

Modelling of Microtube Reactor In Bio-Fuel Production Using CFD

by

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the

Chemical Engineering Programme

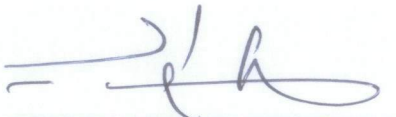
Universiti Teknologi PETRONAS

in partial fulfilment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(CHEMICAL ENGINEERING)

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January 2014

CERTIFICATION OF ORIGINALITY

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



WAN MUHAMMAD AZLI WAN ABDULLAH

ABSTRACT

Nowadays, the biological resources are the best option as alternative to the petroleum-based fuels or petrochemical solvents for renewable energy and green chemistry applications. Over the last 15 years, the production of biodiesel fuels (BDF) mainly composed of fatty acid methyl esters (FAME), had been intensively studied as it is an organic, biodegradable and non-toxic fuels source that is made from renewable resources including animal fats and vegetable oils. In spite of the usage of virgin and food grade oils have proven to be suitable feedstock for biodiesel production, the concern on the proper usage of widespread farmland areas for the production in the detriment of food supply have play an important role on the final chosen feedstock. The usage of non-edible crops like jatropha or castor oil, do not resolve the problem of requiring large plantation area. BDF is defined as the mono-alkyl esters of long-chain fatty acids synthesized by transesterification of triglyceride in vegetable oils or animal fats with alcohol to form fatty acid methyl ester (FAME). This project has theoretically assessed the transesterification of sunflower oil with methanol to produce fatty acid methyl esters (FAME) using KOH catalyst in a micro-channel tube reactor using ANSYS Fluent. Micro-reactor is considered for better heat and mass transfer, also micro-reactor provides admissible control over unwanted side reactions. The exact reaction path of biodiesel production is unknown so the lumped kinetics model is being used instead. Computationally, the volume fraction, the velocity profile, the pressure drop, density profile, and temperature profile are being examined based on the experimental setup which is using the methanol/oil molar ratio = 23.9 at 40 °C. The dimension of microreactor is fixed to 0.8 mm diameter. Based on the experimental result, the flow pattern at the entrance region of the microtube was segmented flow of the methanol and oil phases. As the reaction progress, fine droplets composed of the produced glycerol and methanol were dispersed and circulated in the oil segments. At a methanol/oil molar ratio of 23.9 at 60 °C, a quasi-homogeneous phase form approximately 300mm from the reaction inlet where the oil completely converted to FAME.

ACKNOWLEDGEMENT

The past 28 weeks of my enrolment in this final year project have been truly a valuable experience to me. Therefore, I would like to take this opportunity to express my gratitude to a number of people that have helped me throughout this project.

First and foremost, all praises to the Almighty, Allah S.W.T. for His mercy and grace, I was able to complete this project in good health and in the best condition. Next, I would like to express my gratitude to my Supervisor, Dr. Bawadi B Abdullah, who has supervised me throughout my project period. His willingness to guide and assist gave an opportunity for me in achieving the goals of my project. Besides, he was constantly supportive of the decisions that I make and always share his knowledge and experiences with me.

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CHAPTER 1

INTRODUCTION

1.1 Problem Statement

The alternative of using renewable energy as a substitute for the conventional fuels sources will help in sustaining the environment by reducing the greenhouse effect as well as controlling the environmental pollution. Currently, the bio-oil crops are distributed across the world and the amount are very large including woody and herbaceous crops growing in temperate and subtropical regions. Although the bio-oil resources are abundant, yet the utilization of the technology is very low. With the proper usage of the bio-oil new technology, this will at least counter back the world fuels and energy crisis. In addition bio-oil resources produce less NO₂ and SO₂ emission due to the less content of nitrogen and sulfur.

Nowadays, the biological resources are the best option as alternative to the petroleum-based fuels or petrochemical solvents for renewable energy and green chemistry applications. Over the last 15 years, the production of biodiesel fuels (BDF) mainly composed of fatty acid methyl esters (FAME), had been intensively studied as it is an organic, biodegradable and non-toxic fuels source that is made from renewable resources including animal fats and vegetable oils. In spite of the usage of virgin and food grade oils have proven to be suitable feedstock for biodiesel production, the concern on the proper usage of widespread farmland areas for the production in the detriment of food supply have play an important role on the final chosen feedstock. The usage of non-edible crops like jatropha or castor oil, do not resolve the problem of requiring large plantation area. BDF is defined as the mono-alkyl esters of long-chain fatty acids synthesized by transesterification of triglyceride in vegetable oils or animal fats with alcohol to form fatty acid methyl ester (FAME).

There are many publications on the FAME production available in the current literature and most of the studies focus on multiple aspects of the transesterification reaction. Among the publications, there are reviews of the different ways to catalyze

the transesterification reaction, different means for pre-treating the raw materials before transesterification, and different means to intensify the transesterification reaction for FAME production including emerging process review, acoustic cavitation, microwave, membrane reactors and also reactive distillation. At the end of reaction, they discussed on the methods of separation and purification of FAME at the outlet of the reactor.

The transesterification process is affected by many factors such as molar-to-oil ratio, catalyst type, catalyst amount, reaction temperature, and reaction time. To date, the common producing of commercial BDF is transesterification of triglycerides (found in vegetable oils or animal fats) with methanol in the presence of homogenous base catalysts (KOH, NaOH, KCH₃O, CH₃ONa) to yield FAME and glycerol. It is because it results in adequate reaction rates and product yields. The following reaction occur at temperatures lower than the boiling point of methanol and at normal pressure, definitely reduce the capital and operating costs associated with BDF production.

Microreactor systems designed for continuous production have been studied in recent years for the transesterification of vegetable oils. In the microreactor system, mass and heat transfer may be greatly intensified by the fast fluid flow condition, hence decreasing mass-transfer limitations, avoiding phase separation, as a consequence of the large surface area-to-volume ratio available, affording high process yields that can in the case of supercritical transesterification method prevent the decomposition of fatty acids and decrease the operating conditions.

In order to further improve the production of biodiesel fuels in the micro-channel reactor, the usage of the CFD simulation will show the details of transport processes and chemicals reactions in plant scale reactors. This will allow the design and optimization of the processes while minimizing the need for expensive and time consuming experimental testing.

1.2 Objectives

The objectives of this paper is to study the transesterification of sunflower oil with methanol to produce fatty acid methyl ester (FAME) via KOH catalyzed reaction in micro-channel tube reactor using computational fluid dynamics (CFD). The prime focus is on computational work (ANSYS fluent software) for investigating the behavior of tubular micro-channel tube reactor at elevated temperature.

1.3 Scope

The scope of study is prepared to ensure the project for the FYP will be finish within these two semesters of studying. The scope of study involves as follow:-

- The technique used is transesterification of sunflower oil with methanol via KOH catalyzed chemical reaction.
- The analysis only on the volume fraction, the velocity profile, the pressure drop, density profile, and temperature profile.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel Fuel (BDF)

Current used of fossil fuel as combustion which known to cause global emissions of CO₂ and other harmful gases such as CO, SO_x, NO_x and particulates have led to a serious greenhouse effect, major acid rain, and also deterioration of human health and environment as well. In addition, the increasing in the price of crude oil petroleum-based fuel as well as the depletion of the sources has attract major attention across the globe for the identification of environmentally friendly and renewable sources of alternative energy .

