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EXPERIMENTAL PARAMETRIC ANALYSIS OF BIODIESEL SYNTHESIS IN MICROREACTORS WITH WASTE COOKING OIL

Saxon Paiz

Dissertação de Mestrado apresentada ao Programa de Pós-graduação em Engenharia Mecânica, COPPE, da Universidade Federal do Rio de Janeiro, como parte dos requisitos necessários à obtenção do título de Mestre em Engenharia Mecânica.

Orientadora: Carolina Palma Naveira Cotta

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Dedicated to Raquel and my
family

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ANALISE PARAMÉTRICA EXPERIMENTAL DA SÍNTESE DO BIODIESEL EM MICRORREATORES COM ÓLEO DE COZINHA RESIDUAL

Saxon Paiz

Setembro/2018

Orientadora: Carolina Palma Naveira Cotta

Programa: Engenharia Mecânica

Este estudo investiga a síntese de biodiesel com óleo de cozinha residual usando um dispositivo de microcanais acionado termicamente usando calor rejeitado através de um processo paralelo de troca de calor. Em vez de usar uma análise experimental fatorial completa com uso intensivo de recursos, uma análise fatorial parcial Taguchi foi usada para explorar os efeitos paramétricos e reduzir bastante a quantidade de experimentos necessários. A reduo de ácidos graxos livres no óleo vegetal foi estudada pela primeira vez. Enquanto o teor de ácidos graxos livres do óleo foi reduzido para 0,2%, abaixo do nível recomendado para transesterificação (0,5%), grandes quantidades de emulsões foram criadas durante a purificação, o que torna o processo menos viável para uso em larga escala de produção. Os efeitos paramétricos da transesterificação foram então investigados usando óleo de cozinha residual purificado. Uma conversão de biodiesel de 98% foi alcançada, o que é muito próximo do nível de conversão industrialmente aceitável. Além do alto nível de conversão, o tempo de reação da síntese foi de apenas 2 minutos, o que é muito menor do que os tempos de reação usando reatores tradicionais industriais. A análise sugeriu que a conversão poderia ser aumentada com um aumento na concentração de catalisador.

Abstract of Dissertation presented to COPPE/UFRJ as a partial fulfillment of the requirements for the degree of Master of Science (M.Sc.)

EXPERIMENTAL PARAMETRIC ANALYSIS OF BIODIESEL SYNTHESIS IN MICROREACTORS WITH WASTE COOKING OIL

Saxon Paiz

September/2018

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Department: Mechanical Engineering

This study investigates biodiesel synthesis with waste cooking oil using a microchannel device thermally driven using rejected heat through a parallel heat exchange process. Rather than use a resource-intensive full factorial experimental analysis, a partial factorial Taguchi analysis was used to explore parametric effects and greatly reduce the amount of experiments needed. The reduction of free fatty acids in vegetable oil was first studied. While free fatty acid content of the oil was reduced to 0.2%, below the recommended level for transesterification (0.5%), large amounts of emulsions were created during purification which makes the process less feasible for large scale production use. The parametric effects of transesterification were then investigated using purified waste cooking oil. A biodiesel conversion of 98% was achieved which is very close to the industrially acceptable level of conversion. In addition to the high level of conversion, the reaction time of the synthesis was only 2 minutes which is much lower than the reaction times using traditional batch reactors. The analysis suggested that the conversion could be increased with an increase in catalyst concentration.

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Abbreviations

ANOVA Analysis of Variance

CC Catalyst Concentration

C.F. Correction Factor

DG Diglyceride

DOE Design of Experiments

DOF Degree of Freedom

E Ester or Biodiesel

EU European Union

FAEE Fatty Acid Ethyl Ester

FAME Fatty Acid Methyl Ester

FFA Free Fatty Acid

G Glycerol

HC Hydrocarbon

HPLC High Performance Liquid Chromatography

KOH Potassium Hydroxide

LABCOM Laboratório de Combustíveis e Derivados de Petróleo

MG Monoglyceride

MR Molar Ratio

MSA Methane Sulfonic Acid

MSD Mean Square Deviation

NaOH Sodium Hydroxide

OA Orthogonal Array

OPEC Organization of Petroleum Exporting Countries

PM Particulate Matter

PNPB National Biodiesel Production and Usage Program

PROALCOOL National Ethanol Production Program

RT Residence Time

SLM Selective Laser Melting

S/N Signal to Noise Ratio

TG Triglyceride

WCO Waste Cooking Oil

Nomenclature

A Frequency factor for the reaction $[s^{-1}]$

E_a Activation Energy $[\frac{J}{mol}]$

f Degrees of Freedom

F Variance Ratio

k Kinetic Constant $[\frac{mol}{m^3 * s}]$

n Number of Experiments

P Percent Contribution

R Universal gas constant $[\frac{J}{mol * K}]$

S Sum of Squares

S' Pure Sum of Squares

T Temperature [°C or K]

T Total of Results

V Variance

Y Result of Trial Run

Chapter 1

Introduction

1.1 Background

The worlds energy consumption has steadily increased since the dawn of the industrial revolution. The majority of energy currently produced is derived from fossil fuel energy sources, see Figure 1.1 [1]. These energy sources are of limited supply and their increasing use is detrimental to our environment. Recently, there has been an increase in the use of renewable energy sources which are less harmful to the environment such as solar, wind, hydro, biofuels. One of the most important biofuels is biodiesel. Biodiesel is most used as a replacement or an additive of conventional diesel fuel used in transportation vehicles, as it has near the same energy capacity as diesel [2]. Although biodiesel has several environmental advantages compared to diesel, it is only cost competitive with government subsidies and mandates. Therefore, research and investment has been committed to reducing the cost of biodiesel production [3].

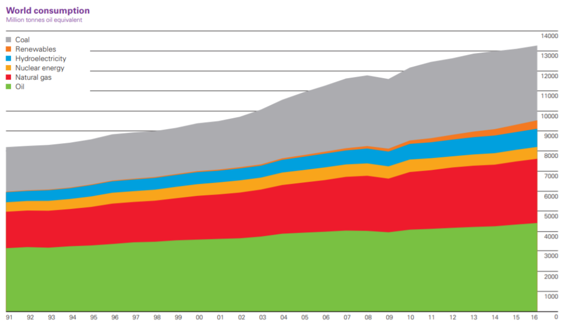


Figure 1.1: World energy consumption by source. (BP World Energy Consumption Report 2018)

Biodiesel is made through the conversion of fatty acids to alkyl esters. Two ways this is done through the transesterification of triglycerides and the esterification of FFAs. The most common method of biodiesel synthesis is transesterification of triglycerides using an oil feedstock, alcohol and alkali catalyst. Biodiesel synthesis through transesterification can be derived from a variety of triglyceride sources (feedstocks) such as plant vegetable oil and animal fat. Esterification of FFAs to esters is synthesized using alcohol and an acid catalyst and is used for feedstocks that are high in FFAs [3].

The largest cost in biodiesel production is the oil feedstock, Figure 1.2, which accounts for 75% of the cost [4]. Refined vegetable oil is most common oil feedstock used for biodiesel synthesis which is in competition with human food production, so several alternate feedstocks have been proposed in research in order to reduce costs, such as non-edible oil and algal oil. One of the most promising methods for reducing oil feedstock cost is to use WCO. Oil degrades with cooking through processes of oxidation at high temperature and hydrolysis from the water in the food which creates FFAs in the oil. WCO therefore contains several contaminates such as water, food particles, and FFAs that must be removed before transesterification. These impurities can have adverse effects on ester conversions during transesterification when present in large quantities. In particular, FFAs present in feedstocks will react with the alkali catalyst during transesterification creating soap. In order to use WCO in alkali catalyzed transesterification biodiesel synthesis several pre-treatment steps are needed to be taken before transesterification [5]. The food particles are removed with vacuum filtering, the water is removed through drying the oil, and the FFAs can be reduced through esterification. Thus it is common to use a two step chemical process: first reduce the FFAs in WCO using an esterification pre-treatment, and then converting the remaining triglycerides using alkali catalyzed transesterification [3].

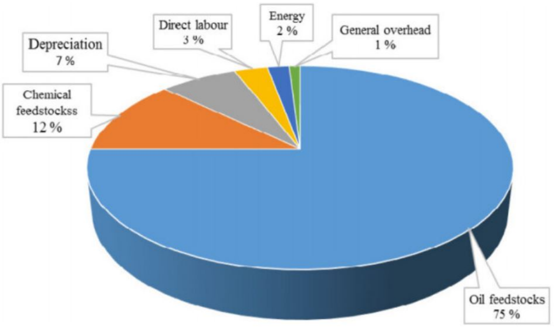


Figure 1.2: Biodiesel production cost breakdown. (Keneni et al. (2017))

The alcohols most commonly used for both esterification and transesterification are methanol and ethanol [6]. Methanol is more widely used in industry for biodiesel synthesis because of its low cost compared to ethanol [7]. In addition, methanol is recoverable and makes purification easier [8]. Ethanol is cost competative with methanol in areas where production is high, such as Brazil [9]. Ethanol also has the advantage of being derived from renewable sources and is safer to handle than methanol [10]. The most common catalyst used in esterification is sulfuric acid, however methane sulfonic acid can also be used and is safer to handle than sulfuric acid [11]. For alkali catalyzed transesterification, KOH and NaOH are the most common catalysts used [12].

Biodiesel production processes are generically divided into batch and continuous processes. In batch processes, a set amount of reactants are reacted while in a continuous process the reactants are continuously fed in to the system [3]. The conventional reactors used in biodiesel production are spinning tank reactors or batch reactors. Many process intensification methods have been proposed for biodiesel synthesis to increase ester conversions in less time using less energy than conventional methods. One of the most promising technologies for process intensification is microreactors [13]. Biodiesel synthesis can be carried out in microsystems faster and more energy efficient in a continuous process. In addition, advances in manufacturing allow for complicated microsystems to be made very efficiently and cost effectively. In a previous study at LabMEMS, a micro device with microreactors in parallel with micro heat exchangers was used to convert triglycerides to biodiesel with 99% purity with a residence time of just 35 seconds. Rejected heat from a parallel thermal system can be used to power the reaction with this microdevice [14].

1.2 Goals and Objectives

The major goal of this study is to experimentally analyze the parametric values for biodiesel synthesis with WCO and ethanol using a 3D printed microreactor device consisting of 10 microchannel reactors in parallel with 11 micro-heat exchangers and the reaction driven with rejected heat from a parallel thermal process. Another goal is to discover the feasibility and experimentally analyze the parameters for esterification of high FFA content oil with ethanol using the same microdevice. In order to realize these goals the following objectives will be met:

- Apply an factorial experimental approach to find the best parameters for esterification of high FFA content oil and transesterification of WCO with ethanol using the microdevice system.

- Conduct the experiments in the proposed sequence and analyze the samples to find the FFA content in the esterification experiments and the ethyl ester conversion for the transesterification experiments.

- Perform a statistical analysis on the results of the experiments to find the best parameters of both the esterification and transesterification reactions.

- Compare the experimental results of both esterification and transesterification reactions to studies in literature.

Chapter 2

Literature Review

2.1 Biodiesel Synthesis in Microreactors

With the insight that physical rules are independent of the choice of system dimensions, scaling analysis on systems in the micro scale show that micro-systems have many advantageous properties on the transport process. The decrease in length cause an increase in the gradients of process parameters such as temperature, pressure and concentration which drive the transport process. The transport processes during transesterification occur at the phase boundaries of the droplets of oil dispersed in the alcohol phase. With a higher specific area and high gradients, micro-reactor transport rates are increased and the equilibrium state is reached much faster. Temperature and concentration differences are homogenized much earlier, which plays a prominent role in mixing and heat transfer. In addition, length scaling often goes along with a time scaling of the relevant processes. In general, the shorter the length, the shorter the characteristic time for transport processes will be. Ultimately, micro-processes for transesterification means much lower residence times, higher energy efficiency, and higher conversion rates [15].

Microreactors generally consist of a mixer followed by a micro-channel or micro-tube to complete the reaction. Various forms of micro-mixers are displayed in Figure 2.5 although many more exist [16]. Advances in manufacturing techniques have made it possible create various micro-channel geometries as well as create objects within the micro-channels to increase mixing [17]. The reaction parameters for biodiesel synthesis, as well as the type of mixer and geometry of the micro-channels will determine the type of flow in the reactor and ultimately determine the quality of the conversion [18]. Complicating the analysis is that the flow will change as oil is converted and the mixture becomes more homogeneous. Figure 2.1 displays some of these flow patterns [19].

Al-Dhubabian (2005) studied biodiesel synthesis using a simple T-mixer

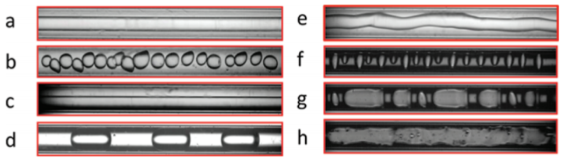


Figure 2.1: Various types of flow patterns in micro-channels: (a) annular flow, (b) bubbly flow,(c) parallel flow, (d) slug flow, (e) wavy annular flow, (f) inverted bubbly flow, (g) inverted slug flow, (h) inverted annular flow from Jovanovic et al. (2012)

microreactor with channel dimensions of 23.3mm length, 10.5mm width, and 0.1mm height as shown in Figure 2.2 generating a simple parallel flow. Under operating conditions of 7.2:1 methanol/soybean oil molar ratio, 1 wt% NaOH catalyst, at atmospheric pressure and 25 °C, a conversion of 91% was obtained in 10 min [20]. Sun et al. (2008) performed transesterification of pre-mixed rapeseed oil and methanol using KOH as a catalyst in quartz capillary of 0.25 mm inner diameter and length of 30 mm. At a catalyst concentration of 1% by weight and methanol to oil molar ratio of 6:1, a fatty acid methyl ester yield of 98.80% was obtained in 6 min at 60 °C [21].

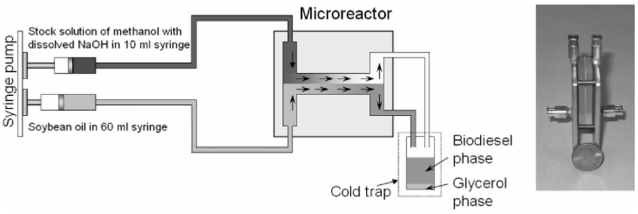


Figure 2.2: Schematic Diagram of Microreactor used by Al-Dhubabian (2005)

To investigate another high efficiency passive micro-structured mixer for biodiesel production, Wen et al. (2009) developed nine different zig-zag micro-channel reactors. The micro-channel reactors were fabricated on stainless-steel sheet by electric spark processing and assembled with a T-shaped three-way mixer. The micro-channels of all reactors were of rectangular cross-section with the same length of 1.07 meters but a different number of periodic turns (10, 50, 100, 200 & 350) and hydraulic diameter (240 to 900μm). Using the micro-channel reactor with a smallest hydraulic diameter (240μm) and most number of turns (350), a maximum yield of 99.5% was reached with methanol to soybean oil molar ratio of 9:1, NaOH concentration of 1.2 wt% in a very short residence time of 28 seconds at 56 °C [22].

