of reaction. Dennis et al. [54] showed the rate constants for the kinetics equations to describe the transesterification reaction of vegetable oil by using an inverse procedure.

This chapter includes the development and utilization of a numerical finite element model for the transesterification reaction in a slug flow in capillary reactor. In the model, the convective and diffusion mass transfer are used in the transesterification reaction to illustrate the improvement of the biodiesel production. To illustrate, a mathematical model is set up with implementation of finite element method to demonstrate the influence of volume flow rate on synthesis of biodiesel. The segmented flow inside capillary will be studied in a lagrangian reference frame. The Navier-Stokes equation and modified convection-diffusion equation will be solved numerically. All reversible reactions during synthesis of biodiesel will be illustrated with different volume flow rate. The relationship between residence time and different volume flow rate will be revealed for biodiesel production in capillary.

7.2 Mathematical model

A mathematical model that governs the multiphase chemically reacting flow through the reactor channel was investigated. The capillary reactor was studied to be the place of occurring reaction. In order to understand the flow behavior of reacting flow, the model was focused on the liquid-liquid phase passing through in the microtube. Due to the axisymmetric nature of flow within a capillary, a slice of quadrant section of capillary is selected as the computational domain to investigate the flow behavior in a capillary microreactor. According to the flow characteristic of two immiscible fluids, a continuous segmented flow forms inside the capillary. Since the two segments form periodically in a continuous loop, a pair of two-segment is selected to be studied; furthermore, the Lagrange in reference frame is chosen to ensure the focus on the two phases. On the other hand, a lot of computational effort will be saved than computing the entire continuous flow. Moreover, there are two adjacent domains of immiscible liquid phases which are methanol and oil phase, respectively.

A constant volume flow rate 3.2:1 of oil to methanol and diameter 500 μm are specified. According to the volume flow rate, this also gives a phase length ratio of 3.2 between oil and methanol. The following 2D picture represents the oil phase in domain 1 and methanol phase in domain 2. Furthermore, the width and the length of rectangles denote the radius of the capillary and the length of phases, respectively.

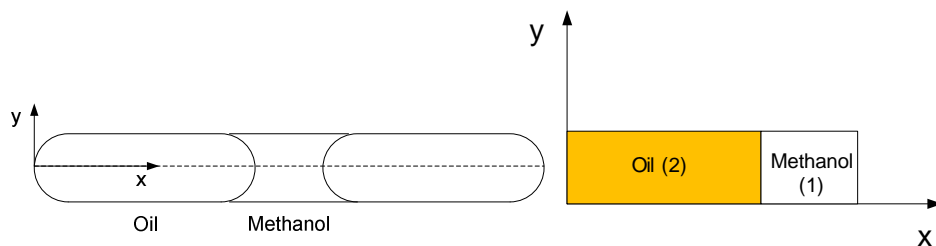


Figure 7.1 Schematic of computational domain; 1 represents methanol phase and 2 represents oil phase

7.3 Governing Equation

Within each phase, the velocity and pressure fields must satisfy the Navier–Stokes equations that governs the motion of viscous incompressible flows. Moreover, the flow is laminar due to the small Reynolds number. The following continuity equation and incompressible and steady Navier-Stokes equations are solved for velocity (u) and pressure (p):

$$\nabla \cdot \vec{u} = 0 \quad (7.1)$$

$$(\vec{u} \cdot \nabla) \vec{u} + \frac{\Delta p}{\rho} + \frac{\mu}{\rho} \nabla^2 \vec{u} = 0 \quad (7.2)$$

We assume the steady state, no body force and axisymmetric in three dimensions.

Where \vec{u} is velocity field

p is pressure

μ is dynamic viscosity

ρ is density

The concentration distribution of all reactants, intermediates and products are obtained by solving the mass convection-diffusion equation for the capillary reactor in biodiesel production.

$$\frac{\partial C_{ij}}{\partial t} + \vec{u} \cdot \nabla C_{ij} - D_{mn} \nabla^2 C_{ij} - R_i = 0 \quad (7.3)$$

The boundary conditions associated with

Where C_{ij} is the concentration of reactant i in domain j

i is the reactants for 6 species e.g. TG, DG, MG, GL, ME, MeOH

j is the two phases, which is oil and methanol phase

\vec{u} is velocity field solved from eq.(6.2)

D_{mn} is the diffusion coefficient of solute m in solvent n

R_{ij} is the reaction rate equation

The diffusion coefficient [55] was calculated from Wilke-Chang correlation in equation 7.4 [46];