Nowadays, the biological resources are the best option as alternative to the petroleum-based fuels or petrochemical solvents for renewable energy and green chemistry applications. Over the last 15 years, the production of biodiesel fuels (BDF) mainly composed of fatty acid methyl esters (FAME), had been intensively studied as it is an organic, biodegradable and non-toxic fuels source that is made from renewable resources including animal fats and vegetable oils. BDF is defined as the mono-alkyl esters of long-chain fatty acids synthesized by transesterification of triglyceride in vegetable oils or animal fats with alcohol. In spite of the usage of virgin and food grade oils have proven to be suitable feedstock for biodiesel production, the concern on the proper usage of widespread farmland areas for the production in the detriment of food supply have play an important role on the final chosen feedstock. The usage of non-edible crops like jatropha or castor oil, do not resolve the problem of requiring large plantation area. To overcome this problem, the effective way is to use cheap and non-edible vegetable oils, animal fats, and waste oils as raw materials. However, the usage of low cost material contains significant amount of free fatty acids (FFA) which later contribute to the depletion of the catalyst, increasing in purification cost and lower yield in alkali catalyzed transesterification.

There are four primary ways to generate biodiesel from vegetable oils or animal fats which are:

- (i) Direct use and blending with diesel fuel
- (ii) Microemulsions with solvents such as methanol
- (iii) Thermal cracking (pyrolysis) by heat with aid of catalyst
- (iv) Transesterification with short chain alcohols with presence of catalyst

But, the most commonly used method is the transesterification of vegetable oil or animal fats with methanol.

BDF and petroleum diesel attain same properties and performance parameters. Compared with petroleum-based diesel, BDF has a relatively high flash point (150 °C) and good lubricating properties. The physical properties and energy content of BDF are also close to the petroleum diesel. Consequently, it can be utilized directly in conventional diesel engines with no modification. Furthermore, BDF burns cleanly, with low emissions of carbon monoxide, sulphur dioxide, particulates and unburned hydrocarbons. Apart from that, the plantation of resources without the destruction of nature would recycle more carbon dioxide by photosynthesis thus resulted in minimizing the effects of greenhouse gases on the earth's surface.

2.2 Fatty Acid Methyl Esters (FAME)

The transesterification of vegetable oils or animal fats producing Fatty acid methyl esters (FAME) as the main product are widely being used as raw materials in the production of fatty alcohols, sulphonated methyl esters, metallic soaps, fatty amines and amides, industrial processes in which it have gradually replaced fatty acids. In addition, FAME are also being used as solvents and as additives in formulations for adhesives and renewable fuels, and as an alternative of petroleum diesel.

The good solvent properties of FAME with relatively low volatility, biodegradable and non-toxic have being useful for various type of industrial applications. The applications of FAME are including:

- (i) Washing metal pieces
- (ii) Printing materials
- (iii) Graffiti
- (iv) Automobiles and plane parts
- (v) Cleaning oil spills
- (vi) Binders in inks
- (vii) Thinning agent
- (viii) Production of pesticides
- (ix) Phytosanitary products

2.3 Micro-Reactors

Since mid-1990, micro-reactions technology both for chemical and biological applications has experienced major technical and scientific development. Nowadays, these improvements in reaction system have proven, through adequate research and industrial practice, to offer innovative and sustainable solutions for the chemical process industries. The application and implementation of chemical engineering concept, make micro-reactor a viable unit.

Due to the small characteristics dimensions, it modifies the surface area to volume ratio of this reactor. Subsequently, the heat and mass transfer which facilitate in mixing are remarkably intensified and the temperature within can be tightly controlled. These advantages make micro reactor adapting to the mixing limited, high exothermic or endothermic or mass transfer limited reactions. As a result, the unwanted reactions are suppressed in the system and getting better parameters controlling in micro reactor compared to the conventional reactor. In addition, upon the better parameter control as the high exothermic reaction could be performed in a well-controlled condition, it ensures a safe operating process.

Mixing through the micro reactor is mainly dominated by laminar flow. In Figure 1 below, the mixing behavior is shown. Normally in large scale the mixing is governed by turbulent regime. In the case of laminar regime, the distance must be reduced so that molecules able to diffuse into each other and achieving good mixing even in laminar flow.

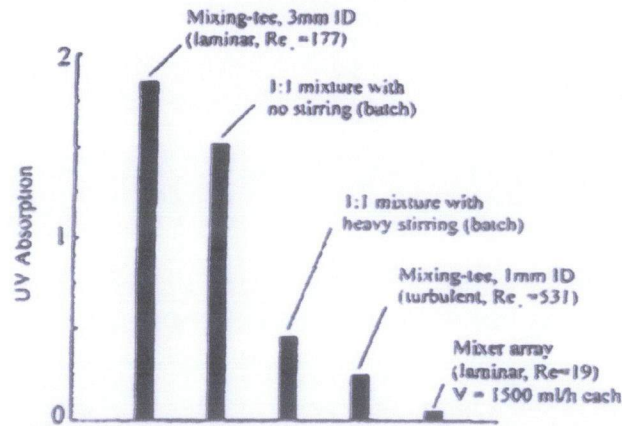


Figure 1: Comparison between micro-reactor and conventional reactor mixing

2.4 Transesterification of Vegetable Oils or Animal Fats

There are many publications on the FAME production available in the current literature and most of the studies focus on multiple aspects of the transesterification reaction. Among the publications, there are reviews of the different ways to catalyze the transesterification reaction, different means for pre-treating the raw materials before transesterification, and different means to intensify the transesterification reaction for FAME production including emerging process review, acoustic cavitation, microwave, membrane reactors and also reactive distillation. At the end of reaction, they discussed on the methods of separation and purification of FAME at the outlet of the reactor. As a conclusion, the possible method for FAME production by transesterification of vegetable oils or animal fats with alcohol can be categorized into following processes:

- (i) Base-catalyst process
- (ii) Acid-catalyst process
- (iii) Non-catalyst process
- (iv) Enzyme-catalyst process

The transesterification process is affected by many factors such as molar-to-oil ratio, catalyst type, catalyst amount, reaction temperature, and reaction time. Table 1 below shows the advantages and disadvantages of using different type of catalyst.

Table 1: Various Catalyst Effect

Type of catalyst	Advantages	Disadvantages
Homogenous base	Very fast reaction rate Mild reaction conditions Inexpensive	Sensitive to FFA content Soap formation (causing yield to decrease and increase difficulty for product and catalyst separation)
Heterogeneous base	Faster than acid-catalyzed reaction Mild reaction conditions Easy separation of catalyst Easy reuse and regeneration of catalyst	Poisoned at ambient air Sensitive to FFA content Soap formation Leaching of catalyst causing contamination of product Energy intensive
Homogeneous acid	Insensitive to FFA and water content Simultaneous esterification and transesterification possible Mild reaction conditions	Very slow reaction rate Corrosive catalysts (e.g. H ₂ SO ₄) Separation of catalyst is difficult
Heterogeneous acid	Insensitive to FFA and water content Simultaneous esterification and transesterification Easy separation of catalyst	Complicated reaction synthesis leading to higher processing costs High reaction temperature, high alcohol to oil molar ratio, long reaction times Energy intensive

To date, the common producing of commercial BDF is transesterification of triglycerides (found in vegetable oils or animal fats) with methanol in the presence of homogenous base catalysts (KOH, NaOH, KCH₃O, CH₃ONa) to yield FAME and glycerol. It is because it results in adequate reaction rates and product yields. The

following reaction occur at temperatures lower than the boiling point of methanol and at normal pressure, definitely reduce the capital and operating costs associated with BDF production. Even though it provide better in term of cost saving process, it also have disadvantages such as it is sensitive to the presence of free fatty acids (FFA) in the oil, which leads to undesired soap formation. Soap formation decreases the reaction yield and facilitates the formation of emulsions. The formation of emulsions caused trouble for the downstream separation process and lead to the increasing in BDF production cost.

2.4.1 Kinetic Model

In an ordinary BDF reactor, oil or fat (triglyceride) is converted to FAME producing glycerol as byproduct through a catalyzed chemical reaction called transesterification. Later on, glycerol is removed from the flow with both products purified subsequently. The purified FAME known as biodiesel and purified glycerol sold as co-product. The step wise reaction of the FAME production is shown in Figure 2 below.