Dai et al. (2014) developed a micro-reactor in which the conventional T-type mixer used by Wen et al. (2009) was replaced by zig-zag micro-channel mixers patterned on stainless-steel sheet along with zig-zag reaction channels. The mixing and reacting channels are linked through a connecting channel as shown in Figure 2.4. Using a hydraulic diameter of 1.5 mm, a biodiesel yield of 99.5% was obtained

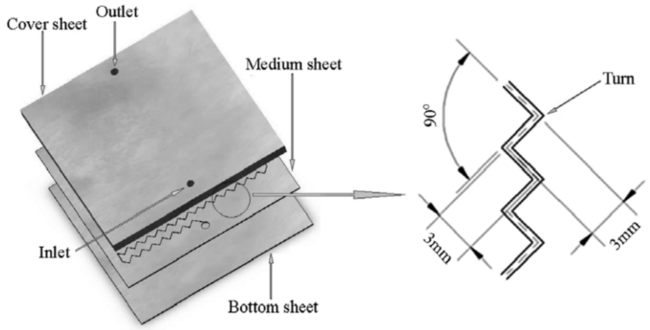


Figure 2.3: Zig-Zag microreactor used by Wen et al. (2009)

at a residence time of 14.9 seconds, methanol to soybean oil molar ratio of 8.5:1 and KOH concentration of 1.2 wt% at 59 °C [23].

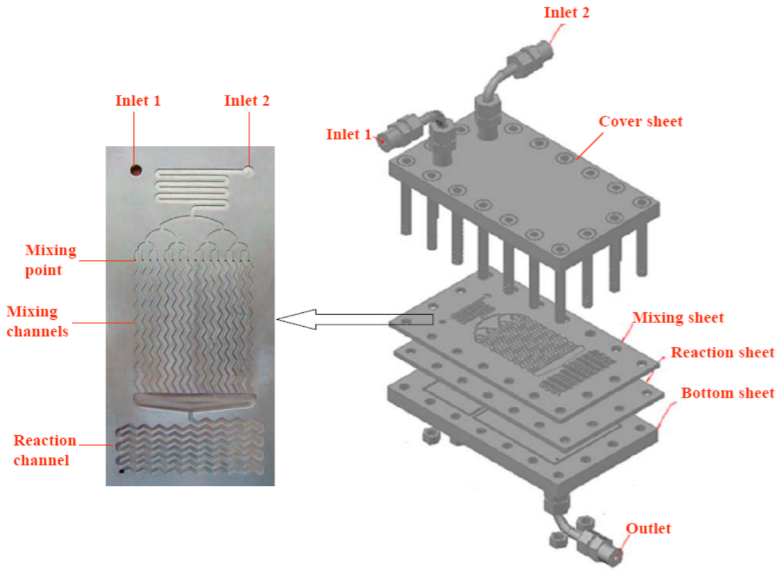


Figure 2.4: Zig-Zag microreactor with zig-zag micro-mixer used by Dai et al. (2014)

Sun et al. (2010) performed experiments on the fast synthesis of biodiesel from cottonseed oil using high throughput micro-structured reactor with various mixer types as shown in Figure 2.5. The FAME yields obtained using the micro-mixers were almost twice of the yields obtained using T- and J-mixers due to more intense mixing in micro-mixers. Using rectangular inter-digital micro-mixer (RIMM) a maximum yield of 99.5% was achieved under the conditions of methanol to oil molar ratio of 8:1, a 1% KOH catalyst concentration, a reaction temperature of 70 °C, the residence time of just 17 seconds and a flow rate of 10 mL/min [16].

Microreactors display several advantages over traditional biodiesel production methods. The use of microreactors allow producers to number up rather than scale up see Figure 2.6. This offers a lot of flexibility in production, as microreactors can be added and removed rather easily while scale-up operations require much more

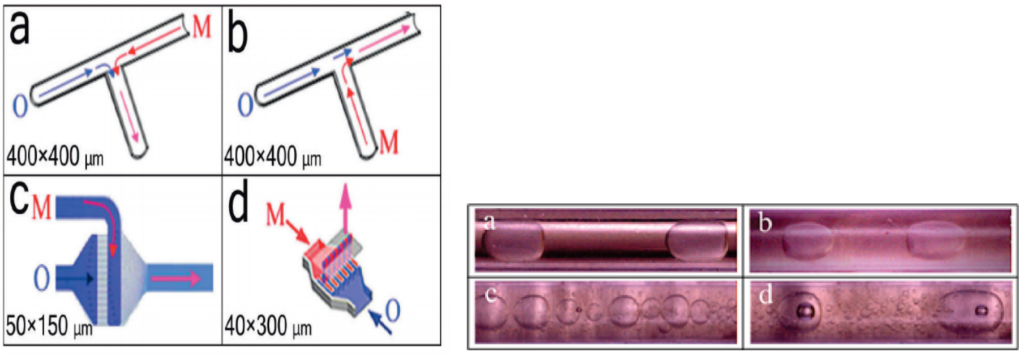


Figure 2.5: Various Forms and Dimensions of Micro-mixers (a)T-mixer (b)J-mixer (c)Rectangular Inter-digital Micro-mixer or RIMM and (c) Split Inter-digital Micro-mixer or SIMM-V2 and their corresponding flow patterns Sun et al. (2010)

investment for more or larger equipment [13]. However, but their use on industrial scales has been minimal. This is largely to due with the difficulty and cost of manufacturing microreactors at mass scale. Traditional manufacturing methods like etching and machining are costly and time consuming. Additive manufacturing, or 3D printing, holds a lot of promise for fabrication of microreactors. Complicated mixing and channel patterns can be mass produced using 3D printing that traditional methods cannot. However, at the moment the technology is still developing and is unfeasible at industrial scale [24].

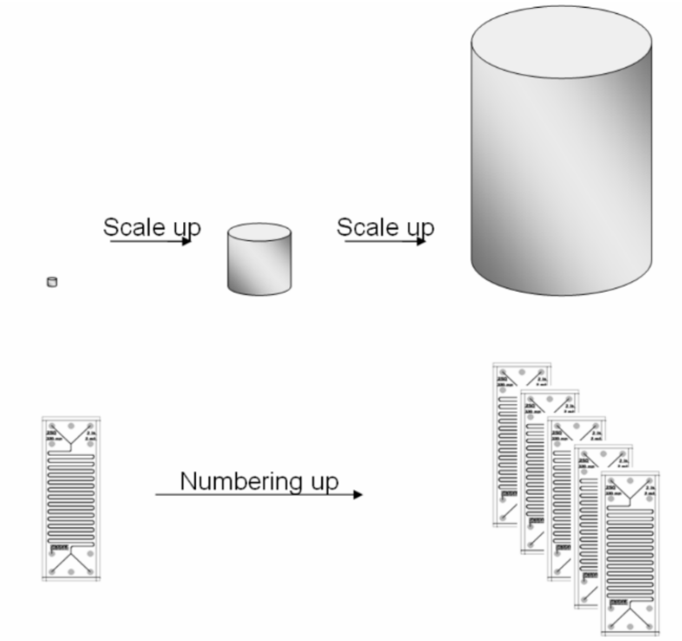


Figure 2.6: Numbering up versus Scaling up, from Salic et al. (2009)

To overcome the high manufacturing costs of microreactors on a mass scale, Billo et al. (2014) developed a cellular manufacturing process for fabrication and assembly of a full-scale microreactor biodiesel plant capable of producing biodiesel at a rate

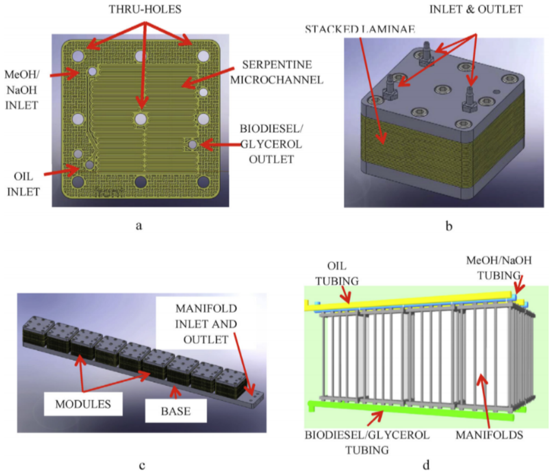


Figure 2.7: Modular microreactor design: (a) Laminae; (b) Module; (c) Manifold; (d) Full-scale microreactor, Billo et al. (2014)

of 2.47 $\frac{L}{min}$ and a capacity to produce 1.2 million liters per year. They fabricated over 14000 individual micro-channel laminae, placing them in a hierarchical system of modules and manifolds. The representative design for a single microreactor lamina is shown in Figure 2.7a. It consists of inlets for the oil and MeOH/NaOH process reactants; microchannels where the reaction takes place, and an outlet for the resultant biodiesel and its glycerol byproduct. Other features on the lamina are thru-holes for later assembly of the laminae into modules and manifolds. The lamina had 0.76 mm thickness and 5.7 cm x 5.7 cm planar dimensions. The microchannel array in the lamina had a serpentine flow pattern, the length of which was designed to correspond with the flow rate and residence time of the biodiesel process to ensure a complete conversion of the reactants to biodiesel fuel. The microchannel had a 500 μm x 500 μm depth and width respectively [25].

To validate the operation of the unit, a test loop with 50 laminae was constructed. Pre-mixed methanol with 0.9M KOH, and vegetable oil were pumped into a heated static mixer at flow rate ratio of 3:1 oil/methanol before being reacted in the microreactors. The mixture was heated at 65 °C and achieved a maximum flow rate of 0.53 L/hr during the 4 day test. The overall residence time was 2.6 minutes including the time spent in the static mixer and a conversion of 99% was achieved [25].

2.2 Biodiesel Synthesis in Microreactors with Ethanol

Arias et al. (2012) employed different channel geometries (Omega, Tesla, and T-shaped), as shown in Figure 2.8, made of polydimethylsiloxane (PDMS) using soft lithography process for producing biodiesel from canola oil and ethanol in presence of NaOH as a catalyst. The micro-channels were of the quadratic cross-section with width and height of 500 μm and length of 1 m. For T-, Tesla and Omega shaped microreactors, ethyl ester conversions of 93.5%, 95.3%, and 96.7% were attained respectively, at ethanol to castor oil molar ratio of 25:1, catalyst loading of 1 wt% NaOH and a reaction temperature of 50 °C in 10 minutes [26].

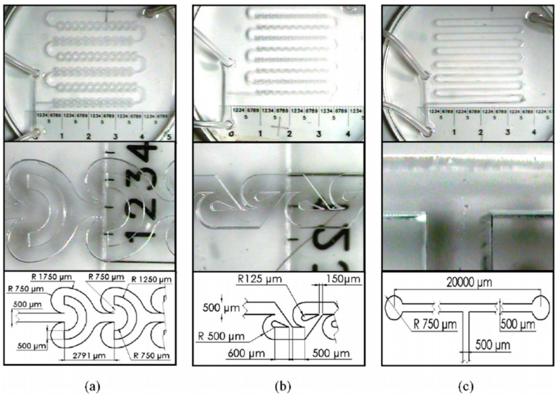


Figure 2.8: PDMS microreactor geometries used by Arias et al. (2012): (a) Omega-shaped (b) Tesla-shaped and (c) T-shaped

Santana et al. (2016) also performed experiments using PDMS microreactors with a T-junction micro-channel of 41.1 cm length, 1.5 cm width, and 0.2 cm height. In their experiments, sunflower oil was used as feedstock with ethanol to produce biodiesel through transesterification with sodium hydroxide as a catalyst. It was observed that minimum residence time of 1 min was needed at room temperature for a conversion of 95.8% as compared to the batch process in which 94.1% conversion was achieved in 180 minutes [27]. In order to increase the conversion and reduce the residence time, the same group performed experiments in a PDMS micro-channel of 35.1 cm length, 1.5 width, and 0.2 cm height with internal rectangular static elements of 1000 μm by 100 μm for the improved mixing, see Figure 2.9. It was found that maximum yield of 99.53% was obtained with 1 wt% catalyst concentration, residence time of 12 seconds and ethanol to oil molar ratio of 9:1 at 50 °C [28].

Schwarz et al. (2013) demonstrated the advantages of applying a continuous process with microreactors to biodiesel production. In the study KOH catalyzed ethanolysis of soybean oil was carried out in continuous and in batch processes. The experimental results and kinetic modeling of the data showed strong mass transfer limitations of the reaction. However, this limitation was reduced by increasing the efficiency of micromixing which lead to performances exceeding the batch process under otherwise identical reaction conditions [29].

Chen et al. (2013) studied biodiesel synthesis using low cost polymeric substrate microreactors, of various microchannel geometries, fabricated using a

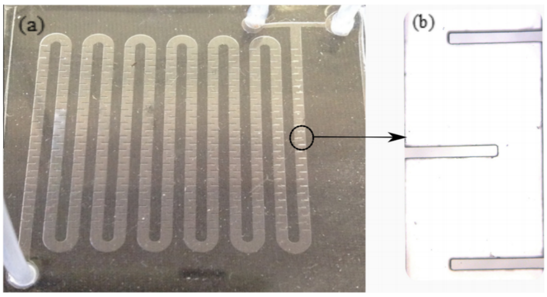


Figure 2.9: The PDMS microreactor used by Santana et al. (2017) (a) and an close view of the rectangular elements placed within the micro-channel.

photolithography technique. Using a tesla shaped geometry, an NaOH catalyst of 1% wt., 12.7:1 ethanol to soybean oil, a residence time of 5.6 minutes at 60 °C a ester conversion of 81% was achieved [30].