R_{ij} is a reaction rate which will be introduced in next section.

$$D_{mn} = 1.17 \times 10^{-16} \frac{T \sqrt{\varphi_n M_n}}{\mu_n (M_m / \rho_m)^{0.6}} \quad (7.4)$$

Where

D_{mn} is the diffusion coefficient of solute m in solvent n

T is temperature in K

φ_n is the association parameter, value of 2.6 is for aqueous phase, value of 1 for other unassociated solvents

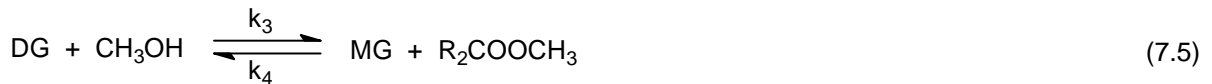
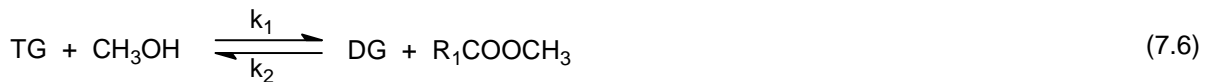
μ_n is the dynamic viscosity of the solvent

ρ_m is the density of solute

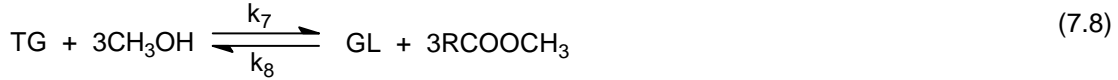
M_m and M_n are the molecular weight of solute and solvent

7.4 Reaction Kinetics

Biodiesel production by transesterification of vegetable oil with methanol (MeOH) consists of a several consecutive, reversible reactions, as shown below. The first step is the conversion of vegetable oil (triglycerides, TG) to diglycerides (DG), which is followed by the conversion of diglycerides to monoglycerides (MG) and finally by the conversion of monoglycerides to glycerides (GL). After the conversion, three mole of methyl ester (ME) are obtained for each triglyceride reacted. The reaction steps are in equation (1) – (3) where k_{1-6} are rate constants[16].



The overall reaction



The general form of the governing set of differential equation characterizing the stepwise reactions involved in the transesterification of triglycerides in equation (4) – (9)

There are six reaction rate equation for biodiesel and they are ordinary differential equations due to the nature of reversibility which are shown following.

$$R_{\text{TG}} = \frac{dC_{\text{TG}}}{dt} = -k_1 C_{\text{TG}} C_A + k_2 C_{\text{DG}} C_{\text{ME}} \quad (7.9)$$

$$R_{\text{DG}} = \frac{dC_{\text{DG}}}{dt} = k_1 C_{\text{TG}} C_A - k_2 C_{\text{DG}} C_{\text{ME}} - k_3 C_{\text{DG}} C_A + k_4 C_{\text{MG}} C_{\text{ME}} \quad (7.10)$$

$$R_{\text{MG}} = \frac{dC_{\text{MG}}}{dt} = k_3 C_{\text{DG}} C_A - k_4 C_{\text{MG}} C_{\text{ME}} - k_5 C_{\text{MG}} C_A + k_6 C_{\text{GL}} C_{\text{ME}} \quad (7.11)$$

$$R_{\text{ME}} = \frac{dC_{\text{ME}}}{dt} = k_1 C_{\text{TG}} C_A - k_2 C_{\text{DG}} C_{\text{ME}} + k_3 C_{\text{DG}} C_A - k_4 C_{\text{MG}} C_{\text{ME}} + k_5 C_{\text{MG}} C_A - k_6 C_{\text{GL}} C_{\text{ME}} \quad (7.12)$$

$$R_{\text{GL}} = \frac{dC_{\text{GL}}}{dt} = -k_5 C_{\text{MG}} C_A + k_6 C_{\text{GL}} C_{\text{ME}} \quad (7.13)$$

The following table is the kinetic rate constant for the soybean oil in biodiesel reaction.

Table 7.1 Kinetic rate constants for soybean oil ($\text{m}^3\text{mol}^{-1} \text{s}^{-1}$)

k1	k2	k3
0.427e-5	0.969e-5	0.200e-4
k4	k5	k6
0.100e-4	0.299e-4	0.904e-6

7.5 Simulation condition

A number of assumptions will be made to simplify the model. This section includes the development of all theoretical elements that are required to build a simulation model for producing biodiesel using Finite Element Method (FEM) with COMSOL on Matlab. In order to solve the numerical equation, the finite element discretization scheme is used in the model. The steady incompressible Navier-Stokes equation is applied to obtain the velocity flow field.