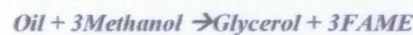


Figure 2: Step wise reaction of FAME production

It is widely studied that the conversion if oil to FAME in the reactor following three consecutive reversible reactions shown in Figure 3 below.

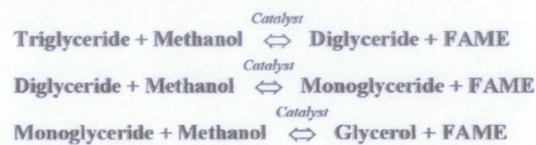


Figure 3: Reversible reaction of FAME production

The reactant intermediate (diglyceride and monoglyceride) appear in small concentrations during the reaction and treated as contaminant in the final product. The studied into the details of transesterification reaction have shown the transitions of the liquid-liquid multiphase mixture (oil and methanol) to another biphasic mixture (FAME and glycerol) through a pseudo-single phase emulsion. A continuous

non-polar phase (Oil, FAME, reaction intermediates) and a dispersed polar phase (methanol, glycerol and catalyst) are present with the composition constantly changing. Due to the nature of the reaction medium, the rate of reactions is affected by chemical kinetics, mass transfer and component solubility.

As the reaction continues, it shows that the reaction progression to be sigmoidal and can be characterized by three stages as shown in Figure 4 below. The first stage show an initial slow rate of reaction, followed by second stage reaction which is a rapid progression up to 80% conversion and the last stage as the equilibrium is approached.

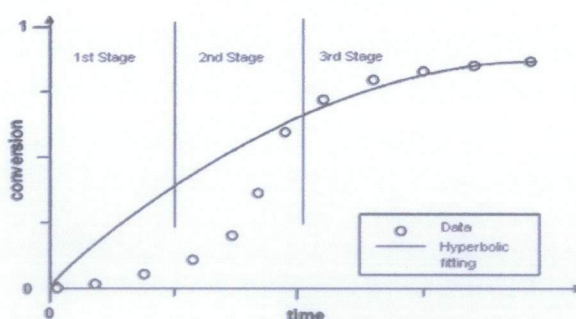


Figure 4: Sigmoidal reaction progression

In the first stage the concentration of oil in the methanol droplets (where the majority of the catalyst resides) is low, requiring significant agitation to reach saturation levels. In this stage it is most likely that the rate of mass transfer between the phases is slower than the chemical rate, thus in this stage, mass transfer is the controlling factor. Although the miscibility of the two phases can be enhanced by increasing the temperature, this is an energy-consuming process.

In the second stage, the reaction rate rapidly increases. It is observed that this increase coincided with a reduction in droplet size. As the droplet size decreases, the area of the polar phase and thus the mass transfer rate increases, explaining the sudden jump in reaction rate. The reaction medium during this stage has been described by some as a pseudo single phase. Different authors have attributed the self-enhanced mass transfer rate to the surfactant action of the reaction intermediates, while others have attributed it to the solvent properties of FAME.

In the third step, the reaction rate rapidly curtails as equilibrium is approached. It is proposed that this sudden drop is due to the breaking of the single phase emulsion as glycerol is formed, resulting in the catalyst dissolving in the polar phase. With almost all of the unreacted glycerides residing in the non-polar phase this results in a very slow approach to equilibrium. It is therefore proposed that in the final stage, it is the solubility of components and not the rate of mass transfer which limits the reaction rate.

It is assumed that the reaction occurs at the interfacial area of two phases. Specific interfacial area with the assumption of spherical droplets is calculated from the Figure 5 below.

$$a = \frac{6\phi}{d_p}$$

Figure 5: Specific interfacial area formula

Where $a(\text{m}^2/\text{m}^3)$ is specific interfacial area, ϕ is dispersed phase hold up, and d_p is the mean drop size. Mean droplet size is calculated from Misek's equation in Figure 5 below.

$$d_p = \frac{16.3 \left(\frac{H}{D} \right)^{0.46} \sigma e^{(0.087D)}}{n^2 d^2 \rho_c}$$

Figure 5: Misek's Equation

d_p (m) is the mean drop size, n (rpm) speed of agitator, d (m) agitator diameter, ρ_c kg/m³ continuous phase density, σ (N/m) surface tension, D (m) reactor diameter, and H (m) is the reactor depth.

Dispersed phase hold up, ϕ , is considered as the volume of methanol to the operational reactor volume. ϕ (N/m) is obtained for the system of sunflower oil and methanol from the following equation in Figure 6 below

$$\sigma = 10^{-7} [TG]^2 - 10^{-7} [TG] + 0.0003$$

Figure 6: Dispersed phase hold up formula

[TG] is the concentration of tri-glyceride during the methanolysis reaction with the unit of kmole/m³. Maximum diameter of droplets is calculated from the proposed equations. When shear forces from the agitator are equal to the surface tension of the drop, the drop will break.

2.4.2 Micro-channel Tube Reactor

In micro-channel reactor, the reaction occurred within the reactor is limited by mass transfer and the small characteristic size of reactor give space for high interfacial areas between phases to be obtained. In transesterification, the reactants (methanol and triglycerides) are immiscible at the beginning of the reaction, an emulsion of fine droplets (or pseudo- homogenous phase) is obtained during the reaction, and then at the end of the reaction the products (esters and glycerol) form two distinct and immiscible phases again. The emulsion of fine droplets formed during the course of the reaction shown in Figure 7 below is specific to transesterification and due to the formation of mono and diglycerides. Table 2 below shows a typical advantage of micro-reactors over batch reactors in the fact that a smaller emulsion droplet size is achieved in a shorter processing time, which means that higher conversion in a shorter time can be achieved in micro-reactors.

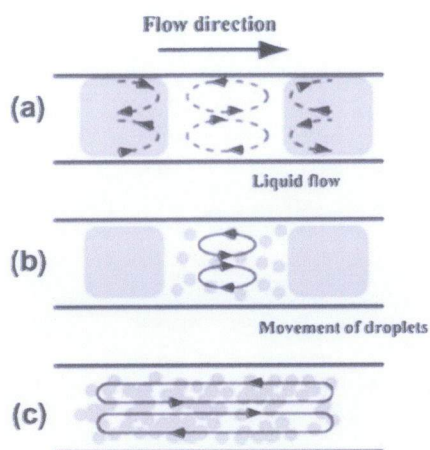


Figure 7: Evolution of liquid–liquid flow patterns over the course of a transesterification reaction in a microreactor. (a) Slug flow whereby the reactants form two distinct phases; (b) Beginning of emulsion formation in the continuous phase due to the production of mono- and di-glycerides; and (c) Emulsion during the course of the reaction, before phase separation of products.

Table 2: Influence of the type of reactor on the droplets mean diameter (dm)

Type of reactor	Operating time (min)	dm (μm)
Batch (250 mL)	3	12.9
(two flat-blade paddle agitator)	60	5.1
Microreactor ($d = 140 \text{ }\mu\text{m}$)	0.5	1.9

A number of studies in the literature have demonstrated the feasibility of using microreactors for improving the performance of transesterification reactions. Table 3 below compares the different data available for a homogeneous base-catalysed transesterification reaction in terms of reaction and flow conditions, microreactor characteristics and reaction performance.