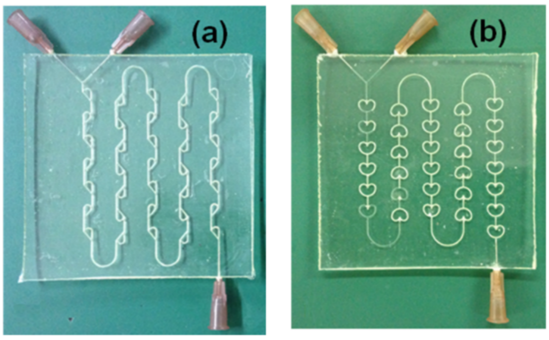


Figure 2.10: Microreactors with (a) Tesla geometry, and (b) Omega geometry; Chen et al. (2013)

Pontes et al. (2016) developed a coupled nonlinear mathematical model for the mass transfer of methanol and soybean oil in a microchannel under parallel flow regime adopted from the work of Al-Dhubabian (2005). See Figure 2.11, where the physical constants are labeled for alcohol (A) and triglycerides (TG). The set of partial differential equations governing the concentration profile were set up from a general mass balance of the species assuming steady state isothermal flow with constant physical properties. The velocity profile was derived from the Navier-Stokes equation assuming stratified laminar flow for two immiscible Newtonian fluids with a planer interface. The second order kinetic equations were developed assuming homogeneous and reversible chemical reactions and written as source terms for the main equations. The equations were solved using the hybrid method known as Generalized Integral Transform Technique (GITT) and compared with numerical results using COMSOL Multiphysics platform. The results showed good agreement with the COMSOL results as well as the previous work done by Al-Dhubabian (2005) [31].

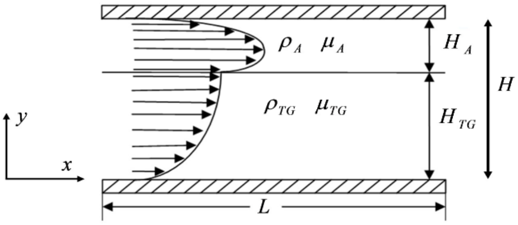


Figure 2.11: 2D schematic of stratified flow; Pontes et al.(2016)

Chen (2015) investigated the effects of two main types of flows that occur in microchannels during transesterification: stratified and segmented flow. These mathematical models for the coupled mass transfer and concentrations were solved using a finite element method with COMSOL Multiphysics computational software. A parallel plate microchannel geometry, similar to the microreactor in the work of Al-Dhubabian (2005), was used for analysis of stratified flow. For segmented flow, a circular microchannel geometry was used. The results agreed with literature that greater conversions occur with a segmented flow, and the smaller the droplet size the faster the conversion [32].

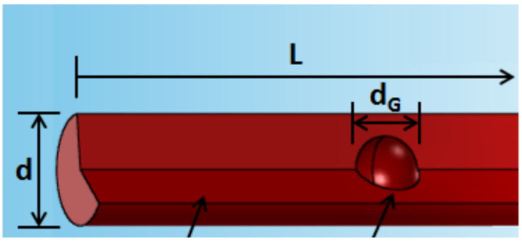


Figure 2.12: Schematic of segmented flow used in Chen (2015). A spherical droplet of oil is dispersed within alcohol in a circular microchannel.

Costa Junior (2017) studied the continuous synthesis of biodiesel with microreactors using the rejected heat of a parallel thermal process to heat the reaction and improve conversions, see Figure 2.13. An experimental analysis using a single microreactor manufactured using a micro-milling technique yielded a ethyl ester conversion of 92.56% at a residence time of 46.56 seconds. A superior reactor design was conceived, coupling 10 microreactors in parallel with 11 micro-heat exchangers, and fabricated using additive manufacturing. This reactor yielded a ethyl ester conversion of 99.61% with a residence time of 34.92 seconds. A 3D mathematical model describing the diffusive, convective, and reactive interactions of the species was reformulated using the Coupled Integral Equations Approach (CIEA). The new model reduced the system to a set of coupled compound non-linear ODEs,greatly reducing computational costs. The kinetic constants were then estimated using the Markov Chain Monte Carlo method with experimental data with low conversion rates, to better estimate the constants of intermediary species [14].

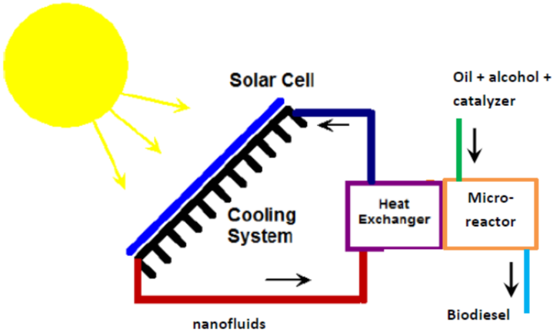


Figure 2.13: Schematic showing a photo-voltaic thermal process running parallel with a biodiesel process

2.3 Contribution of Present Study

The present study will contribute in the following ways which current literature lacks:

- Attempt to reduce FFAs through esterification with ethanol and MSA catalyst using microreactors.
- Synthesize biodiesel in microreactors using WCO and ethanol.

Chapter 3

Biodiesel Synthesis

3.1 Biofuels

Global demand for fossil fuels has increased exponentially since the beginning of the industrial revolution. The demand is expected to increase in the future as developing nations such as India and China continue to industrialize [33]. These resources are finite and disruption in their supply can cause economic and political instability throughout the world. In addition, the combustion of fossil fuels results in the deposit of particulates and greenhouse gases into the atmosphere. This has adverse effects on human society, such as poor air quality and climate change associated with greenhouse gases. It is therefore important to increase renewable energy capacity worldwide in order to mitigate these effects. Technologies such as solar, wind, geothermal and biofuels help increase renewable energy capacity as well as reduce carbon emissions [34].

The majority of road transport fuels are derived from fossil fuels. Combustion of these road transport fuels account for about 25% of CO_2 emissions globally. Road transport-related emissions will continue to increase due to ever-increasing rates of road transport. The transport industry accounts for nearly 60% of world fossil fuel demand, and approximately 50% of this was consumed in road transport. The demand for fuel in the transport sector is likely to increase in the future as developing countries improve their infrastructure and grow their transportation industries. The International Energy Agency predicts that ownership of cars and trucks will increase from 700 million in 2005 to 2 billion in 2050 worldwide. This massive increase in demand will increase greenhouse gases and place pressure on governments to develop sustainable energy policies. Biofuels will be a part of these emerging policies and appear promising as an alternative to a portion of fossil fuel derived combustibles [33].

Vegetable oil such as soybean, peanut and palm oil are biofuels that have been used throughout history. In fact, peanut oil was used as diesel engine fuel when Rudolf Diesel ran his first prototype diesel engine in Augsburg, Germany in 1893 [34]. However, the use of pure vegetable oil as diesel fuel is not recommended for use long term. Plant oils, animal fats, and greases used in diesel engines, even at concentrations as low as 1%, can cause long-term engine deposits, ring sticking, lube oil gelling and other maintenance problems, and can reduce engine life or even cause engine failure. These problems are caused mostly by the much higher viscosity of the raw fats and/or oils (around 40mm^2/s) compared to that of diesel fuel, for which the engines and injectors were designed (1.3 to 4.1mm^2/s). Higher viscosity can lead to polymerization of the oil and create various engine problems. The significantly higher boiling point of raw fats and oils may also lead to failure of the fuel to fully evaporate, especially during cold start, leading to harmful engine deposits and engine oil sludging. Through the process of transesterification or esterification, plant oils (as well as animal fats and waste oils) can be used to create fatty acid alkyl esters or what is termed biodiesel [3].

3.2 Biodiesel Advantages

Biodiesel has a viscosity of 4-5mm^2/s allowing it to operate in compression ignition engines like petroleum diesel, thereby requiring no essential engine modifications. In addition, biodiesel maintains the payload capacity and range of conventional diesel. The fuel is miscible with petrodiesel in any proportion and possesses several stand-alone technical advantages over conventional petrodiesel fuel, such as inherent lubricity, low toxicity, superior flash point, biodegradability, negligible sulfur content, and lower overall exhaust emissions [35]. Biodiesel comes from renewable sources allowing non-oil rich countries to become more energy independent and potentially more secure. Also, biodiesel researchers have measured a significant reduction in CO_2 emissions. CO_2 is the greenhouse gas believed to be the main cause of global warming. However, biodiesel has important disadvantages to consider when compared to petrodiesel, these include high feedstock cost, inferior storage and oxidative stability, lower volumetric energy content, inferior low-temperature operability versus petrodiesel, and in some cases, higher NOx exhaust emissions [36]. Many of these deficiencies can be mitigated through cold flow improver; additives, blending with petro-diesel, and/or reducing storage time [35].

Feedstock acquisition currently accounts for over 75% of biodiesel production expenses, which is a serious threat to the economic viability of the biodiesel industry [37]. One potential solution to this problem is employment of alternative feedstocks which are much cheaper than pure vegetable oils which are commonly used. These feedstocks may include soap-stocks, acid oils, tall oils, used cooking oils and waste restaurant greases, various animal fats, non-food vegetable oils, and oils obtained from trees and microorganisms such as algae [38]. However, many of these low-cost feedstocks are of poor quality and may contain high levels of free fatty acids (FFA), water, or insoluble matter, which necessitate quality improvement before biodiesel production [39].

3.2.1 Environmental/Emissions

Industrialized countries worldwide have emissions standards for combustion engines and these standards continue to become more strict as governments take action on global warming and populations demand cleaner air. Because of the ever increasing emissions standards, car manufactures and operators are interested in any way to reduce emissions. Emissions from the use of pure biodiesel in compression ignition engines are greatly reduced compared to conventional petroleum diesel fuels. Reductions up to 100% sulfur dioxide (SO_2), 50% carbon monoxide (CO), 47% particulate matter (PM), 67% total unburned hydrocarbons (THC), and up to 90% reduction in mutagenicity have been reported, dependent on the quality of the biodiesel [40].

Diesel engines emit relatively small quantities of CO and THC compared to conventional gasoline vehicles and are well below the compliance threshold of these pollutants in most jurisdictions, regardless of the type diesel fuel being used. However, diesel engines emit significant amounts of PM and oxides of nitrogen (NOx) [34]. It is almost universally agreed upon that running a diesel engine on either pure biodiesel or biodiesel blended fuel will reduce the emission of PM. This is mostly due to the more complete combustion of biodiesel in the combustion chamber and the absence of soot producing aromatics in biodiesel. Conversely, the physical properties of biodiesel lead to advanced injection and an advanced combustion process in the combustion chamber which increases NOx emissions,see Table 3.1 [41]. Selecting biodiesel with favorable properties and adjusting the engine tuning are the most common methods used to reduce the NOx emissions. The addition of additives and blending the biodiesel with petro diesel are methods also commonly used [40]. Perhaps the most significant reduction based on life cycle analysis is the 78% reduction in carbon dioxide, which is considered the most important greenhouse gas affecting climate change in climatic models. In addition, biodiesel has much higher biodegradability than low-sulfur diesel fuel and the addition of biodiesel to petrodiesel fuels actually promotes the biodegradability of the diesel fuel, making the blends more environmentally friendly in this regard [34].

Table 3.1: Average Emissions of Biodiesel, Biodiesel Blend, and Diesel Fuel; Luque et al. (2008)

Emission (kg/100km)	Biodiesel 100%	Biodiesel 30%	Diesel
CO	0.37	0.43	0.46
Hydrocarbons	0.03	0.04	0.04
NOx	3.78	3.64	3.37
Particulate Matter	0.62	1.48	1.85
CO_2	0.87	3.53	4.67
SO_2	0	1.14	1.62

3.2.2 Biodiesel Global Outlook

Biofuels production has increased globally since 2000, with the most significant contributions from USA, Brazil, the EU, Malaysia and India [33]. The majority of these biofuels are bio-ethanol and biodiesel, which are used as liquid fuels for automobiles. Bioethanol is produced commercially at an industrial scale for use either on pure form or blended with gasoline for liquid transport fuel. During the oil crisis of the 1970s, Brazil instituted the program PROALCOOL and to this day continue to have the most comprehensive supply, domestic consumption and export of bio-ethanol worldwide. The substantial bio-ethanol program in Brazil was due to the availability of raw materials from sugarcane and molasses from sugar industry [42]. Because of the experience and success gained from PROALCOOL, the Brazilian government launched the program PNPB in 2004 [43]. Biodiesel production has since continued to expand in Brazil with soybean oil the most common feedstock used in biodiesel production in Brazil. With production at just 47% total capacity, biodiesel will continue to be part of the energy solution in the country [42].

Biodiesel began to gain interest from government officials and customers in the United States since the 1970s with the Organization of OPEC oil crisis. Biodiesel production has steadily increased since that time but biodiesel was minuscule compared to petrodiesel consumption [34]. During the 21st century, biodiesel production has increased greatly, with the market reaching an all time high of approximately 2.8 million gallons in 2016 [33]. In the near term, plans are to increase capacity and production levels. Governmental legislation continues to support biodiesel, through tax incentives and some mandated use. Biodiesel is seen as a major part of US energy policy going forward to reduce dependence of foreign oil, create domestic jobs, and reduce the impact of diesel fuel related activities on the environment [34].

The EU has been the most aggressive in promoting the use of biodiesel through legislation and government mandates. Proposals from the EU Biofuels Action Plan Summit called for increases in biodiesel consumption through 2020. The countries in the EU continue to produce and consume the most biodiesel in the world. While the EU is certainly the leader in biodiesel development followed by the United States, many countries in Asia are embarking on their own biodiesel programs. Among these are China, India, Japan, South Korea, Taiwan, Thailand, The Philippines, Malaysia, Indonesia and Singapore. This development bodes well for the future of biodiesel as part of the worlds energy solution [34].

3.3 Biodiesel Production

3.3.1 Pyrolysis

This refers to a chemical change caused by the application of thermal energy in the absence of air or nitrogen. It involves the cleavage of chemical bonds into small molecules. Thermal decomposition of triglycerides produces compounds of several classes, including alkanes, alkenes, alkadienes, aromatics, and carboxylic acids. Different types of vegetable oils reveal large differences in composition when they are thermally decomposed. The liquid fractions of the thermally decomposed vegetable oil are almost the exact chemical composition of conventional diesel fuel [44]. Pyrolyzed soybean oil, for instance, contains 79% carbon and 12% hydrogen. It also has low viscosity and a high cetane number compared to pure vegetable oils [45]. However, while pyrolyzed vegetable oils possess acceptable amounts of sulfur, water, and sediment, as well as giving acceptable copper corrosion values, they are unacceptable in terms of ash, carbon residues, and pour point. In addition, though the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during thermal processing also eliminates any environmental benefits of using an oxygenated fuel [46].

3.3.2 Dilution

Dilution of vegetable oils to reduce their viscosity can be accomplished with such materials as diesel fuels, solvents or ethanol. Several studies have been conducted on the effects of vegetable oil dilution on diesel fuel properties. Physical and chemical properties of these fuel blends allow the blends to function in diesel engines, however, the blends do not meet regulatory fuel standards are not recommended for long term use [46].