Moreover, the modified convection-diffusion is solved including the implementation of flow field.

The entire domain is discretized by a structured mesh topology with clustering on the boundary.

The following assumptions are for all simulations considering:

1. Constant viscosity, density and temperature
2. Front and back interface of each slug are the same: periodical boundary condition
3. The slug size is the same for all velocities or undeformed shape of two phases during the mass transfer process and reaction
4. The problem is considered axis symmetric in three dimension
5. The fluid in each slug is considered to be The Newtonian fluid, incompressible, and isothermal

For the flow field, the assumption is decided by considering the moving wall of capillary with a constant average flow velocity while the oil and methanol phase are held to be the stationary part. Moreover, a constant average flow velocity is computed by using the volume flow rate of oil and methanol with the division of capillary reactor area. During the reaction process at the interface between two phases, the slip boundary condition is applied in the equation.

The modeling for the convection-diffusion, we define the boundary conditions to be independent for each species by nature of consecutive. The reversible reactions are also included in the equation reaction. The axial symmetry was applied at the origin of radius ($r=0$) for all species. Moreover, because of no mass flux across the wall, the insulated boundary condition of capillary wall is established. During the diffusion process from glycerol to methanol phase and reversible reaction, constant mass flux of glycerol is employed at the interface between oil and methanol. During the continuous phases between two phases, a periodic boundary condition is applied between the interfaces of two phases to solve the glycerol equation. In addition, the methanol concentration will be reduced by time. The physical properties of methanol phase and oil phase are presented in table 2.

Table 7.2 Fluid Properties

	<i>Density</i> (kgm ⁻³)	Dynamic Viscosity at 40°C (Pa.s)
Soybean oil	897.9	26.0e-3
Methanol	791.8	0.399e-3

7.6 Results and Conclusion

The simulation model by using Finite Element Method (FEM) with COMSOL on Mathlab was developed for the biodiesel synthesis in capillary reactor. The results of mathematical model were compared with the experimental results to support the agreement.

The unstead convection-diffusion equation is used to find the average concentration of TG, DG, and MG, respectively from figure 7.2. The figure 7.2 depicts the relationship between the conversion of TG, DG, MG, and residence time. As expected, the amount of Triglyceride in the sample is rapidly decreasing with increased residence time. Moreover, at the beginning, there is no diglyceride and monoglyceride in the oil phase until triglyceride is converted to diglyceride as well as diglyceride is converted to monoglyceride and it is gradually reduced by the time to produce biodiesel or methyl ester. The triglyceride is slightly decreased after 4 min. This is consistent with rapid mass transfer that occurs during the first 4 min in the reactor. The results obviously illustrate that it is the dependence of oil conversion on the residence time for capillary reactor.

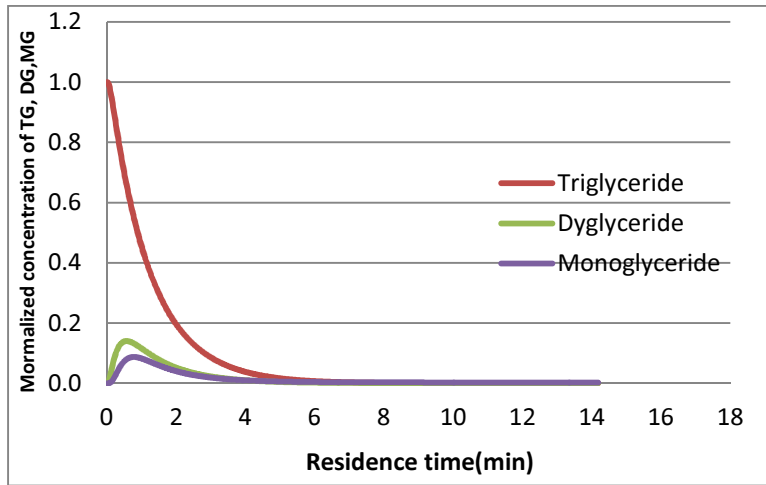


Figure 7.2 The concentration of TG, DG, and MG on residence time at flow rate 1.3 ml/h

The effects of oil concentration of TG, BD, and GL on the residence time are shown in figure 7.3. From the figure, the triglyceride is rapidly decreased while the biodiesel and glycerol are dramatically increased in the biodiesel production. As the theory, the simulation gives that one molecule of oil always gives three molecule of methyl ester and one molecule of glycerol.