Table 3: Results obtained for homogeneous base-catalyzed transesterification in microreactors. c: conversion (%), R: molar ratio methanol:oil, t: residence time (min), w: weight fraction of catalyst (%), T: temperature ϕ : reactor dimension (mm), F: flow-rate (mL/h). I: beginning of the reaction, II: during the reaction, III: end of the reaction, s-f: slug-flow, e: emulsion, p: parallel flow

Oil	Catalyst	Reaction conditions				Type of reactor	Performance c	Flow-pattern			Material	ϕ	F
		R	t	w	T			I	II	III			
Sunflower	KOH	23.9	1	4.5	60	T-joint + tube	100	s-f	e	e	FEP	0.8	8.2
		4.6	3.7	4.5	60	T-joint + tube	59.3	s-f	e	s-f	FEP	0.8	8.2
		23.9	1.6	4.5	40	T-joint + tube	100	s-f	e	s-f	FEP	0.8	8.2
		11.3	0.83	4.5	60	T-joint + tube	97	.	.	.	FEP	0.8	8.2

Table 4: Advantages and drawbacks of microreactor for transesterification

Microreactors	Advantages	Drawbacks
Transesterification	short reaction times control of the flow pattern to increase mixing during the reaction and to facilitate the separation at the outlet of the reactor	Low flow rates (10–200 mL/)

2.5 Turbulent Flow

In single phase flow, the dimensionless Reynolds number (Re), shown in Figure 8 below, is used to predict the turbulent flow.

$$Re_{2\text{Phase}} = \frac{\rho_m D_p U}{\mu_m}$$

Figure 8: Reynolds number formula

To account for two phase flow, the volume averaged densities and viscosities were used as shown in Figure 9 and Figure 10 below.

$$\rho_m = r_c \rho_c + r_d \rho_d$$

Figure 9: Volume average densities formula

$$\mu_m = r_c \mu_c + r_d \mu_d$$

Figure 10: Volume average viscosity formula

2.6 Turbulence Model

The two equations k-epsilon (k-ε) turbulent model is considered because the flow in micro-reactor varies from laminar to turbulent. Turbulence is one of the characteristics of fluid motion in which eddy formation (void spacing) takes place because of irregularity of the fluid. This behavior normally happens at high Reynolds number of the flow. The turbulence model is a computational procedure to close the system of mean flow equations (Bakker 2002), therefore it is also very important to know that how the mean flow affected by turbulence. The sum of the mean kinetic energy and turbulent kinetic energy can be known as instantaneous kinetic energy. The k-epsilon model mostly put emphasis on mechanism by which turbulent kinetic energy can be affected. This model has some practical advantages for instance ease of implementation, facilitate in convergence of calculations, reliable predictions for fluid. The transport equation of standard k-epsilon model is shown in Figure 11 below.

$$\frac{\partial}{\partial t}(\rho k) + \frac{\partial}{\partial x_i}(\rho k u_i) = \frac{\partial}{\partial x_j} \left[\left(\mu + \frac{\mu_t}{\sigma_k} \right) \frac{\partial k}{\partial x_j} \right] + G_k - \rho \epsilon + S_K$$

$$\frac{\partial}{\partial t}(\rho \epsilon) + \frac{\partial}{\partial x_i}(\rho \epsilon u_i) = \frac{\partial}{\partial x_j} \left[\left(\mu + \frac{\mu_t}{\sigma_\epsilon} \right) \frac{\partial \epsilon}{\partial x_j} \right] + C_{1\epsilon} \frac{\epsilon}{k} G_k - C_{2\epsilon} \rho \frac{\epsilon^2}{k} + S_\epsilon$$

Figure 11: Transport equation of standard k-epsilon model

Where 'k' is turbulent kinetic energy and epsilon 'ε' is turbulent dissipation rate. S_K and S_ε are the source term; G_k is produced kinetic energy because of mean velocity

gradient. The μ_t is turbulent viscosity, ρ is the density and the model constants are $C_1=1.44, C_2 = 1.92, \sigma_k= 1.0$ and $\sigma_\epsilon=1.3$.

2.7 Turbulence Intensity

Practically it is observed that the importance of T.I is vital for prediction of the flow. The core purpose is to avoid back flow problem. The back flow mainly happens at flow inlets and outlet, therefore T.I needs to be defined as boundary conditions of the system. T.I value is in percent when 1 is the lowest and 10 is the highest. 'Re' is the Reynolds number and dh is hydraulic diameter (inlet diameter).

$$T.I=0.16Re_{DH}^{-1/8}$$

Figure 12: Turbulence Intensity formula

2.8 Multiphase Model

The software ANSYS fluent provides a wide range of multiphase model, which are mixture model, Eulerian model, and volume of fluid (VOF) model. Based upon case to case the application of these models varies. The VOF is basically for large surface area of disperse phase for instance floating oil on water. Whereas the Eulerian and mixture are almost same, the basic difference is that the mixture model use segregated solver for ease phase and solidification problems could not be modeled. However Eulerian model could use segregated and coupled solver both but it needs more computational resources than mixture model and sometimes it has problem related to convergence of the solution due to instability. Therefore the selected model is mixture multiphase model. The mixture model is a multiphase model and has better convergence properties. It is easy to implement as compare to Eulerian Model. The stability of mixture model is better than Eulerian model and it solves most of the engineering problem concerning to multiphase. It is applicable with phases at different velocities and if the velocities are same then mixture model consider the fluids as single phase. This model simulates fluid or particle and solves momentum,

energy, and continuity equations for mixture. It also solves volume fraction equations for secondary phase and algebraic expression for relative velocities.

2.8.1 Continuity Equation of Mixture Model

$$\frac{\partial}{\partial t}(\rho_m) + \nabla \cdot (\rho_m v_m) = 0$$

v_m is mass average velocity:

$$v_m = \sum_{K=1}^n \alpha_K \rho_K v_K / \rho_m$$

ρ_m is the mixture density

$$\rho_m = \sum_{K=1}^n \alpha_K \rho_K$$

Figure 13: Continuity equation

α_k is volume fraction of phase k, ρ is the density, n is the number of phases and v is the velocity

2.8.2 Momentum Equation of Mixture Model

The momentum equation for all phases is:

$$\frac{\partial}{\partial t}(\rho_m v_m) + \nabla \cdot (\rho_m v_m v_m) = -\nabla p + \nabla \cdot [\mu_m (\nabla v_m + \nabla v_m^T)] + \rho_m g + F + \nabla \cdot \left[\sum_{K=1}^n \alpha_K \rho_K v_{dr,k} v_{dr,k} \right]$$

Figure 14: Momentum equation

Where n is the number of phases, F is body force and μ_m is mixture viscosity.

$$\mu_m = \sum_{K=1}^n \alpha_K \mu_K$$

Figure 15: Mixture viscosity equation

$v_{dr,k}$ is the drift velocity for disperse phase k, it is equals to $v_k - v_m$

2.8.3 Energy Equation of Mixture Model

For mixture the equation of energy could be elucidated as:

$$\frac{\partial}{\partial t} \sum_{k=1}^n (\alpha_k \rho_k E_k) + \nabla \cdot \sum_{k=1}^n (\alpha_k v_k (\rho_k E_k + p)) = \nabla \cdot (k_{eff} \nabla T) + S_E$$

Figure 16: Energy equation

K_{eff} is effective conductivity ($\sum \alpha_k (K_k + K_t)$), S_E is the volumetric heat source.

CHAPTER 3

METHODOLOGY

3.1 General

Computational fluid dynamic (CFD) modeling is done to simulate the transesterification of sunflower oil with methanol in a microtube reactor via KOH catalyst reaction. CFD is used to predict the volume fraction, the velocity profile, the pressure drop, density profile, and temperature profile. In CFD the ANSYS fluent simulation software is used for fluid dynamics and ANSYS Geometry and Mesh for geometry and meshing. The core purpose of using CFD is to optimize the operating conditions and to visualize the output parameters.

3.2 Selection and Construction of Physical Model

The 2-Dimensional geometry is created in ANSYS Geometry and Mesh to save computational resource and time saving. The constructed geometries are imported into ANSYS fluent software for fluid dynamics. The solution is not dependent upon mesh convergence is improved by mesh refinement. For physical model, initially the geometry of different dimensions is constructed in ANSYS Geometry. Special consideration is given at inlets and outlet boundaries by mean of decreasing mesh size. In two dimensions the XY coordinates are considered and Z-axis is equal to zero. The mesh size and spacing plays integral role on the simulated results therefore adequate considerations are being considered while making geometry. The key quality parameter of mesh is orthogonal quality; 0 is (worst) and 1 is (best). It is a thumb rules that a good geometry leads to good simulation. Since the liquid-liquid multiphase flow is predominated in the system, therefore the substrate is incompressible flow. The velocity of the methanol and sunflower oil is fixed at 0.41m/s.