3.3.3 Microemulsion

Microemulsion is another method used to reduce high viscosity in vegetable oil. The use of microemulsions with solvents such as methanol, ethanol, and 1-butanol have been studied in depth. A microemulsion is defined as a colloidal equilibrium dispersion of an optically isotropic fluid microstructure with dimensions generally in the 1150 nm range formed spontaneously from two normally immiscible liquids and one or more ionic amphiphiles. In other words; microemulsions are clear, stable isotropic fluids with three components: an oil phase, an aqueous phase and a surfactant. The aqueous phase may contain salts or other ingredients, and the oil may consist of a complex mixture of different hydrocarbons and olefins. This ternary phase can improve spray characteristics by explosive vaporization of the low-boiling-point constituents in the micelles. All microemulsions with butanol, hexanol and octanol meet the maximum viscosity limitation for diesel engines. Microemulsion-based fuels are sometimes also termed hybrid fuels, although blends of conventional diesel fuel with vegetable oils have also been called hybrid fuels. Microemulsions are classified as nonionic or ionic, depending on the surfactant present. Microemulsions containing for example, a basic nitrogen compound are termed ionic while those consisting for example, only of a vegetable oil, aqueous ethanol, and another alcohol, such as 1-butanol, are termed non-ionic. Nonionic microemulsions are often referred to as detergentless microemulsions, indicating the absence of a surfactant [47].

3.3.4 Transesterification

The transesterification, or alcoholysis, process involves the reaction of a feedstock containing triglycerides (the main constituent in vegetable oils and animal fats) with short chain primary alcohols (methanol, ethanol, butanol etc.) to produce fatty acid esters and by-product glycerol (G) via three stepwise reversible removals of the fatty acid moieties from the triglyceride (TG), diglyceride (DG), and monoglyceride (MG), see Figure 3.1.

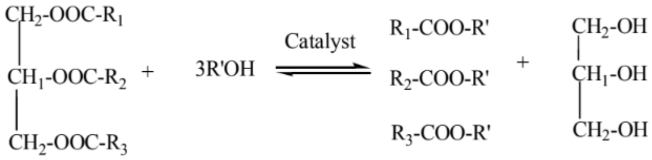


Figure 3.1: Transesterification Reaction

An ester is produced from each step and thus three esters are made from a single TG along with one glycerol molecule. The R1, R2, and R3 are long chain hydrocarbons (HC), sometimes called fatty acid chains, see Table 3.2 [48]. These fatty acid chains can vary depending on which type of feedstock is being used, see Table 3.3 [49]. The length and the amount of double bonds of the fatty acids have a noticeable effect on the combustion and emission properties of the finished biodiesel [7]. Methanol is the most common alcohol used in biodiesel production because of its wide availability, low cost, and ease of separation and recovery in the purification stages of production [50]. However, ethanol is also used especially in high ethanol-production areas such as Brazil, where it is cost competitive with methanol [51]. Ethanol is also less toxic and safer than methanol and is derived from renewable resources, while methanol is produced from fossil fuels (researchers are beginning to implement production methods of green methanol, however these technologies are in their infancy) [52]. To achieve the activation energy of this reaction high temperatures and/or pressures are required in absence of a catalyst. Therefore, a catalyst is typically used to facilitate the reaction at atmospheric pressure. These catalyst are broadly divided into categories of homogeneous acid or base catalysts, heterogeneous catalysts (usually solid), and enzymatic catalysts [53].

Table 3.2: Common fatty acids and their chemical structures, Lin et al. (2011)

Fatty Acid	Chemical Structure
Lauric (12:0)	$CH_3(CH_2)_{10}COOH$
Myristic (14:0)	$CH_3(CH_2)_{12}COOH$
Palmitic (16:0)	$CH_3(CH_2)_{14}COOH$
Stearic (18:0)	$CH_3(CH_2)_{16}COOH$
Oleic (18:1)	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$
Linoleic (18:2)	$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
Linolenic (18:3)	$CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$
Arachidic (20:0)	$CH_3(CH_2)_{18}COOH$
Behenic (22:0)	$CH_3(CH_2)_{20}COOH$
Erucic (22:1)	$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}COOH$

Table 3.3: Fatty acid content of common feedstock, Aransiola et al. (2014)

Feedstock	Fatty Acid ($\frac{\%w}{w}$)									
	12:0	14:0	16:0	18:0	18:1	18:2	18:3	20:0	22:0	22:1
Sunflower	-	-	-	4.5	21.1	66.2	-	0.3	-	-
Soybean	-	0.1	11.0	4.0	23.4	53.2	7.8	-	-	-
Cottonseed	0.1	0.7	22.1	2.6	19.2	55.2	0.6	-	-	-
Canola	-	-	4.0	2.0	62.0	20.0	9.0	-	-	-
Corn	-	-	11.7	1.9	25.2	60.6	0.4	0.2	-	-
Palm	0.2	1.1	44.0	4.5	39.2	1.0	0.4	-	-	-
Coconut	46.5	19.2	9.8	3.0	6.9	2.2	-	-	-	-
Tallow	0.1	2.8	23.6	19.4	42.4	2.9	0.9	-	-	-

The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Figure 3.2 [44]. The first step is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate from which the alkyl ester and the corresponding anion of the diglyceride are formed. The latter deprotonates the catalyst, thus regenerating the active species, which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol [51].

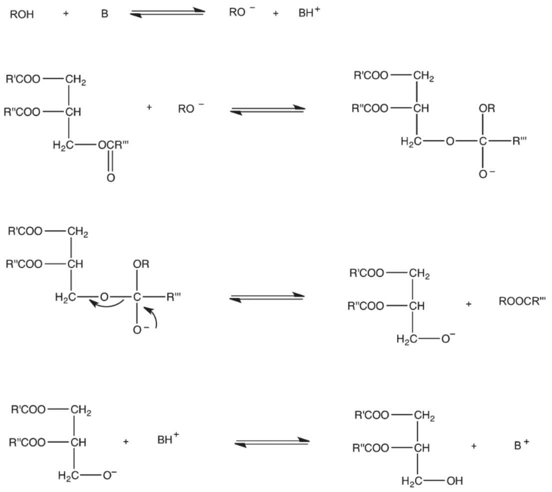


Figure 3.2: Transesterification Mechanism; Sarin (2012)

Kinetics of Transesterification

Transesterification occurs in three reversible steps represented in Equation (3.1) with k the kinetic constant. When solving for the reaction kinetics, one must consider that vegetable oil and alcohol are not miscible. Therefore the mass transfer of the mixture must be considered before the reaction is kinetically controlled. The mass transfer will depend on the reactor type being used for conversion. The miscibility between the oil and alcohol can also be increased with the use of co-solvents, however the co-solvent must be removed which complicates the purification steps. Most conventional kinetic models assume the reaction is kinetically controlled with use of a batch reactor where the stirring speed is set high enough to consider the reaction mixture homogeneous and ignore the mass transfer effects. Some studies have shown that the use of ethanol as the reacting alcohol also reduces the effect of the initial mass transfer stage [54]. In addition, conventional models assume side reactions (saponification, FFA neutralization) are negligible.

$$TG + ROH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} DG + E \tag{3.1a}$$

$$DG + ROH \underset{k_4}{\overset{k_3}{\rightleftharpoons}} MG + E \tag{3.1b}$$

$$MG + ROH \underset{k_6}{\overset{k_5}{\rightleftharpoons}} G + E \tag{3.1c}$$

Using the law of mass action, a set of differential reaction rate equations can be written (Equation (3.2). When the molar concentration of alcohol is much higher than the concentration of oil, the concentration of alcohol is considered constant, therefore the kinetic constants $k_1, k_3, k_5 >>> k_2, k_4, k_6$ and only the forward reactions are considered [55].

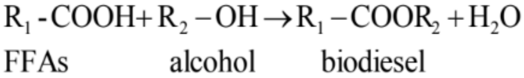
$$\begin{align}
\frac{d[TG]}{dt} &= -k_1[TG][ROH] + k_2[DG][E] \tag{3.2a}\\
\frac{d[DG]}{dt} &= k_1[TG][ROH] + k_4[MG][E] - k_2[DG][E] - k_3[DG][ROH] \tag{3.2b}\\
\frac{d[MG]}{dt} &= k_3[DG][ROH] + k_6[G][E] - k_4[MG][E] - k_5[MG][ROH] \tag{3.2c}\\
\frac{d[E]}{dt} &= k_1[TG][ROH] + k_3[DG][ROH] + k_5[MG][ROH] \nonumber\\
&\quad - k_2[DG][E] - k_4[MG][E] - k_6[G][E] \tag{3.2d}\\
\frac{d[G]}{dt} &= k_5[MG][ROH] - k_6[G][E] \tag{3.2e}\\
\frac{d[ROH]}{dt} &= -\frac{d[E]}{dt} \tag{3.2f}
\end{align}$$

Once the rate constants are found, the activation energy can be determined using the Arrhenius equation (3.3).

$$k = Ae^{\frac{-E_a}{RT}} \tag{3.3}$$

3.3.5 Esterification

Esterification of FFAs can also be used to create biodiesel and is frequently used as a pretreatment for oils of poor quality [56]. Chemically, esterification is a reversible reaction of carboxylic acids with alcohol to produce alkyl esters and water in the presence of acid catalysts, see Figure 3.3 [57].



$$R_1\text{-}COOH + R_2-OH \rightarrow R_1-COOR_2 + H_2O$$

Figure 3.3: Esterification Reaction

FFAs are created through the process of hydrolysis. This process occurs most commonly during cooking with vegetable oil as the water in food reacts with the triglycerides in the vegetable oil at high temperature which leaves FFA and glycerol molecules in the oil [58]. This makes esterification useful as a pretreatment to WCO before transesterification.

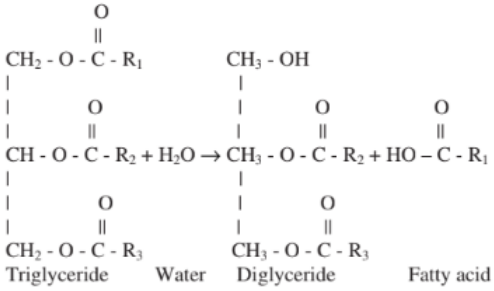


Figure 3.4: Hydrolysis Reaction

The mechanism of esterification reaction involves a process related to nucleophilic substitution. First, the carboxylic acid is protonated initially by the strong inorganic acid catalyst. Then, the alcohol nucleophile (two lone pairs on the oxygen) adds the sp2 carbon and the alcohol proton is lost. The new ester bond between the carboxyl group carbon and the alcohol oxygen is formed, the water molecule is eliminated at one site or the other, and finally, the excess proton leaves, regenerating the inorganic acid catalyst. The esterification mechanism is shown in Figure 3.5 [59].

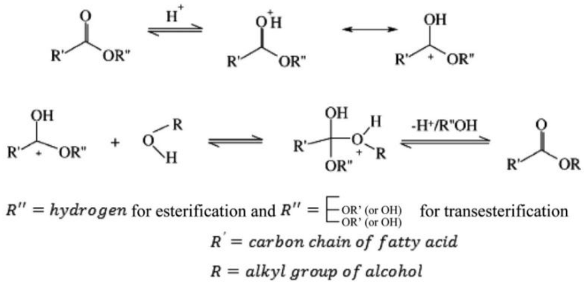


Figure 3.5: Esterification Mechanism

Kinetics of Esterification

The kinetics of esterification of FFA are found much the same way as with transesterification. Using the reaction in Equation 3.4 where a free fatty acid molecule reacts with an alcohol molecule to create an ester (biodiesel) molecule and a water molecule. Ignoring the mass transfer effects, rate equations can be written for the species. When the amount of alcohol is very large in comparison to the other species, the reverse reaction can be considered non significant and the equation can be solved for k. Form here, the activation energy can be found using the Arrhenius equation (3.3) [60].

$$FFA + ROH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} E + H_2O \tag{3.4}$$

3.4 Parameters Affecting Biodiesel Production

3.4.1 FFA Content

The free fatty acid and moisture content are key parameters for determining the viability of the feedstock used in the transesterification process. To carry the base catalyzed transesterification reaction to completion, a FFA value lower than 1.5% and a water content of less than 0.1% is needed. An FFA content of lower than 0.5% and completely anhydrous oil are preferred for consistent conversion results [34]. FFAs are present in high quantities in feedstocks such as animal fats, coconut oil, and palm oil. FFAs are also present in WCO through the oxidation of triglycerides, which are created while cooking foods [61]. The higher the acidity of the oil the smaller is the conversion efficiency because of the saponification reaction that occurs between FFAs and base catalysts during transesterification. FFAs react with an alkali catalyst, creating soap and water as seen in Figure 5.5 [62].

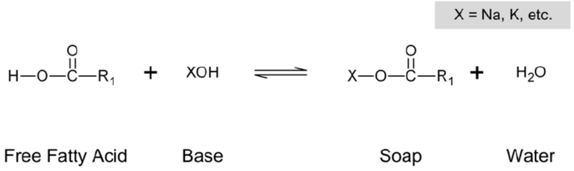


Figure 3.6: Saponification Reaction

This reaction occurs much faster than the transesterification of the triglycerides and can diminish the overall yield of biodiesel product by using up the base catalyst in the reaction mixture. The resulting soap can also complicate mass transfer during conversion and downstream processing of the finished biodiesel [63]. The FFA content is reduced using several methods but the most common method is to react the FFAs with alcohol with a acid catalyst to create esters (esterification). Esterification can be done on any type of oil with high FFA content [64].

Many different oils have been used across several esterification studies. For example, Arora et al., (2016) reduced FFAs in rice bran oil from 12% to 1.8% using 0.5% weight-oil H_2SO_4, a 20 to 1 methanol to oil molar ratio, a temperature of 333K and for 90 minutes in a spinning tank reactor [65]. Likewise, Brinks et al., (2013) reduced FFAs in rapeseed oil from 5% to 0.2% using 0.1% H_2SO_4, 20:1 methanol to oil molar ratio, a temperature of 70 °C, in 240 minutes [66]. In another study, Kostic et al., (2016) was able to reduce the FFA content from 15.8% to 0.24% in plum stone oil using 2% H_2SO_4, 8.5:1 methanol to oil molar ratio, a temperature of 45 °C in 60 minutes [67]. Neumann et al., (2016) used pure oleic acid (a common FFA) and converted 75% to esters (biodiesel) using a 1.5% H_2SO_4, a 6:1 ethanol to oil molar ratio at 347K and 120 minutes [68]. Neeharika et al., (2017) used a different acid catalyst and reduced the FFA content in jatropha oil from 22.52% to 0.5% using 1% MSA, a 20:1 methanol oil molar ratio at 60 °C in 270 minutes [69].

3.4.2 Water Content

The starting materials used for base catalyzed alcoholysis should be substantially anhydrous. The feedstock used in transesterification with more than 0.1% water will yield poor results [34]. Water in the system will react with the triglycerides to form FFAs via hydrolysis which will cause soap formation. Extra water in the system will also quench the catalyst in both the transesterification and esterification reactions which has an adverse effect on yield. One part of water can quench up to 4.67 parts of catalyst. Therefore commonly used alkali catalysts in transesterification, methoxide and hydroxide of sodium or potassium, should be maintained in anhydrous state. Prolonged contact with air will diminish the effectiveness of these catalysts through interaction with moisture and carbon dioxide [58].