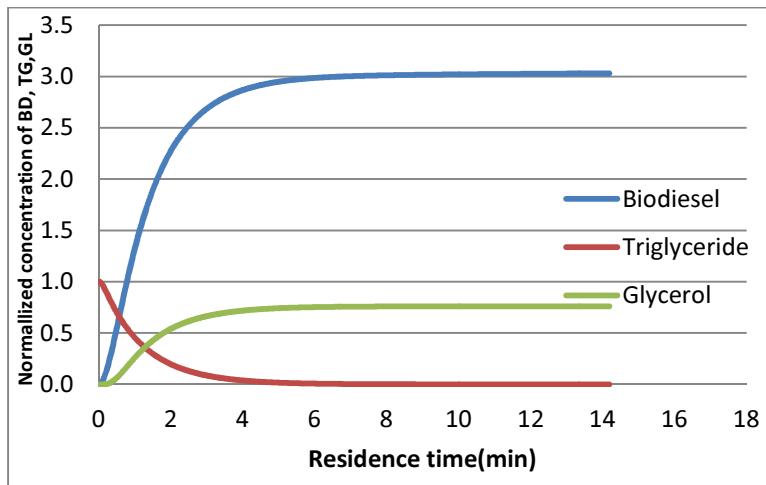


Figure 7.3 The concentration of TG, BD, and GL on residence time

The figure 7.4 presents the conversion of oil with the residence time. The tendencies of biodiesel synthesis are the same on the function of residence time. To illustrate, the higher

residence time gives the higher oil conversion. It is clearly that the volume flow rate is the significant effect on the biodiesel synthesis.

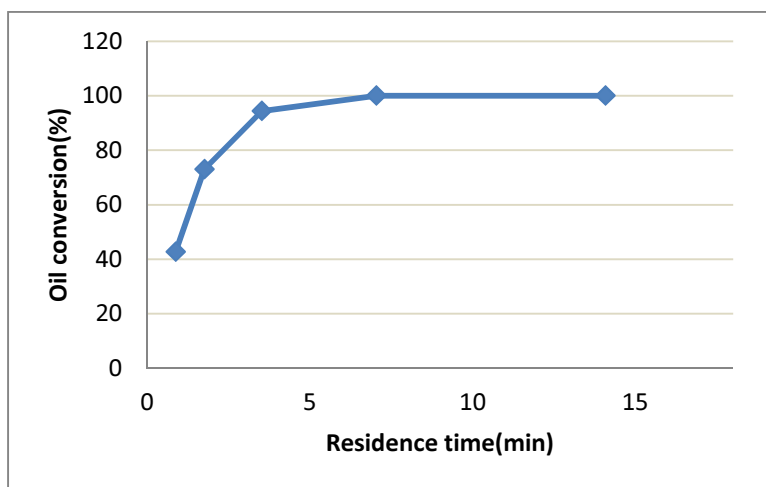


Figure 7.4 The oil conversion on the residence time at flow rate 21 ml/h

Figure 7.5 represents the relationship between experiment and modeling data. To illustrate, at 7.0 and 14.0 min of residence time, the trends is 2% higher. However, at 1.0 and 2.0 min residence time is approximately 50% higher. Because the rate constants of the experiment had an effect of the reaction, we calculated the rate constants by hands which these numbers were not précising. The future work will find the précising rate constant values for this model.

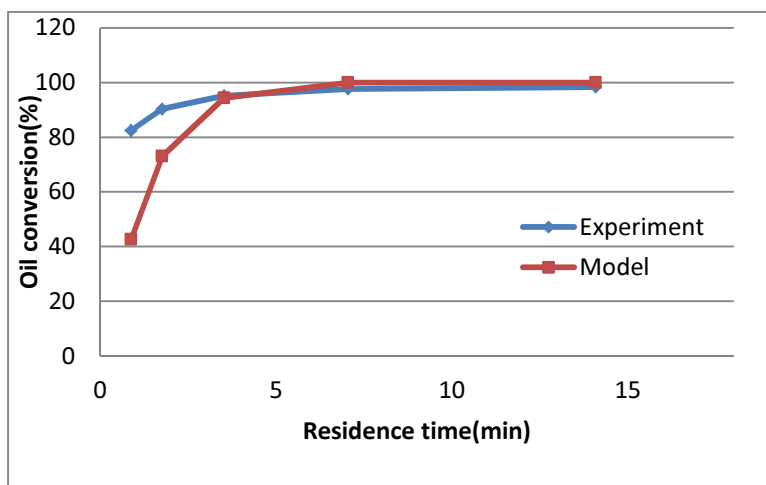


Figure 7.5 The comparison between experiment and modeling data at flow rate 21 ml/h