3.3 Modeling of Reaction

The pressure-based solver is used in ANSYS fluent to solve the momentum, energy, species transport and continuity equations. The SIMPLE algorithm is considered for the coupling of pressure-velocity. The order of discretization schemes is second for reliable prediction of continuity, momentum, species and energy equations. The under-relaxation factor for species is 1 to facilitate the convergence. The boundary conditions for all inlets are velocity based and for outlet it is pressure based. The velocity-pressure combination gives stable results. The turbulence model k-epsilon is used for turbulence. The turbulent intensity as a function of inlets and outlets opening diameter is considered. The volumetric reaction with finite rate and eddy dissipation are being considered. For temperature gradient inside the system, the energy equation is enabled. The scheme used is Green-Gauss Node Based with second order momentum, volume fraction, turbulent kinetic energy and turbulent dissipation rate. The modeling of model components sunflower oil, methanol, FAME and glycerol is done by ANSYS fluent. In fluent software, the finite rate species transport model is considered because the rate of reaction is well defined by Arrhenius equation. The finite rate transport model requires stoichiometry coefficient and rate exponent of each chemical species along with Arrhenius parameters. The stoichiometry of each of the reactants and products are set as the literature review discussed on 2.4.1 Kinetics Model.

The properties of the materials are as follows:

Table 5: Fluid Properties. MW: Molecular weight (kg/kgmol), ρ : Density (kg/m³), μ : Viscosity at 313.15K, TC: Thermal Conductivity (W/mk), SSE: Standard State Enthalphy (J/kgmol), SSER: Standard State Entrophy (J/kgmolK)

Species	MW	ρ	μ	TC	SSE	SSER
methanol	32.04	773.3431	0.000447	0.1973	-201448	-160134
SO	850.41	901.1101	5.128	0.1642	-2.6E+8	5.5E+5
glycerol	92.09	1247.737	2.85E-01	0.2927	-583701	-441503
fame	142.2	894.4378	2.47E-03	0.1131	-421979	-201606

CHAPTER 4

RESULT AND DISCUSSION

4.1 Selection and Construction of Physical Model

As mentioned before the 2-Dimensional geometry is made in ANSYS Geometry software. The diameter of main body is set to 10mm, whereas the diameter of inlet and outlet is set to 0.8mm. In Figure 17 below, the important geometries are showed. The type of mesh is Quadrilaterals, locating near boundary conditions. The density of mesh at boundaries is double ratio to ensure realistic fluid flow. The mesh density is controlled by double ratio. The overall quality of the geometry is admissible with orthogonal quality range of 0.59 on a scale of 1(best) to 0 (bad) and aspect ratio of 3.77. The solution convergence does not depend upon mesh refinement which shows that there are no miss or uneven distribution of mesh.

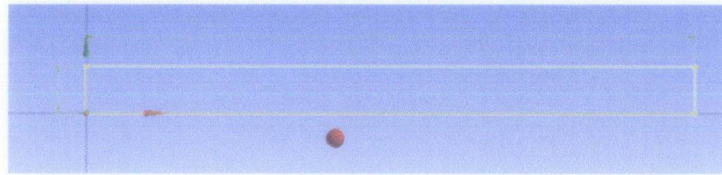


Figure 17: Geometry build (H5=10mm, V6=0.8mm)

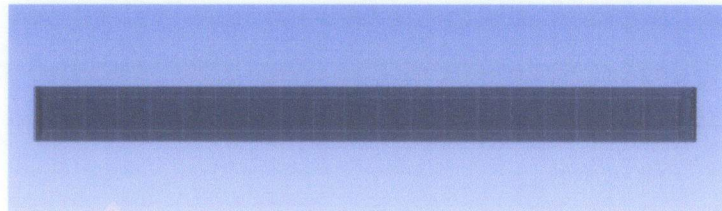


Figure 18: Mesh build

Table 6: Mesh report

Domain	Nodes	Elements
surface_body	16310	7776

4.2 Modeling of Reaction

Based on the ANSYS setup discussed on 3.3 modeling of reaction, the solution converge less than half an hour under CPU Quad Core processor with 4Gb ram. The time step are set to be 1 second and the total number of time step equal to 250 with maximum 5 time iterations per time step. The solution converge at flow time = 195s with 195 time steps and 970 complete iterations.

4.2.1 FAME Mass Fraction

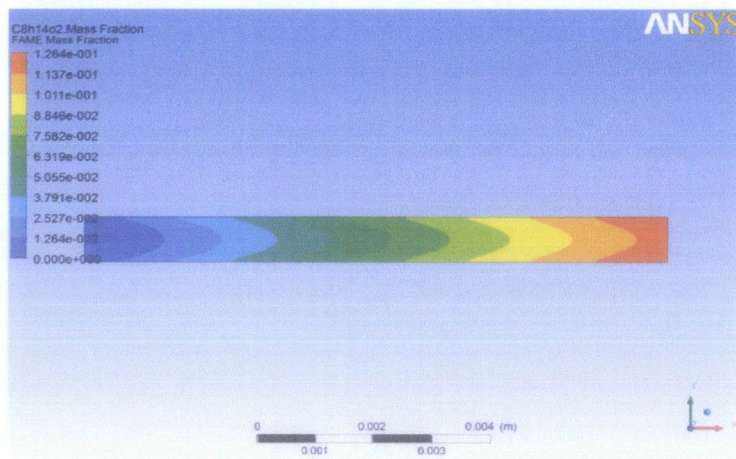


Figure 19: FAME Mass Fraction

Based on the contour shown in Figure 19, Fatty Acid Methyl Ester (FAME) are 100% converted at the outlet of the reactor under 195 second of reaction. By using the methanol oil molar ratio of 23.9 at 313.15 K, the simulation shows that 100% FAME are converted on par with the experimental result done in the literature review. The detail of the conversion shown in Figure 20 below:

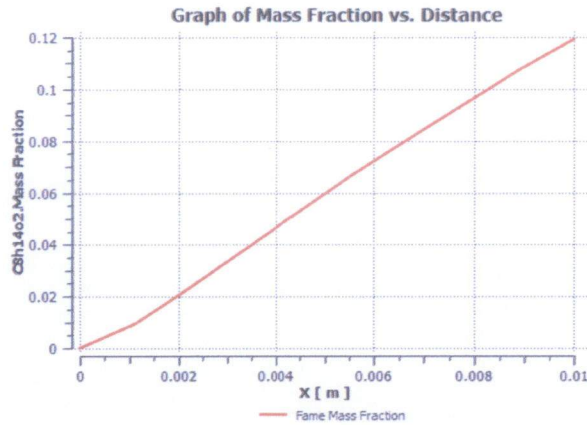


Figure 20: Graph of Mass Fraction vs. Distance (FAME)

4.2.2 Methanol Mass Fraction

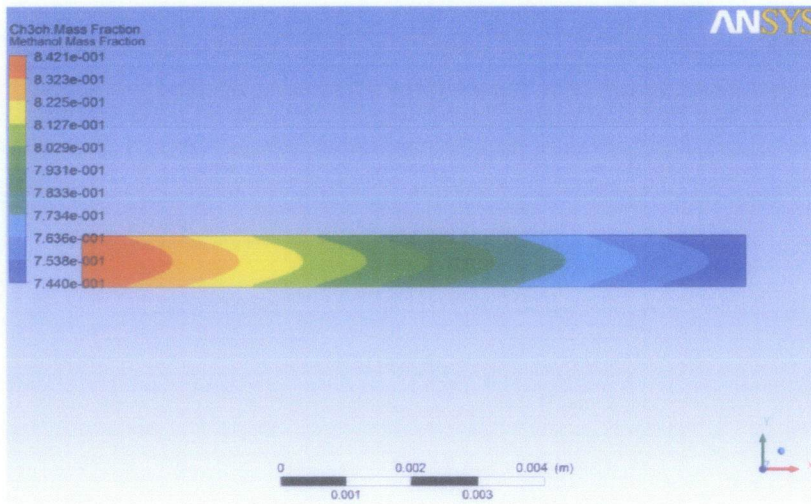


Figure 21: Methanol Mass Fraction

Based on the contour shown in Figure 21, the methanol are being consume and the reduction in the mass fraction can be noticed. In the reaction, it shows that the methanol as the excess reactant as well as the component solubility that determine the yielding of FAME at the outlet of the reactor. The detail of methanol mass fraction shown in Figure 22 below:

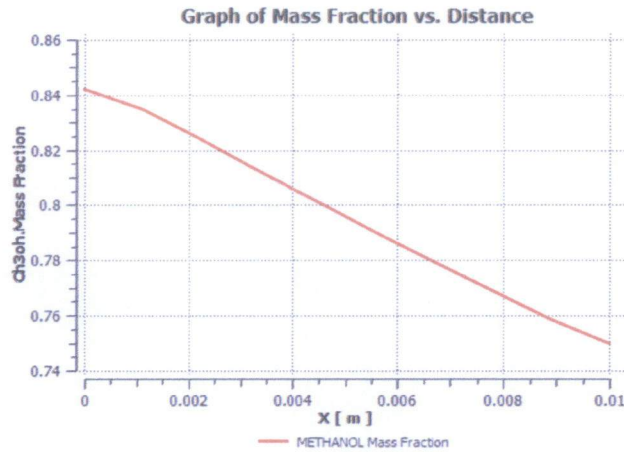


Figure 22: Graph of Mass Fraction vs. Distance (methanol)

4.2.3 Sunflower Oil Mass Fraction

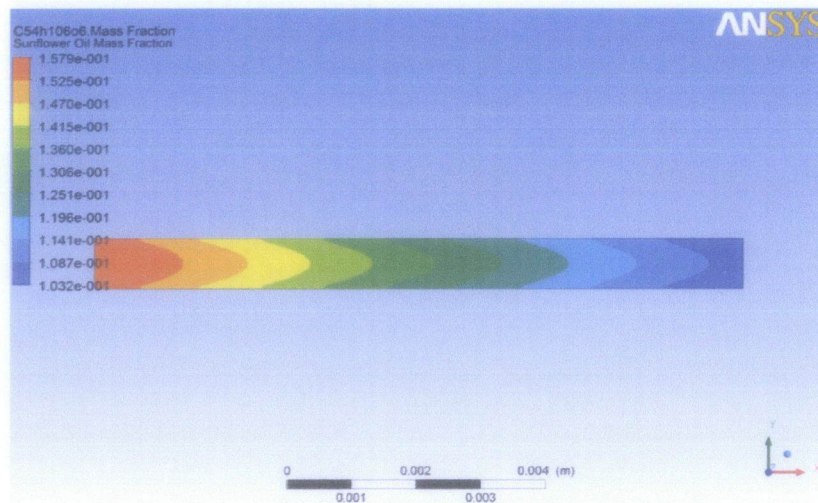


Figure 23: Sunflower Oil Mass Fraction

Based on the contour shown in Figure 23, the mass fraction of the Sunflower Oil are reduced at the end of the reactor, prove that the reaction occur inside the reactor transforming the molecule into Glycerol and FAME by slow rate of reaction and the remaining at the reactor outlet will be treated as residual. The detail of Sunflower Oil are shown in Figure 24 below.

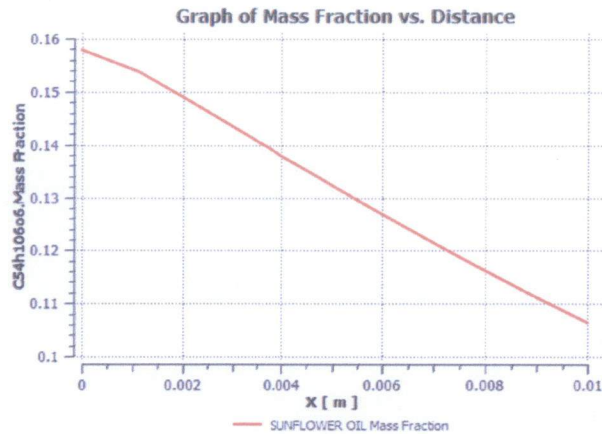


Figure 24: Graph of Mass Fraction vs. Distance (Sunflower Oil)

4.2.4 Glycerol Mass Fraction

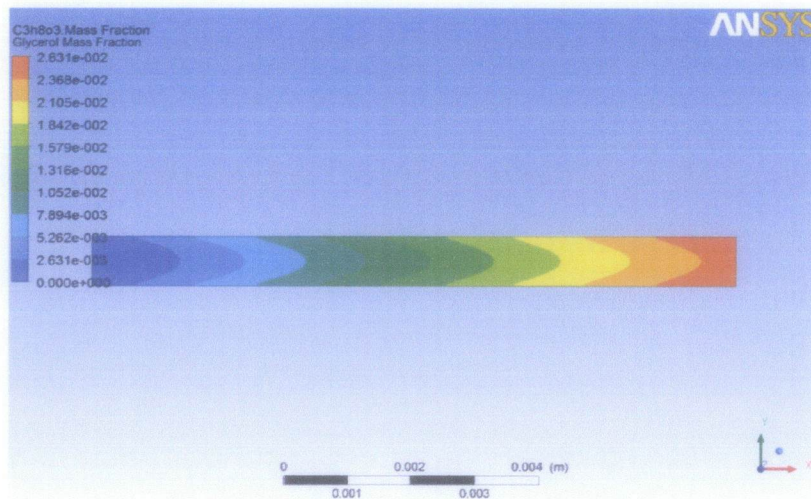


Figure 25: Glycerol Mass Fraction

Based on Figure 25 above, the formation of Glycerol at the reactor outlet clearly can be observed. The increasing of the Glycerol mass fraction shows that the chemical reaction of methanol and sunflower oil produce glycerol at the reactor outlet as by product. The details of the glycerol mass fraction shown in Figure 26 below.

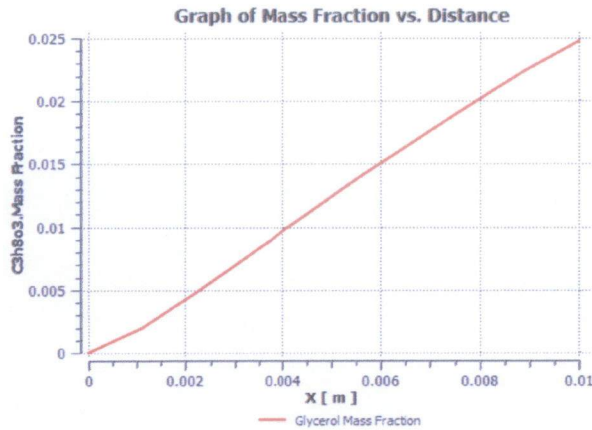


Figure 26: Graph of Mass Fraction vs. Distance (Glycerol)

4.2.5 Reactor Density Profile

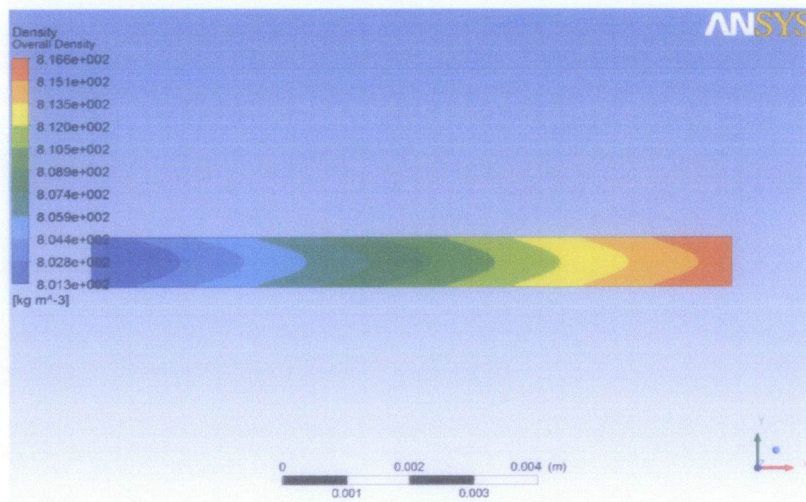


Figure 27: Density Profile

Based on Figure 27, the contour clearly show that the density at the outlet of the reactor are higher compared to the inlet of the reactor. This simulation prove that the density of FAME as product formation at the reactor outlet having much higher density compared to methanol. As the density of non-polar phase (FAME, oil) are higher compared to the polar phase (methanol glycerol) as in the literature study, the simulation successfully shown the properties. The details of the density profile across the reactor shown inFigure 28 below.