3.4.3 Catalyst Concentration

The activation energy of the transesterification reaction requires high temperatures and pressures without the use of catalysts. Therefore, catalysts are used to facilitate the reaction at more manageable operating conditions. Catalysts used for the transesterification of triglycerides are classified as alkali, acid, enzymatic or heterogeneous catalysts [70]. Alkali catalyzed transesterification reaction is relatively quick and the downstream products separate easily when methanol is used as the alcohol [61]. For these reasons, as well as low cost, alkali catalysts are used in nearly every industrial biodiesel application. Commonly used alkali catalysts include sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide. NaOH is the most used catalyst because of its low cost. However, KOH is also very common and typically yields better triglyceride conversions at a slightly higher cost compared to NaOH. Vincinte et al. (2004) compared these common catalysts using 6:1 methanol to sunflower oil molar ratio, stirred in a batch reactor for three hours at 65 °C, and 1% catalyst. These experiments resulted in biodiesel yields of 87%, 92%, 99%, and 98% for NaOH, KOH, CH_3NaO, and CH_3KO respectively [70].

An increase in catalyst concentration will typically increase product yield due to the enhancement in rate of reaction. However, homogeneous alkali and acid catalysts are difficult to recover, so to minimize costs the optimal concentration is the lowest that will yield 100% triglyceride conversion. Excess catalyst will also increase the viscosity of the reaction mixture which makes purification more difficult and has adverse effects on yield. In addition, excess catalyst in the system can potentially increase saponification of triglycerides shown in Figure 3.7 [71].

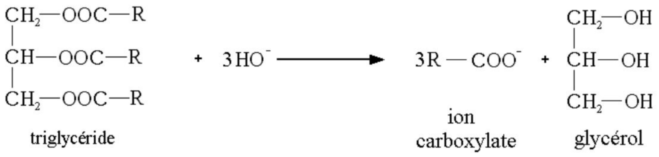


Figure 3.7: Saponification of triglycerides reaction

Although alkali catalysts are almost exclusively used in industry, they do cause some problems when used with low quality oil because of the saponification of FFA and hydrolysis side reactions [72]. If the oil has high free fatty acid content an acid catalyzed esterification step is added before transesterification. The acids used can be sulfuric, phosphoric, hydrochloric or sulfonic acids with the most common being sulfuric and hydrochloric. Acids can also be used to facilitate the transesterification reaction but the reaction times are much larger than alkali catalysts [73].

Although chemical transesterification using an alkaline catalysis process gives high conversion levels of triglycerides to their corresponding esters in short reaction times, the reaction has several shortcomings: it is energy intensive, recovery of glycerol is difficult, the alkaline catalyst has to be removed from the final product, alkaline wastewater requires treatment, and free fatty acid and water can interfere the reaction. The drawbacks can be overcome using enzymatic catalysts like lipase which are able to effectively catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems. However, the reaction time using enzymatic catalysts is much greater than alkaline catalysts. In addition, the cost of enzymatic catalysts greatly exceeds that of traditional alkaline catalysts which make their use cost ineffective [50].

Two other catalyst technologies are commonly researched, solid heterogeneous catalysts, and performing the transesterification reaction with no catalyst using supercritical conditions. Solid heterogeneous catalysts are attractive because they can be used to convert poor quality oils containing large amounts of FFAs into biodiesel without pretreatment. The high cost of these catalysts make their use on the industrial scale inviable [53]. Performing transesterification with no catalyst at supercritical conditions drastically simplifies downstream processing as there is no catalyst to remove and the alcohol is easy to recuperate. However, the high pressures and temperatures needed to achieve supercritical conditions greatly increases the costs of production and these techniques continue to be used only for research purposes [5].

3.4.4 Alcohol to Oil Molar Ratio

The most common type of alcohol used in biodiesel production is methanol (creating FAME) because of its low cost and availability worldwide as well as ease of downstream separation and recovery. Ethanol is the second most used alcohol (creating FAEE) in biodiesel production and is less expensive than methanol in regions where ethanol production is high, such as Brazil [43]. Ethanol also has the added benefit of being produced from renewable sources, such as corn and sugarcane, rather than methanol which is produced from fossil fuels [74]. It is also less toxic than methanol. Butanol, propanol, isopropanol, and pentanol are other alcohols used in biodiesel research [34].

The base catalyzed formation of ethyl ester is more difficult compared to the formation of methyl esters. Specifically the formation of stable emulsion during ethanolysis is a problem. Methanol and ethanol are not miscible with triglycerides at ambient temperature, and the reactants are mixed to enhance mass transfer [75]. During the course of reaction, emulsions usually form. In the case of methanolysis, these emulsions quickly and easily break down to form a lower glycerol rich layer and upper methyl ester rich layer. The lower layer can be easily removed from simple draining or centrifugation and then the methanol can be recovered by heating the mixture and capturing the vapor. In ethanolysis, these emulsions are more stable and severely complicate the separation and purification of esters. The product mixture remain in one phase with ethanolysis so the alcohol must be washed out and removed along with the glycerol and is not easily recoverable [3].

The emulsions in the product are caused in part by formation of the intermediates monoglycerides and diglycerides, which have both polar hydroxyl groups and non-polar hydrocarbon chains. These intermediates are strong surface active agents. In the process of alcoholysis, the catalyst, either sodium hydroxide or potassium hydroxide is dissolved in polar alcohol phase, in which triglycerides must transfer in order to react. The reaction is initially mass-transfer controlled and does not conform to expected homogeneous kinetics. When the concentrations of these intermediates reach a critical level, emulsions form. The larger non-polar group in ethanol, relative to methanol, is assumed to be the critical factor in stabilizing the emulsions. However, if the concentration of mono- and diglycerides is very low, the emulsions become unstable. This emphasizes the necessity for the reaction to be as complete as possible, thereby reducing the concentrations of mono- and diglycerides [3].

Verma et al. (2006) compared the biodiesel yield on karanja oil using both methanolysis and ethanolysis. Methanol was shown to be the superior alcohol of the two in terms of biodiesel yield. This was shown by optimizing the process variables of transesterification of both methanol and ethanol using response surface methodology. For methanol, a biodiesel yield of 91% was achieved using a 10.44:1 molar ratio, 1.22% KOH, and a residence time of 91 minutes at 68.6 °C. This was compared to ethanol which had a biodiesel yield of 77.4% with a 8.42:1 molar ratio, 1.21% KOH, and a residence time of 120 minutes at 61.3 °C [76].

One of the most important variables affecting the yields of ester formation during transesterification is the molar ratio of alcohol to vegetable oil employed. The stoichiometric ratio for this reaction requires 3 moles of alcohol per mole of triglyceride to yield 3 moles of fatty esters and 1 mole of glycerol, however, transesterification is an equilibrium reaction [77]. According to Le Chatelier's principle, the rate of the formation of product increases with increase in reactant concentration, therefore large excess of alcohol is required to drive the reaction to the right [3].

All else being equal, higher molar ratios result in higher ester conversions in shorter time. However, in industry, the alcohol molar ratio is optimized to reduce costs which means using lowest amount of alcohol to convert the feedstock to market grade fuel [34]. Several studies have also mentioned that very high alcohol molar ratios complicate the separation of glycerin as there is an increase in solubility at such ratios [56].

3.4.5 Residence Time

The residence time is the amount of time the reactants spend in the reactor. The transesterification reaction occurs very quickly but because the alcohol and oil are not miscible, the reaction only occurs at the interface of the two separate phases. Therefore, in order to make biodiesel that meets regulatory standards, the reactants must be mixed for an extended period of time to make sure that all triglycerides and intermediates have been converted. The conversion rate obviously increases with an increase in residence time. However, production plants look to keep the reaction time as low as possible while still achieving full conversion, in order for the plant to produce as much biodiesel as possible at the lowest possible operating costs [3].

3.4.6 Temperature

Transesterification can occur at different temperatures, depending on the types of catalyst, alcohol, oil, and type of reactor being used. Generally, higher temperatures will result in an increase in conversion up until the temperature reaches the boiling point of the alcohol being used in transesterification. However in industry, temperature is optimized to achieve complete conversion at lowest cost [3]. Freedman et al., (1984) studied the transesterification of refined oil with methanol at 6:1

methanol/oil ratio and 1% NaOH, the reaction with three different temperatures. After half an hour, ester yields were 94%, 87% and 64% for 65 °C, 45 °C, and 32 °C respectively. After one hour, ester formation was identical for 60 °C and 45 °C runs and only slightly lower for the 32 °C run. It is therefore evident that temperature clearly influenced the reaction rate and yield of esters with a longer residence time needed for lower temperatures [78].

The effect of temperature on the conversion of waste cooking oil to biodiesel at was studied by Al-Hamamre et al., (2014). In order to investigate the effect of reaction temperature the transesterification of WCO was carried out using a 9.5 methanol to oil molar ration and 1% KOH at different reaction temperatures(40 °C, 50 °C, and 60 °C) and analyzed at different time intervals (5, 10, 20, 40, and 80 min). They observed that by increasing the temperatures from 40 °C to 60 °C increased the conversion from 92% to 98% at 5 minutes conversion time and the lower temperature reactions increasing steadily to 98% conversion after 30 minutes and remaining steady during the 80 minutes. However, at 60 °C, a slight reduction in the conversion was observed after 60 minutes. This is because high temperature enhances both transesterification and saponification reactions [79].

3.5 Biodiesel Reactor Types

The reaction rate of transesterification is limited by the mass transfer of the between the oil and alcohol because they are immiscible. Therefore the type of reactor used to overcome the mass transfer will greatly effect the yield and quality of the biodiesel as well as have an effect on the overall cost of the biodiesel production operation. Reactors are deployed in either continuous or batch operations. In continuous operations, the reactants are constantly fed into the reactor at a certain rate. While in batch processes, a fixed amount of the reactants are placed in the reactor, reacted, emptied, and then the process is repeated [80].

3.5.1 Spinning Tank Reactors

Spinning tank reactors, or simply batch reactors are the most commonly used reactors in biodiesel production and research [81]. The reactants are placed in a vassal and mechanically sired at a desired temperature for times ranging from 30 minutes to several hours. These reactors vary in size depending on the specific application, ranging from laboratory scale of a few ml to industry scale of several thousand liters. Batch reactors are relatively cheap and provide a simple and consistent method of producing biodiesel, however they have some limitations [82]. Because of the reversible nature of the transesterification reaction, long reaction times are needed to achieve a high biodiesel yield using batch reactors. This makes their use energy intensive compared to other methods currently being researched [23].

3.5.2 Static Mixers

Static mixers consist of a cavity with static elements within which create the effect of mechanical mixing as the immicible reactants flow through. The static element designs are numerous and range from fixed metal designs to more packed bed type elements such as various fibers or foams. These reactors offer the advantage of being low maintenance and more energy efficient compared to traditional batch reactors since they have less moving parts. However, high yields using these reactors have been achieved with low flow rates, keeping the flow in the laminar regime, therefore the residence times are still long much like batch reactors [80]. In addition, some static mixers are complicated in design and difficult to manufacture [83].

3.5.3 Oscillatory Baffled Reactors

Oscillatory baffled reactors (OBR) are tubular reactors in which orifice plate baffles are place in the tube, equally spaced and attached to a piston, in order to produce an oscillatory flow. This oscillatory flow creates a recirculation flow pattern near the baffles thus enhancing mass and heat transfers. The recirculating flow also allows for flexibility in reactor design as well, as the length to diameter ratio can be small. For base catalyzed transesterification, under similar conditions as traditional industrial scale batch reactor operations, residence times are dramatically reduced to a matter of minutes. One drawback for OBRs is their lack of a integrated separation unit for the end products which makes process planning more difficult on the industrial scale [83].

3.5.4 Cavitation Reactors

The phenomena of cavitation occurs when the local pressure is less than the saturation pressure. Cavitation reactors use acoustic or flow energy to create the cavitation phenomena, this creates high temperatures and pressures which augment the transesterification reaction. The high temperatures and pressures caused by the collapsing cavities create a dispersion of molecules and the resulting cavity is filled with the surrounding fluid. This mechanism greatly increases mass transfer which greatly reduces residence times to ranges of 5-20 minutes for conversions in the upper nineties at ambient temperatures for acoustic cavitation reactors and residence times in the milliseconds with hydrodynamic cavitation reactors [83].

The main drawback with acoustic cavitation reactors is the difficulty in scaling up. The ultrasound probe generates the cavitation phenomena in the vicinity of the probe tip and the major difficulty is then obtaining a homogeneous ultrasonic field throughout the entire reactor volume. Therefore, as the reactor volume increases, an increased amount of ultrasound power must be dissipated to the reaction mixture [84]. A complex design with several powerful probes is required in order to obtain a homogeneous acoustic field in larger reactors. Hydrodynamic cavitation reactors appear more promising for industrial use but more research must be conducted to ultimately determine their adaptability to industrial scale [83].

3.5.5 Spinning Tube Reactors

Spinning tube reactors consist of a narrow inner tube placed inside an outer tube, leaving a narrow annular gap between the two. The reactants are placed within the gap while the inner tube spins rapidly and the outer tube remains static. This action induces a Couette flow which ultimately leads to a high mass transfer rate and much lower residence times compared to traditional reactors [80].

3.5.6 Microwave Reactors

Microwave reactors utilize microwave irradiation to transfer energy directly to the reactants thus accelerating the chemical reaction. The two major mechanisms involved in microwave reactors are dipolar polarization and ionic conduction. Dipolar polarization occurs when dipoles are forced to align with the direction imposed by the electric field, which is caused by the microwave irradiation [85]. The electric field, however, rapidly oscillates and the dipole therefore tries to realign itself with this electric field as fast as possible by rotation. The frequency of microwaves is sufficiently high to cause a phase difference between the field and the dipole orientation and the resulting frictional and collision forces between the molecules thus generate heat. Ionic conduction occurs as the charged dissolved particles oscillate under the influence of the microwave field. When the direction of the electric field is changing, the ions slow down and change direction thereby dissipating kinetic energy as heat. This action can reduce residence times to a matter of minutes while maintaining high conversion rates for a base catalyzed transesterification reaction [83].

The drawbacks of microwave reactors are he difficulty scaling up as well as safety issues. These have been mitigated through the use of microwave irradiation in continuous systems but many results have not been reproducible as well, this could be because of a poor understanding of the dielectric phenomena. These issues have greatly inhibited the use of microwave reactors on the industrial scale [83].