7.7 Conclusion

The capillary reactor is the enhancement of mass transfer to mix and separate the methyl ester production. According to the intensification of process, the capillary reactor is used to reduce the residence time in the biodiesel synthesis. A numerical model was developed and utilized for the transesterification reaction in a slug flow in capillary reactor. In a model, the convective and diffusion mass transfer are applied in the transesterification reaction to illustrate the improvement of the biodiesel production. To illustrate, a mathematical model is set up with implementation of finite element method to demonstrate the influence of volume flow rate on synthesis of biodiesel. As we expected, the predictions made by the model follow the same trends observed in the experiments. To illustrate, the dependence of oil conversion is significant effect on the residence time in capillary reactor for biodiesel production. Moreover, the biodiesel process can be reduced the residence time by continuous process of capillary reactor.

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CHAPTER 8

CONCLUSION

8.1 Discussion and Conclusion

The transesterification of vegetable oil with methanol in a presence of homogeneous alkali-catalyst via stirred batch reactor and continuous flow capillary reactor were studied in the experiment. The results clearly showed that, at the same Reynolds number, the conversion of vegetable oil greater than 98% could be achieved for continuous flow capillary reactor. However, there was no reaction in the stirred batch reactor case. Because of effective process, the capillary reactor used 0.55% of energy input of stirred batch reactor technology. This enhanced performance was due to the intensification of mass and heat transfer enabled by the use of the capillary reactor. Since channels were very small, resulting the less residence time was obtained by microreactor. The titanium microreactor of transesterification with homogeneous alkaline catalyst was conducted and compared with the capillary reactor. The results indicated that the smaller channel gave the shorter residence time. In addition, this work was also interested in the heterogeneous acid catalyst because of no saponification reaction, no more washing step and also esterification of the free fatty acid in vegetable oil simultaneously. The titanium oxide sulfate particle was one of the most attractive catalysts because it showed the acidity. In order to reduce the biodiesel production, the transesterification of vegetable oil with TiOSO_4 as a packed bed of micro-particles catalyst was conducted by using capillary reactor. The results presented that the 84% of oil conversion was reached in 1 h. for the residence time. Because of the greatly improvement of biodiesel synthesis, the TiOSO_4 had a promising of heterogeneous acid catalyst for biodiesel synthesis. Since the particles were packed, the pressure drop had become the major problem of TiOSO_4 catalyst. The results were

also indicated that the pressure drop increased by the time and no stability. In this reason, there are some future works for the titanium dioxide catalyst and we will talk in the further work in the next section. Finally, the simulation model using finite element method for the slug flow in capillary reactor of transesterification will be investigated for the new modeling in capillary reactor. In the model, the convective and diffusion mass transfer are used in the transesterification reaction to illustrate the improvement of the biodiesel production. The model the convective and diffusion mass transfer are used in the transesterification reaction to illustrate the improvement of the biodiesel production. The predictions made by the model followed the same trends observed in the experiments.

8.2 Future Work

There are many advantages of using solid acid catalyst. To illustrate, the solid acid catalysts not only promote the transesterification of vegetable oils but they also treat the esterification of free fatty acid in the vegetable oil as well. In addition, capillary reactor favors the intensifying process as well as separates the methyl ester and glycerol from the product. The research will be focused on transesterification of vegetable oil with acid catalyst in capillary tube or micro-reactor. Because of high pressure drop of TiOSO_4 particles in capillary reactor, the catalyst can be changed to TiO_2 nanotube by anodization method to increase the surface area and make the sulfate on nanotube surface. Currently, we have experimentally studied the transesterification of vegetable oil with TiO_2 nanotube. The results showed that the anodization of TiO_2 wire could be the catalyst for transesterification of vegetable oil in capillary reactor. The results significantly indicated the feasibility of biodiesel synthesis with TiO_2 nanotube in the future.

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