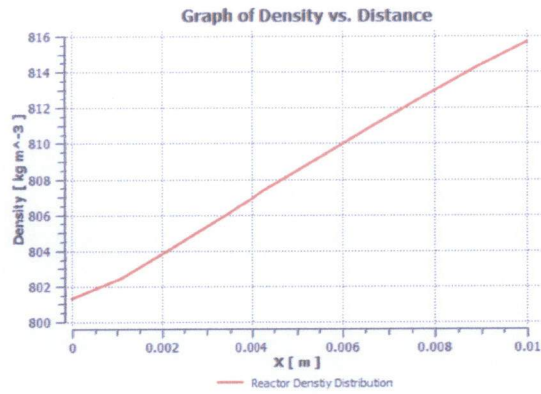


Figure 28: Graph of Density vs. Distance

4.2.6 Reactor Pressure Profile

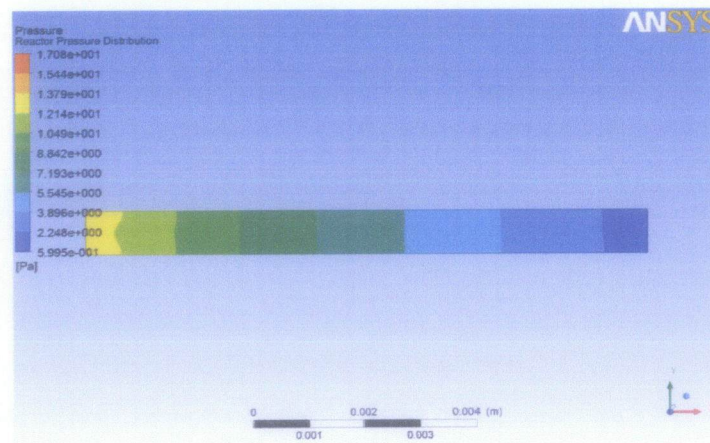


Figure 29: Pressure Profile

Based on Figure 29, the simulation indicates the pressure drop occurs inside the reactor. This can clearly be noted by the contour of yellow at the inlet and blue at the outlet of the reactor. The details of the pressure distribution across the reactor shown in Figure 30 below.

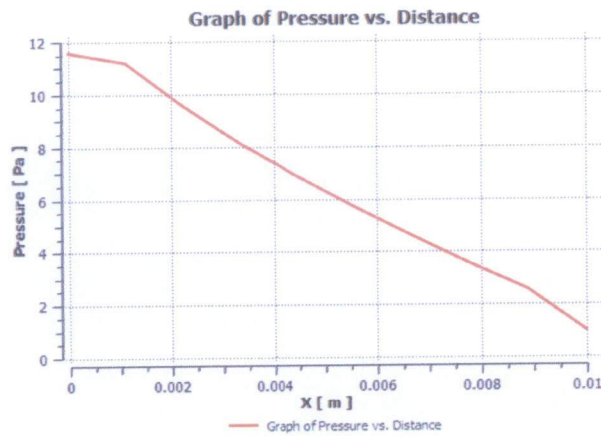


Figure 30: Graph of Pressure vs Distance

4.2.7 Reactor Temperature Profile

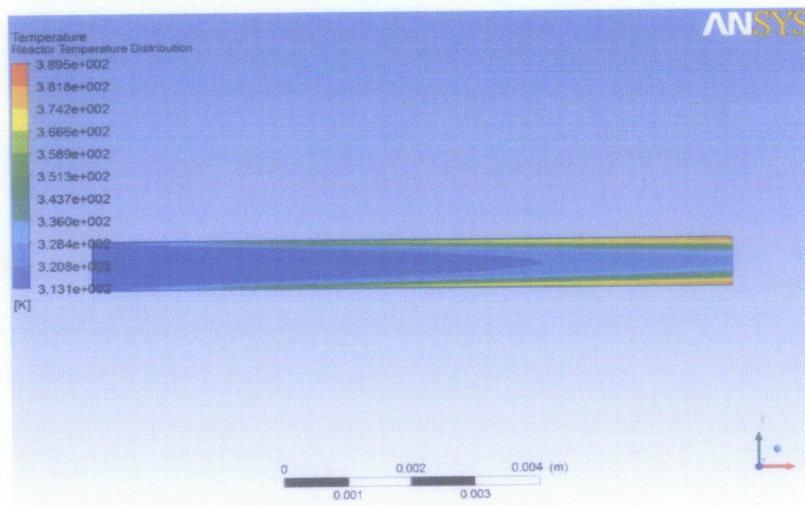


Figure 31: Temperature Profile

Based on the Figure 31, the contour of temperature across the reactor shown an increasing of temperature. This is basically prove that the reaction produce heat and it is exothermic reaction. The detail of the temperature distribution across the reactor shown in Figure 32 below.

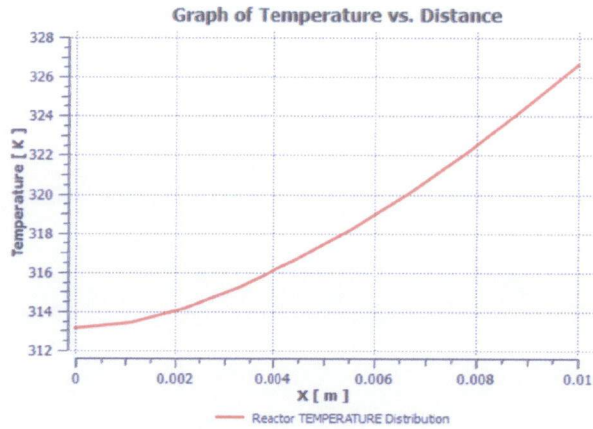


Figure 32: Graph of Temperature vs Distance

4.2.8 Reactor Velocity Profile

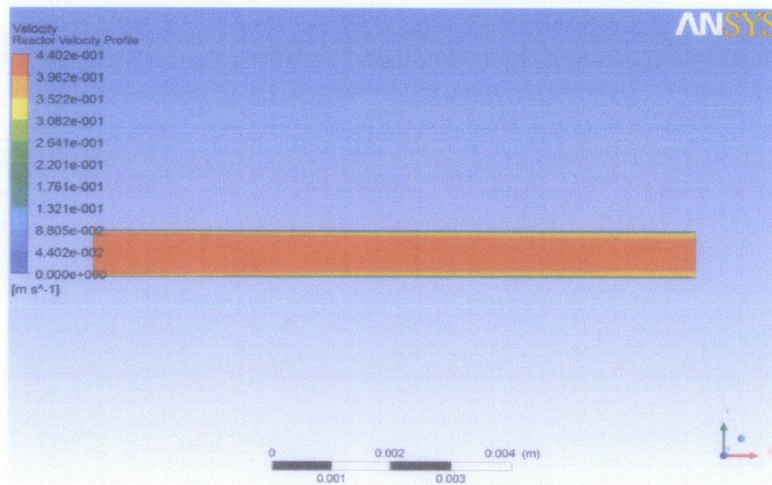


Figure 33: Velocity Profile

Based on the contour shown in Figure 33, the velocity are the highest at the middle of the middle of the reactor and the lowest at the wall of the reactor. This is as result of drag force and surface tension occur between the liquid-liquid and liquid-wall friction. The detail of the velocity across the reactor shown in Figure 34 and the velocity across the reactor outlet at y axis shown in Figure 35.