3.5.7 Membrane Reactors

Membrane reactors use micro-porous inorganic membranes that enable product separation by a molecular sieving effect. These membranes can be made of carbon, ceramics, zeolites, silica, or polymers, however, carbon membranes are most commonly used due to their low cost. The main upside of membrane reactors is how they improve the purification steps [86]. During transesterification, membrane reactors are able to retain and separate the various components of the reaction such as the triglycerides, diglycerides, monoglycerides, esters, and glycerol. Soap from the saponification reaction can also be retained making the technology good for use with poorer quality oils that are high in FFA. Although gains are made in terms of ester purification, membrane reactors do not significantly improve the reaction rate [83].

3.5.8 Microreactors

Biodiesel production with microreactors is discussed in depth in Chapter 2.

3.6 Biodiesel Purification

After transesterification, the reacted mixture will consist of biodiesel, glycerol, unreacted alcohol, catalyst, and any soaps created during the reaction. Biodiesel must be separated and purified in order to meet governmental fuel standards. Biodiesel purification steps often take much longer than the reaction steps so any technologies improving purification are of high interest. However, not much progress has been made on reducing the time for purification as compared to progress made in process intensification of biodiesel synthesis by transesterification. When methanol is used as the alcohol in transesterification the purification is made easier because two phases form after the reaction mixture has settled, a biodiesel phase on top of a glycerol phase. The glycerol phase can be easily be removed from a bottom drain. When ethanol is used, the glycerol remains suspended in the mixture so the glycerol is more difficult to remove. By far, the most common purification method in use today is simple water washing followed by a drying stage. Dry-washing using ion-exchange resins are also used for purification in specific cases [47].

3.6.1 Water Washing

Water washing is the most common method used for biodiesel purification and used almost exclusively in industry. The glycerol, catalyst, and unreacted alcohol in the reaction mixture are highly soluble in water and can effectively be removed with water washing along with any other contaminates present. Water washing consists of adding water to the reacted mixture, dispersing it to collect the unwanted products and contaminates, letting the mixture settle into a top biodiesel phase and bottom water phase, draining the contaminated water, and repeat until the drain water is clear indicating it is free of contaminates. The most common methods of dispersing the water through the mixture during water washing is by agitation through stirring, bubbling, or misting. The settling times normally range from several hours to multiple days, the mixture will settle faster the less contaminates are present [7].

While water washing is very affective in removing unwanted products from the biodiesel, the inclusion of water into the system creates some problems. The main problems are the treatment and disposal of the wastewater (which adds to costs), and the creation of emulsions during agitation. Biodiesel that is not fully reacted will have diglycerides, and monoglycerides present. Both monoglycerides and diglycerides are used in the food industry as emulsifiers, and their presence in large amounts will create emulsions during water washing. Excess soap in the biodiesel can also aid in the creation of emulsions. The conversion of WCO can have excess soap because of its high FFA content. Emulsions are created during agitation, both bubble washing and mist washing are gentler than stirring and can mitigate the creation of emulsions. Once emulsions have formed, they take several days to settle out if they settle out at all. Heating the mixture and adding salt water to the mixture can break up emulsions faster than settling [87].

After water washing the biodiesel, microscopic water particles will still be suspended in the biodiesel. Even a small amount of water in the biodiesel can damage diesel engines during combustion and with corrosion. The biodiesel must therefore be dried after washing. This is typically done by simply heating the biodiesel to above the boiling point of water so the excess water evaporates. Heating the mixture can create conditions where the water reacts with the esters via hydrolysis, creating FFA and diminishing the quality of the biodiesel. Therefore the mixture is stirred during drying to minimize hydrolysis. The biodiesel can also be dried using desiccants such as sodium sulfate. In this process the desiccant is added to the biodiesel and mixed, absorbing the excess water, and then simply filtered out, avoiding the problem of hydrolysis [88].

3.6.2 Dry Washing

Dry washing is done by ion-exchange resins. Berrios et al. (2008) investigated the effectiveness of water washing and ion-exchange resins using biodiesel made from vegetable oil and methanol. The study found that the resins were able to remove the free glycerol and soap to fuel grade levels, but did a poor job of removing the methanol from the mixture. Only water washing was able to lower all the contaminates to fuel grade level. Therefore, the use of ion-exchange resins must be coupled with an additional stage to remove the methanol [89].

Chapter 4

Materials and Methods

4.1 Introduction

This chapter will describe the experimental methods and materials used in this study. The purpose of this study is to optimize the parameters for esterification of high FFA content oil and transesterification of WCO. To do this accurately and efficiently a Taguchi experimental methodology was implemented. Experimental procedures were put in place to obtain accurate and meaningful results. The following sections outline the procedures used as well as the decision making involved in choosing the methodological and procedural steps.

The chemicals used in this study were chosen considering the advantages and disadvantages common chemicals used to conduct the esterification and transesterification reactions. Ethanol was used as the alcohol for the esterification and transesterification studies, its advantages and disadvantages compared to methanol are shown in Table 4.6.

4.2 Experimental Methods

4.2.1 Design of Experiments

Design of experiments (DOE) are a set of experimental designs that test certain conditions to the variation of the outcome. In this present work it will be the parameters (factors) of esterification and transesterification tested over a specified range (levels) for the outputs of FFA conversion and biodiesel conversion (results). The most the thorough design for optimization is a full factorial design, where the factors at each level are tested against all possible combinations. However, this method is extremely resource intensive. Several other methods have been developed to reduce the amount of experiments needed to optimize factors (surface response, box etc.). The method used in this work will be the Taguchi method.

4.2.2 Taguchi Method

Taguchi method (or robust design method) are a set of DOE statistical methods developed by Genichi Taguchi to improve the quality of manufactured goods. The Taguchi method makes use of the properties of orthogonal arrays which are defined as an array of s elements, denoted by $L_N(s^m)$, in an Nxm matrix whose columns have the property that in every pair of columns each of the possible ordered pairs of elements appears the same number of times. In other words the OAs make the rows of the experiment matrix. This allows for maximum experimental efficiency, using the least number of test runs [90].

The Taguchi method is applied in five steps:

1. Determine the parameters (factors) important to esterification/transesterification.
2. Design the experiments to test the parameters.
3. Conduct the experiments.
4. Analyze the results and determine the optimal conditions.
5. Run a confirmatory test with the optimal conditions.

4.2.3 Determination of Factors - Esterification

The principal parameters that affect the esterification reaction are: residence time, temperature, catalyst concentration, and alcohol to oil molar ratio. The esterification experiments take longer than the transesterification experiments because of the quantity (5ml) of final product required to perform an accurate analysis. Purification of the oil is more difficult, and can last multiple days. Therefore, in order to reduce the amount of experiments needed a 3-factor (L-9) experiment matrix was used. The factors chosen of the principal parameters were catalyst concentration, molar ratio, and residence time. The best results in nearly all biodiesel/esterification literature were achieved at the temperature just below the boiling point of the alcohol used. Therefore, the temperature control in the experiments (electrical tension) was set to the maximum (17.5V) without the system reaching the boiling point of ethanol (78 °C), keeping the reactants in liquid phase.

4.2.4 Determination of Levels - Esterification

The factor levels for this study were determined using previous experimental studies in literature, as well as specific knowledge of the microreactor to be used, to approximate what parametric range will yield the best results. Unfortunately, the parameters used in literature vary widely and no study converting FFA to esters through esterification was found. For example, looking at a study with WCO with FFA content of 5%, Chai et al. (2014) achieved optimum results (0.5% FFA) with a residence time of 2 hours, a 40:1 methanol to FFA molar ratio, a temperature range of 55-65 °C, and a sulfuric acid concentration of 10% (wt.) [91]. In another study using surface response methodology Goyal et al. (2012) converted 14.6% FFA content jatropha curcas oil to 0.34% FFA with a 6.5:1 methanol to oil molar ratio, a 1.5% wt. sulfuric acid concentration, 125 minute residence time, and at 50 °C [92]. Using the same catalyst as this study, Hayyan et al. (2012) reduced 9% FFA crude palm oil to 0.5% FFA using 8:1 methanol to oil ratio, 1% wt. methane sulfonic acid, for 30 minutes at 60 °C [93]. Marchetti et al. (2008) converted 95% of the FFAs in using using a 6.126:1 ethanol to oil molar ratio, 2.261% wt. sulfuric acid, at 55 °C for 250 minutes [94]. Khan et al. (2010) optimized esterification parameters using a Taguchi method DOE and achieved a 95% reduction in FFA of a blend of crude rubber oil and crude palm oil with a 15:1 methanol to oil ratio, 0.5% wt sulfuric acid, at 65 °C for 3 hours [95]. Ouachab et al., (2012) used a high acid concentration of 20% sulfuric acid and was able to reduce FFA of olive pomace oil from 2.3% to 0.3% using a 35:1 methanol to oil ratio 40 °C for 60 minutes [96].

The catalyst concentration levels were chosen taking a relativity low value in literature of 1% as the first level value. A relatively high value in literature of 5% was chosen as the upper bound for level 3. Level 2 value of 2.5% was used as a middle value between the level 1 and 3. The stoichiometric value of the reversible esterification reaction is a one to one alcohol to FFA molar ratio, however, the alcohol to molar ratio is set above the stoichiometric value to drive the reaction to the right side. Also, we are dealing with two immicible fluids in the oil and alcohol mixture and the reaction will only occur at the interface between the two liquids therefore the mass transfer of the mixture becomes very important when determining the alcohol to oil molar ratios to be used. The mass transfer of the system is largely determined by the reactor design. Using the same reactor used in this study (detailed description in Section 4.3.2), Costa Junior (2017) converted soybean oil to biodiesel using alcohol to oil molar ratios as low as 5:1 with his best conversions being achieved at a 20:1 ethanol to oil molar ratio. Although his study was with transesterification rather than esterification the oil dispersion in the alcohol mixture is the same. Therefore we can use a lower bound (level 1) of 5:1 ethanol to oil molar ratio and an upper bound (level 3) of 20:1 with level 2 between the two at 10:1. The experimental studies in described in the previous paragraph all used laboratory batch reactors, therefore the residence times are much larger than necessary for the experiments in this study using microreactors. Again we use the study of Costa Junior (2017) to help determine the range of residence times to be used. Setting level 1 to 1 minute, level 2 to 2.5 minutes, and level 3 to 5 minutes. Larger residence times than 5 minutes make the experiments more tedious and had minimal effect on the results in Costa Junior (2017). Experiments with residence times below 1 minute, while possible, are extremely strenuous on the equipment used in the experiments (equipment described in detail in Section 4.3.1) and can result in malfunction. Table 4.1 summarizes the factors and values of the levels used in this study. Table 4.2 displays the orthogonal array matrix used in this study.

Table 4.1: Factors and level values for esterification experiment matrix

Level	Catalyst Concentration (%wt-oil)	Molar Ratio (Ethanol:Oil)	Residence Time (Minutes)
1	1	5:1	1
2	2.5	10:1	2.5
3	5	20:1	5

Table 4.2: Levels to be used for factors of each trial for esterification experiments

Trial #	CC	MR	RT
1	1	1	1
2	1	2	2
3	1	3	3
4	2	1	2
5	2	2	3
6	2	3	1
7	3	1	3
8	3	2	1
9	3	3	2

4.2.5 Determination of Factors - Transesterification

The parameters affecting transesterification are the same as esterification: residence time, alcohol to oil molar ratio, catalyst concentration, and temperature. The analytical methods used in this study require much less product (1ml) compared to the esterification experiments (5ml), therefore the transesterification experiments are quicker and the biodiesel is easier to purify. Because of this all five parameters were used as factors.

4.2.6 Determination of Levels - Transesterification

The determination of the levels for the transesterification DOE were devised using the previous work of Costa Junior (2017). In his study he was able to convert 99% of soybean oil triglycerides to ethyl esters with a residence time of 34 seconds, 1%

NaOH catalyst, 20:1 ethanol to oil molar ratio and a electrical tension (temperature control) of 17.5V. Residence times under 1 minute are strenuous on the equipment used for the experiments, therefore the lowest residence time of 1 minute is chosen for level 1 with increases of 1 minute for each of the other levels up to 5 minutes for level 5. In order to observe the effects of catalyst concentration the best result from Costa Junior (2017) is taken as the middle value (level 3) and two lower values of 0.5% and 7.5% are placed in levels 1 and 2 respectively, and two higher values of 1.25% and 1.5% are placed levels 4 and 5 respectively. For the ethanol to oil molar ratio the molar ratio from the best result in Costa Junior was placed in level 3. Two values below of 10:1 and 15:1 were placed in level 1 and 2 respectively and two values above of 25:1 and 30:1 were placed in level 4 and 5 respectively. To observe the effect of temperature we set the electrical tension of the resistance connected to the heat exchanger (described in Section 4.3.3) that will be used in the transesterification experiments. The maximum value is observed when the electrical tension is set to 17.5V. When the resistance is set higher than this value, the reaction can reach temperatures above the boiling point of ethanol (78 °C). Therefore, the first level is set to 6V and increased to 9V for level 2, 12V for level 3, 15V for level 4 and the maximum of 17.5V for level 5. The factors and level values are summarized in Table 4.3. The orthogonal array matrix used is displayed in Table 4.4.

Table 4.3: Factors and level values for transesterification experiment matrix

Level	Catalyst Concentration (%wt-oil)	Molar Ratio (Ethanol:Oil)	Residence Time (Minutes)	Tension (V)
1	0.50	10:1	1	6
2	0.75	15:1	2	9
3	1.00	20:1	3	12
4	1.25	25:1	4	15
5	1.50	30:1	5	17.5

4.2.7 Analysis of Results

The objective of the analysis of the experimental results is to seek answers to the following three questions:

1. What is the best condition?
2. What factors influence the variability of the results and by how much?
3. What will be the expected result at the best condition and how much does each factor contribute to the improvement?

Table 4.4: Levels to be used for factors of each trial for transesterification experiments

Trial #	CC	MR	RT	T
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	1	4	4	4
5	1	5	5	5
6	2	1	2	3
7	2	2	3	4
8	2	3	4	5
9	2	4	5	1
10	2	5	1	2
11	3	1	3	5
12	3	2	4	1
13	3	3	5	2
14	3	4	1	3
15	3	5	2	4
16	4	1	4	2
17	4	2	5	3
18	4	3	1	4
19	4	4	2	5
20	4	5	3	1
21	5	1	5	4
22	5	2	1	5
23	5	3	2	1
24	5	4	3	2
25	5	5	4	3

The average performance of factor A is calculated for each level given response Y for each run at the specified level:

$$\overline{A_i} = \frac{\sum_{i=1}^{n_i} Y_i}{n_i} \tag{4.1}$$

Where n is the number of runs at the specified level, i. The average performance is plotted for visual inspection, called the main effect plot. Given the desired quality characteristics:

- Bigger is better
- Smaller is better
- Nominal is better

From the performance factor or main effect plot, the probable optimal characterization can be determined except for possible interactions between the factors. The relative influences of factors to the variation of results are determined by comparing their variances. The technique popularly known as the analysis of variance is used for this purpose. ANOVA method computes several quantities and organizes them in a tabular format. These quantities are calculated for each factor and their interrelationships are defined as shown in Table B.1. The calculations for the values in Table B.1 and be found in Appendix B. The ANOVA quantities are calculated for an error term, e, as well which is a measure of the contribution of the variance from causes other than the data spread of the factors chosen.