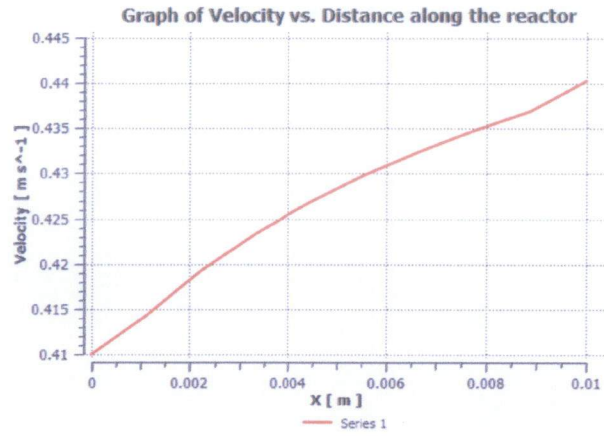


Figure 34: Graph of Velocity vs Distance along the reactor

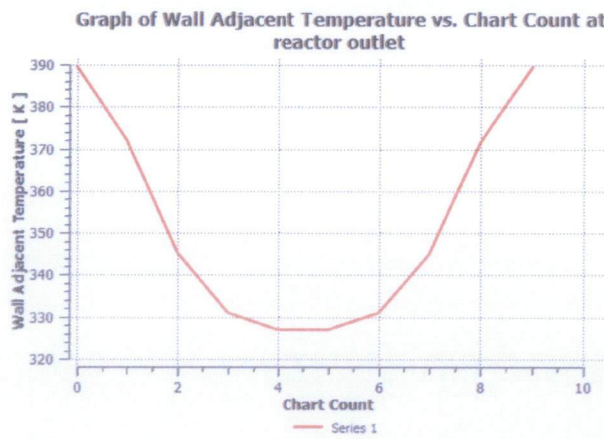


Figure 35: Graph of Velocity vs Chart Count at reactor outlet

4.2.9 Tracking Line

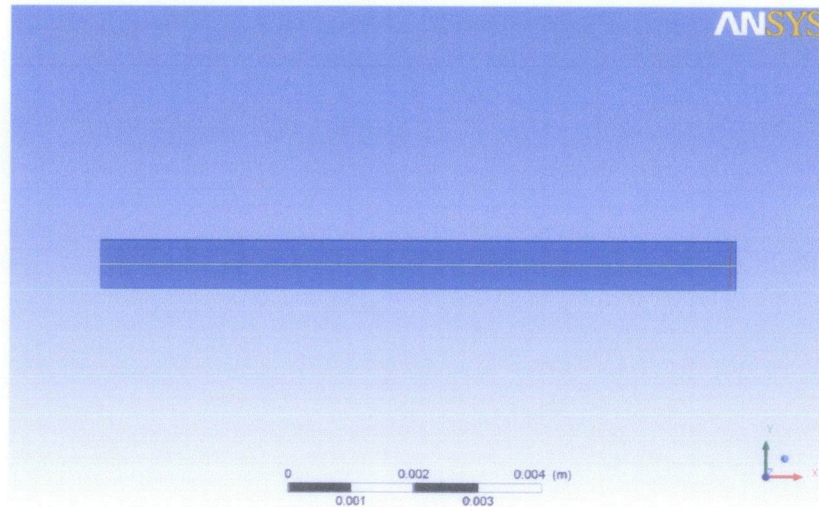


Figure 36: Tracking Line

The tracking line shown in Figure 36 are being used to create the graph. The yellow color line for the tracking of data across the reactor while the purple color for tracking of data at the reactor outlet.

CHAPTER 5

CONCLUSION

Based on the result obtained, the simulation of the reactor condition of reaction between sunflower oil and methanol to produce FAME and glycerol is on a good agreement with the experimental setup done by Guoqing Guan, et. al. The result of their experiment shown in Figure 37 below.

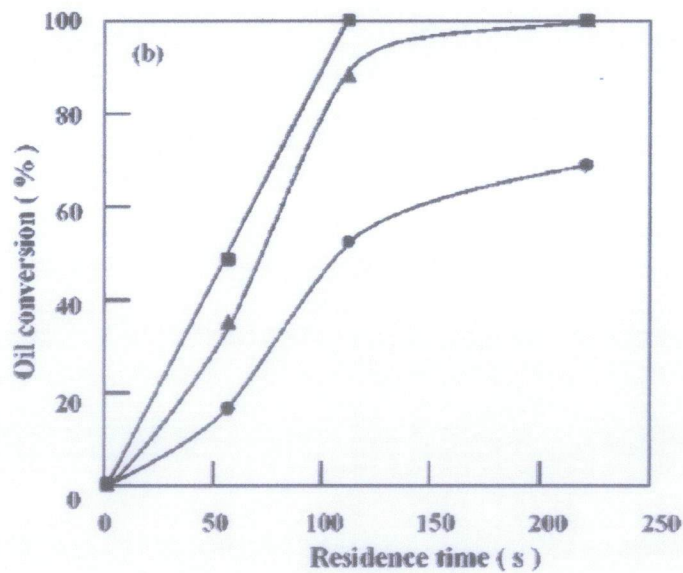


Figure 37: Oil conversions as a function of residence time at 40 °C

Methanol/oil molar ratio: ●, 4.6; ▲, 11.3; ■, 23.9.

In Figure 37 above, it shows that at 40 °C, with methanol to oil molar ratio of 23.9 the oil conversion is achieving 100% within the residence time in the range of 100 – 150 seconds while in the simulation done in this study, it required 195 seconds for the solution to converge and achieving target oil conversion. This indicates that the simulation is in good agreement with the experimental setup with relative error of 26%.

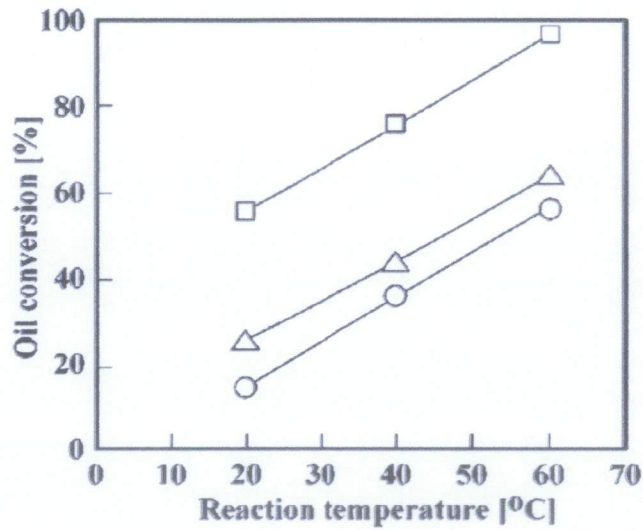


Figure 38: Oil conversion as a function of reaction temperature with residence time of 56 seconds

Based on Figure 38 above, at 40 °C and residence time of 56 seconds with methanol to oil molar ratio of 23.9, the experimental result shows that the oil conversion is achieving around 60% – 80% conversion which is also in good agreement with the simulation done in this study.

The simulation done on this study is still in need of improvement and further study should be required to simulate the exact and accurate reaction of methanol with sunflower oil to produce FAME. This study can be served as basis for the simulation using CFD of the reaction. For further study, it is recommended to take into consideration the buoyancy effect as well as drift force along the wall in order to achieve better convergence.

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