Table 4.5: ANOVA quantities and notation

V	mean square (variance)	P	percent influence
S	sum of squares	T	total (of results)
S'	pure sum of squares	n	number of experiments
f	degrees of freedom	$C.F.$	correction factor
e	error (experimental)	f_T	total degrees of freedom
F	variance ratio	Y	result of trial run

4.3 Esterification of High FFA Content Oil

4.3.1 Materials

To conduct the esterification parametric analysis experiments the main reactants needed are high FFA content oil, alcohol and acid catalyst. In order to create an oil with a high FFA content, chemical grade oleic acid, which is a very common FFA found in vegetable oils, was purchased and mixed with refined soybean oil. This mixture is chemically identical to poor quality WCO for the purpose of this study and allowed control and consistency over the mixtures initial FFA content.

The two main alcohols used in both esterification and transesterification are methanol and ethanol. Their advantages and disadvantages in relation to one another are summarized in Table 4.6. Ethanol is the alcohol used in this study and was ultimately chosen because it is derived from renewable sources and is safer to handle than methanol.

Methane sulfonic acid, chemically CH_3SO_3H, was used as the catalyst in the esterification experiments. Sulfuric acid, chemically H_2SO_4, is the most common catalyst used for esterification, the advantages and disadvantages in relation with MSA are shown in Table 4.7. MSA was ultimately chosen for this study because of its safety and availability.

The full list of chemicals, materials, and equipment needed to conduct esterification experiments as well as the titration analysis is summarized in Table 4.8.

Table 4.6: Advantage and disadvantages of common alcohols

Alcohol	Advantages	Disadvantages
Ethanol	-Made from renewable resources -Safer, less toxic -Reduces mass transfer effects	-Higher cost -Purification more difficult
Methanol	-Lower Cost -Easier purification	-More dangerous to handle

Table 4.7: Advantage and disadvantages of common acid catalysts

Catalyst	Advantages	Disadvantages
CH_3SO_3H	-Safer than common acid catalysts -Good results in literature	-High cost
H_2SO_4	-Low Cost -Good results in literature	-Dangerous in large quantities -Changes color of oil

Table 4.8: Chemicals and materials used in esterification experiments

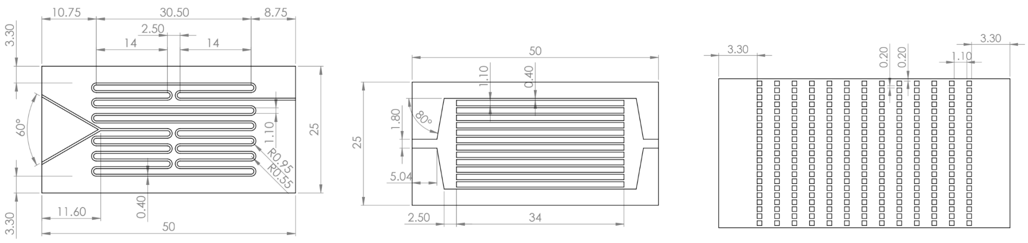
	Chemicals	Equipment
Esterification	Ethanol (99%) Methane Sulfonic Acid (>99%) Oleic Acid (75%) Soybean Oil Sodium Sulfate Distilled Water	Beakers (25ml, 50ml) Polyethylene Hoses Syringes (28mm diameter) Syringe Pumps Water Tank Water Pump Current Source Thermocouples Computer Microreactor Micro-Heat Exchanger Filter Paper Magnetic Stirrer Scale Volumetric Flask (25ml) Separation Funnel
Titration	Phenolphthalein Ethanol (95%) NaOH pellets (98%) Potassium Biphthalate Ether Distilled Water	Erlenmeyer Flask (250ml) Burette Burette Stand Magnetic Stirrer Dropper Scale Volumetric Flask (100ml)

4.3.2 Reactor Design

One thing holding back wide adoption of using microreactors for large industrial scale chemical processes is the difficulty manufacturing high quality microreactors at mass scale. Traditional manufacturing methods, such as laser etching, machining, and casting, are limited in design flexibility and time consuming when employed on mass scale. Advances in additive manufacturing, 3D printing, may revolutionize several industries including chemical processing. The ease and complexity additive manufacturing is capable of is unparalleled compared to other manufacturing techniques.

The microreactor device used in this study has 10 microreactors stacked in parallel with 11 micro-heat exchangers. This is the same device used in another study (Costa Junior, (2017)) to use a parallel thermal process to heat a working fluid that is then passed through the micro-heat exchangers, heating the chemical process (transesterification) taking place in the microreactors. The dimensions of the microreactor device is shown in Figure 4.1.

The microreactor design uses a Y-mixer, of channel length 13.34mm, for the alcohol/KOH and oil reactants. The reaction takes place in a meandering square (400μm x 400μm) microchannel reactor of 432.57mm length. The micro-heat exchangers, heated water is distributed to 13 microchannels and transfer heat to the microreactors in placed in parallel on the surfaces.



(a) Microreactor (b) Micro-Heat Exchanger (c) Side Cut View

Figure 4.1: Dimensions of microreactor device in millimeters

The reactants and heating fluid are attached to the entrance of the device by three barbed circular fittings with an interior diameter of 2mm and length of 6mm. The three fluids are distributed to the various microreactors and heat exchangers and the products are exited via two barbed circular fittings. One for the reacted final product and one for the water exiting the heat exchangers. A 3D view of the microreactor is shown in Figure 4.2.

This specific design would be impossible to manufacture as a single homogeneous unit, but with additive manufacturing, the 3D drawing of the device was all that was needed to produce the device. The 3D printing method of selective laser melting was employed for the production of the device. This method makes use of laser power

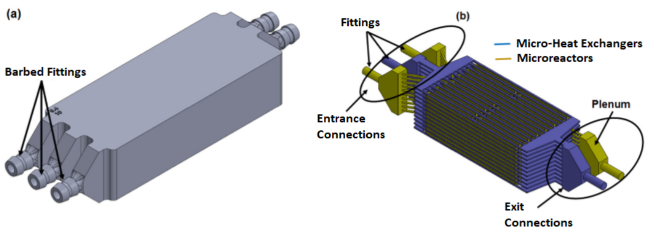
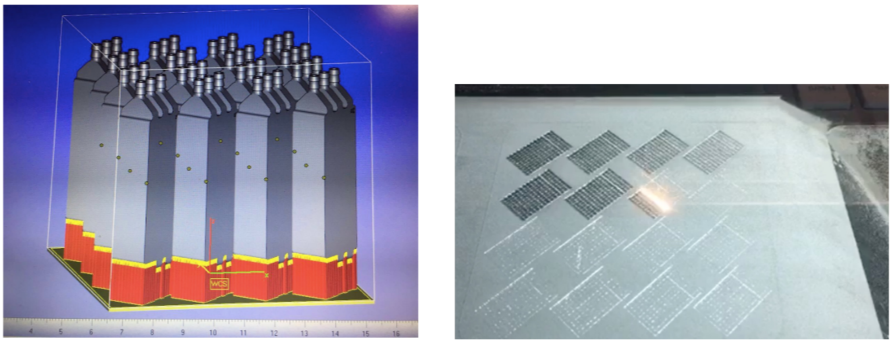


Figure 4.2: 3D view of the microreactor device used in this study. (a) external view and (b) internal view

source to melt powdered metallic material (in this case a chrome-cobalt alloy) into the specified part. Figure 4.3 shows the software used for the manufacturing of the device and the actual SLM process in action.



(a) SLM software

(b) SLM in action

Figure 4.3: Layout in SLM software and the SLM printer in action

4.3.3 Experimental Setup

To conduct the esterification experiment we need reliable ways to control the flow rate of the reactants entering the microdevice as well as the temperature of the water entering the microdevice. Figure 4.4 displays the schematic of the experimental setup used in this study.

The main components of the esterification experiments are as follows:

- The chrome-cobalt microdevice described in section 4.3.2. The material chrome-cobalt is non-corrosive allowing us to use acid catalysts worry free of corrosion to the microdevice.
- Polyurethane foam used as insulation and support for the microdevice. The insulation allows for minimum heat loss to the outside environment, utilizing the rejected heat from the parallel electrical resistance thermal process to be maximally used for the heating of the reaction.

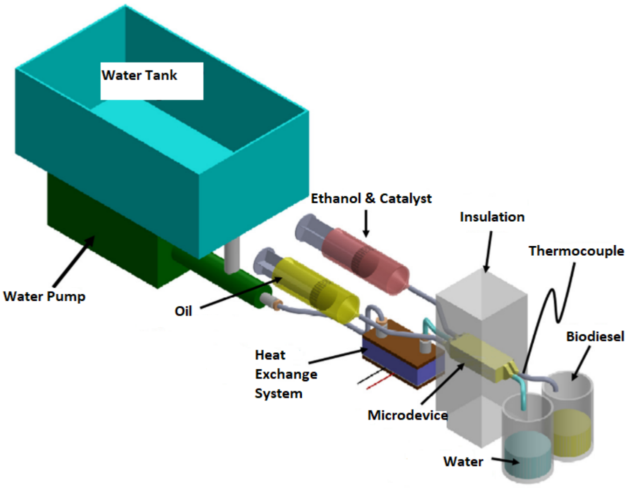


Figure 4.4: Schematic of experimental setup

- Two syringe pumps (New Era Pump Systems Inc., model NE 1000) are used to control the flow rate of the reactants (oil and ethanol/catalyst mixture) into the microdevice.
- Two collection reservoirs for the final reacted product and the water exiting the microdevice. The final product is collected in a beaker immersed in an ice water bath. This is so that the temperature will be low enough to stop any reactions from taking place while the final product is being collected.
- A heat exchange system is run parallel to the esterification process. This system consists of a micro-heat exchanger and electrical resistance to heat water that will then pass through the microdevice, driving the esterification reaction. a schematic drawing of the heat exchange system is show in Figure 4.5. The heat exchanger used in the system is shown in Figure. The rectangular metal heat exchanger has a length of 25mm and a width of 40mm.

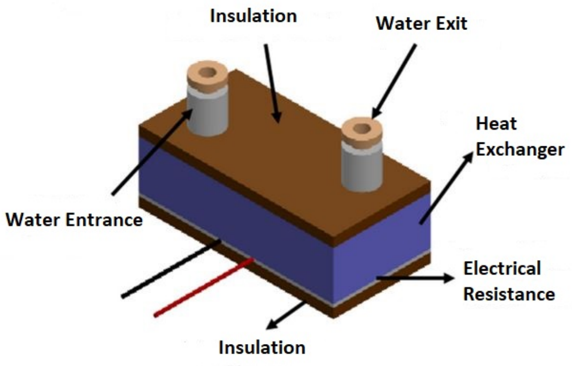


Figure 4.5: Schematic of micro-heat exchanger system

The interior consists of 9 1mm length and height channels with a 28mm length. Electrical resistance is placed on the bottom of the heat exchanger and the heat from the resistance is used to transfer heat to the water which is then used to drive the reaction. The system is surrounded with insulation to minimize heat loss.

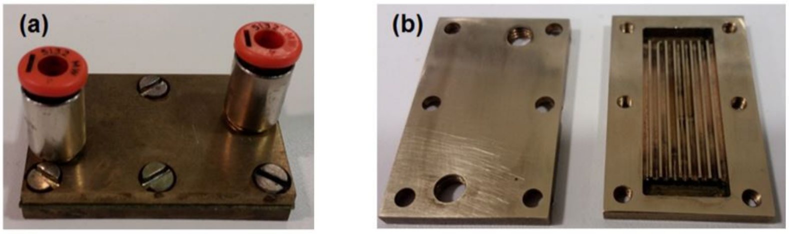


Figure 4.6: Heat exchanger used in water heating system (a) Outside of heat exchanger, (b) interior of heat exchanger

- To supply the electrical resistance, a simple continuous current source (ICEL, model PS-6100) with controlled electrical tension of 0-30V and a maximum current of 6A is used.
- A water tank to hold the water that will be passed through the electrical resistance heat exchange system.
- A helical rotor pump (NEMO Pumps, model NM003BY11S12B - NETZSCH) is used to deliver the water to the heat exchanger system. The flow rate of the pump is controlled by a frequency inverter where each frequency corresponds to a motor speed and ultimately a flow rate of the water.
- Eight thermocouples are used to monitor and collect temperature data of the experiment. These thermocouples are placed at each face of the microdevice, at the exits of both the final product and water exiting the microdevice, at the entrance of the water entering microdevice, and one to measure the ambient temperature.
- The data from the thermocouples is collected with a data collection system (Agilent 34970-A).
- The data is then analyzed using the data collection system software and a desktop computer.

The experimental setup used is shown in figure 4.7.

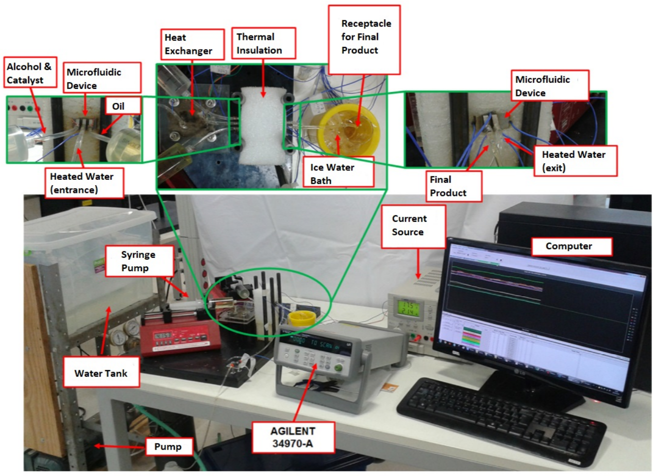


Figure 4.7: Experimental setup

4.3.4 Experimental Procedure

The esterification experiments conducted in this study were done with the following steps:

1. Prepare the ethanol/catalyst solution: Weigh out the proper amount of methane sulfonic acid (CH_3SO_3H) using an electronic scale and pipette. Add the acid to ethanol (99%), stir. Transfer the contents into a volumetric flask and fill the rest with ethanol. Pour the solution into a beaker and fill a syringe which is to be placed on a syringe pump and connected with a hose to the microdevice.

2. Prepare the oil: In a large beaker pour approximately 500ml of refined soybean oil and approximately 30ml of oleic acid, agitate. This oil will have a FFA content of about 5% (most WCOs have FFA content of 2-7%) and will be used for all the esterification experiments. The actual FFA content will be measured with a titration. Pour 50ml of oil into a beaker and fill a syringe with the oil, to be placed on the syringe pump and connected with a hose to the microdevice.

3. Connect a hose from the water pump to the entrance of the electrical resistance heat exchanger. Connect a hose from the heat exchanger exit to the microdevice water entrance (middle fitting). Connect another hose to the microdevice water exit (middle fitting) to a collection receptacle. Turn on the helical pump and make sure the water is flowing through the heat exchanger and microdevice with no leaks and no air entering the flow.

4. Connect all the thermocouples to the microdevice and turn on the data acquisition system and start the program on the computer to make sure there

are no thermocouples with defects.

5. Set the syringe pumps to the desired flow rates dependent on the alcohol/oil molar ratio. Turn on the pumps and make sure the reactants enter at the same time to insure a smooth laminar flow for the reaction.
6. Turn on the water pump and the current source and set the electrical tension to the proper voltage.
7. Let the system run while monitoring the temperature. Once the temperatures have stabilized (20 min), start the experiment and let run until the desired amount of product is collected into a beaker immersed in an ice water bath.
8. With roughly 5 minutes remaining in the experiment heat approximately 60ml of distilled water to about 70 °C. This water will be used for the first water wash of the product. The water is heated to better collect the impurities in the final product as most are more soluble in water at higher temperatures.
9. Once the experiment is done, the final product is placed into a separation funnel and immediately water washed for the first time.
10. To wash the product simply pour the water into the funnel and agitate. The product is left to settle and should have two distinct phases of an oil phase on top of a water phase. Drain the waste water and continue with water washes until the waste water has a neutral pH which indicates that all the catalyst has been removed. The pH of the waste water is measured using simple pH color indicator strips.
11. Drying the treated oil: Transfer the oil into a large beaker and add enough sodium sulfate to roughly fill a quarter of the oil level. Use a mechanical stirrer to mix for about 15 minutes.
12. The dried oil is then filtered using filter paper placed in a funnel. The filtered oil is collected and ready for titration.

4.3.5 Analytical Methods - Titration

To determine the FFA content of an oil, a simple titration was used for this present work. The basic idea is to use a alkaline solution of known molarity to react with the FFAs present in the sample. The alkaline solution is added slowly to the sample and a color phenolphthalein indicator is used and changes color when the solution is neutral. Then the FFA content can be calculated using the volume of the alkaline solution used and the weight of the sample. To prepare the reagents used in the titration the following steps are taken:

1. Phenolphthalein solution: Weigh 1.0g of phenolphthalein in a 50ml beaker. Add enough ethanol (190 proof) to the mixture to just dissolve the phenolphthalein and transfer the contents into a 100ml volumetric flask. Fill the rest of the flask with ethanol, shake. Store the solution in a dropper bottle.
2. Sodium hydroxide solution (0.01M): Weigh 0.1125g of NaOH in a 25ml beaker. Dissolve the NaOH in distilled water and transfer the contents into a 250ml volumetric flask. Fill the rest of the flask with distilled water and shake. Store the solution in a polyethylene bottle.

The actual molarity of the solution is not 0.01M and in our calculations we use a correction factor f to correct for the disparity. To find f we do the following: Weigh approximately 0.05g of potassium biftalate in a 125ml Erlenmeyer flask and dry at 105 °C for 1 hour. Add 50ml of water and mix until dissolved. Add 3 drops of phenolphthalein solution. Place 25ml of the NaOH solution into a burette and titrate the solution until it turns a dull pink color. We can then solve for the normality correction factor f using equation (4.2).

$$f = \frac{W}{0.2042VM} \tag{4.2}$$

Where:

- W = weight of potassium biftalate used in g
- V = volume of NaOH solution used in ml
- M = molarity of the NaOH solution (0.01)

After the reagents are made, the titration of the oil sample is done using the apparatus in Figure 4.8. A burette is used to easily control the flow rate into the sample as well as provide an easy way to read the volume amount of the NaOH solution used. The titration is completed in the following steps:

1. Weigh 5 to 10 grams of the oil sample in a 250ml Erlenmeyer flask.
2. Add 25 ml of ethanol and 25ml of ether and stir until solution is homogeneous.
3. Titrate the the sample using the NaOH solution. Slowly add NaOH while stirring the sample flask and stop when the solution is a dull pink color and remains so for at least 30 seconds

The dull pink color of the sample indicates that the solution is neutral or that all the FFAs in the sample have reacted with NaOH molecules. If the solution is clear it indicates the presence of FFAs. If the sample is a dark pink, it indicated the

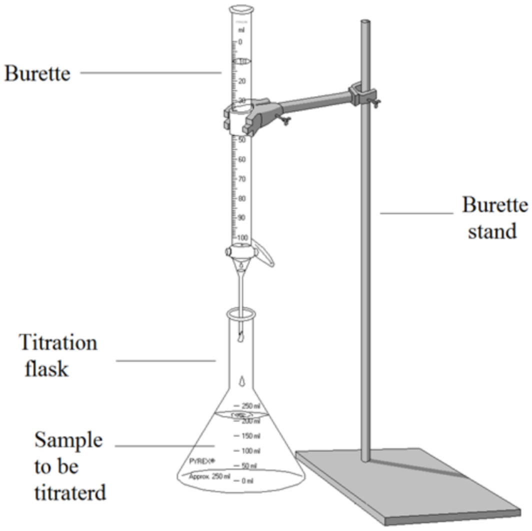


Figure 4.8: Titration apparatus used for analyzing FFA content

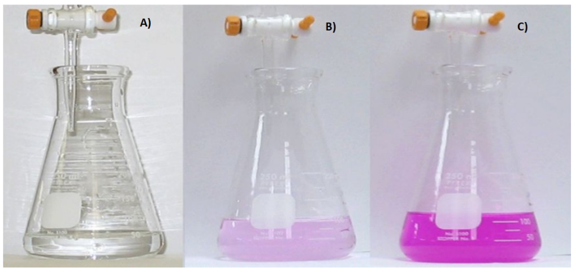


Figure 4.9: A): Titration not far enough, B): Good Titration, C): Titration went too far

presence of NaOH molecules and that too much NaOH solution was added during the titration. Figure 4.9 shows the different cases described.

The amount of FFA in the sample can be calculated using equation (4.3).

$$\%FFA = \frac{V_{NaOH} M_{NaOH} f (0.282)(100)}{W_{Oil}} \tag{4.3}$$

Where:

- V = volume of NaOH solution used in milliliters
- M = molarity of NaOH solution
- f = normality correction factor
- W = weight of sample used in grams

4.4 Transesterification of WCO

4.4.1 Materials

The transesterification experiments were carried out using WCO from a local restaurant (Adega Perola in Copacabana), potassium hydroxide as a catalyst, and ethanol. Ethanol is the alcohol of choice for the reasons presented in Section 4.3.1.

KOH was chosen as the catalyst over sodium hydroxide because of its superior performance converting WCO according to several previous studies. The advantages and disadvantages are summarized in Table 4.9.

Table 4.9: Advantage and disadvantages of common alkali catalysts

Catalyst	Advantages	Disadvantages
KOH	-Better results in literature -Less emulsions	-Higher cost
NaOH	-Low Cost	-Increase fluid viscosity in large quantities -Difficult to fully dissolve

The materials used to conduct the transesterification experiments as well as the HPLC analysis are summarized in Table 4.10.

4.4.2 Preparation of WCO

The WCO used in this study was obtained from a local restaurant. WCO is full of food particles and water from cooking and these impurities must be removed before transesterification. In order to remove food particles, the WCO is filtered using a vacuum filter with paper shown in Figure 4.10.

To remove water from the WCO, the WCO is place into a large beaker and heated to roughly 120 °C for 1 hour. While the WCO is heated, the oil is magnetically stirred the entire time to avoid hydrolysis, increasing the FFA content in the oil. Stirring the oil also allows the water in the oil to evaporate more quickly. Figure 4.11 shows the drying process.

After drying the WCO was titrated to determine the FFA content. The FFA content for this WCO was very low compared to other WCO used in literature, but to bring down the FFA content further, the WCO was esterified using 5% wt. methane sulfonic acid, 20:1 alcohol to oil molar ratio, and residence time of 2 min using 17.5V of electrical resistance tension to heat the reaction. This was done several times over several days to accumulated a sufficient amount to perform transesterification analysis. The oil is dried after each reaction. Once a sufficient amount was accumulated, a titration was performed to discover the new FFA content. The new

Table 4.10: Chemicals and materials used in transesterification experiments

	Chemicals	Materials/Equipment
Transesterification	Ethanol (99%) Potassium Hydroxide pellets (85%) Waste Cooking Oil Sodium Sulfate Distilled Water	Beakers (25ml, 50ml) Polyethylene Hoses Syringe Pumps Water Tank Water Pump Syringes (28mm diameter) Current Source Thermocouples Computer Microreactor Micro-Heat Exchanger Filter Paper Magnetic Stirrer Scale Volumetric Flask (50ml) Separation Funnel Pestle and Mortar
HPLC	Phenolphthalein Ethanol (95%) NaOH pellets (98%) Potassium Biphthalate Ether Distilled Water	Erlenmeyer Flask (250ml) Burette Burette Stand Magnetic Stirrer Dropper Scale Volumetric Flask (100ml)

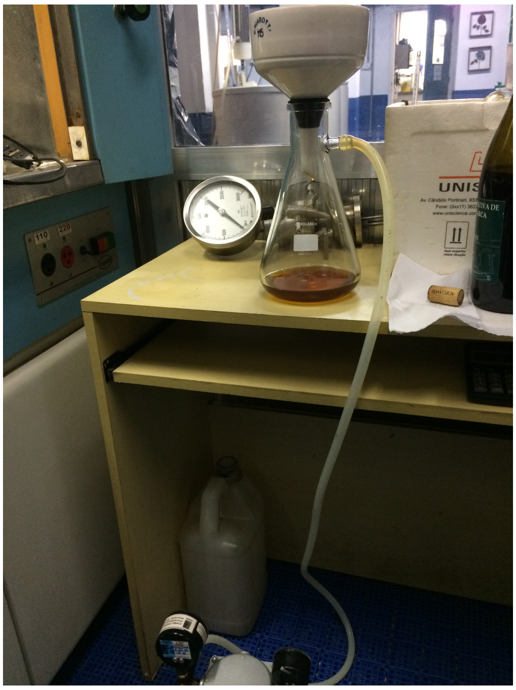


Figure 4.10: Vacuum filtering system used to remove particulates

Figure 4.11: Heated magnetic stirring apparatus used to dry the WCO

FFA content met the standard of 0.5% FFA that is recommended in literature [97]. Transesterification also of the triglycerides in the oil via acid catalyst also occurs during the esterification of FFAs. The transesterification with acid catalyst is much slower than with an alkali catalyst but intermediary species (MGs and DGs) will be created. Table 4.11 summarizes the final FFA and intermediary species content before the WCO was used for the alkali catalyzed transesterification experiments.

Table 4.11: FFA content and intermediary species of WCO used in transesterification experiments.

FFA Content in WCO		WCO Composition		
Before Esterification	After Esterification	MG	DG	TG
1.07%	0.50%	4%	3%	93%

4.4.3 Experimental Setup

The equipment and experimental setup for the transesterification experiments is the same as the esterification experiments as described in Section 4.3.3 and shown in Figure 4.7.

4.4.4 Experimental Procedures

The transesterification experiments were conducted in the following steps:

1. Preparation of ethanol/KOH solution: Use the mortar and pestle to grind a small amount of KOH pellets into a fine powder. Quickly weigh the predetermined amount of KOH powder on an electric scale for the desired catalyst concentration. Once weighed note the actual weight and pour about 40ml of ethanol into the beaker. Use a magnetic stirrer to mix the KOH and the ethanol until the KOH is completely dissolved (20 min). Use a funnel to pour the mixture into a volumetric flask and fill the rest with ethanol, agitate. Pour the solution into a beaker and fill a syringe with the solution. Secure the syringe on the syringe pump and connect the syringe to the microdevice with a hose.

2. Pour some WCO into a beaker and fill a syringe with the oil. Secure the syringe onto a syringe pump and connect the syringe to the microdevice with a hose.

3. The rest of the experiment is run the same as the esterification experiments as described in Section 4.3.4.

4. When washing the biodiesel, the water is added slowly or with a mister to minimize the creation of emulsions. Figure 4.12 shows the phases in the separation funnel after four separate washes.

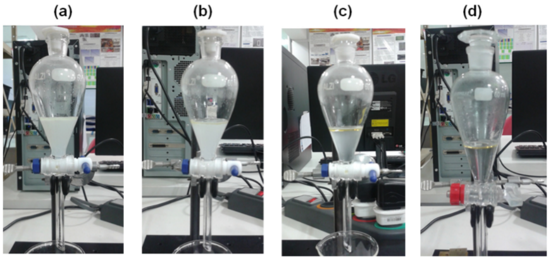


Figure 4.12: Biodiesel purification (a) 1st wash, (b) 2nd wash, (c) 3rd wash, (d) 4th wash

4.4.5 Analytical Methods - HPLC

The analysis of the biodiesel was done using high performance liquid chromatography. HPLC involves passing a high pressurized liquid mobile phase (the sample) through a column with a stationary phase (typically a granular absorbent). The components of the mobile phase interact differently with the stationary phase and are separated. This analysis was done in conjunction with the staff and equipment of LABCOM using a Thermo Scientific Ultimate^{TM} 3000 to analyze the biodiesel samples, shown in Figure 4.13. This analyzer is equipped with four pumps, an ultraviolet spectrum detector (DAD-3000), and an automatic injector

(WPS-3000SL). A mobile phase composed of the sample to be analyzed, methanol, and a mixture of i-propanol/n-hexane (5:4 v/v) is passed through a Thermo Scientific Acclaim^{TM} 120 C18 column of 4.6mm internal diameter and a 250mm length with 5μm particulates of a 120 Å pore diameter. The samples are run for at 40 °C for 40 minutes with a flow rate of 1 ml/min and a UV detection wavelength of 205nm.

Figure 4.13: Thermo Scientific Ultimate^{TM} 3000

The results of the analysis are displayed in a chromatogram and analyzed with the software package Chromeleon 6.80. A sample chromatogram is shown in Figure 4.14. Each peak corresponds to a particular glycerol of the sample and the area of the peak corresponds to the amount of the specific glycerol present in the sample. The red highlighted peak in Figure 4.14 corresponds to ethyl ester-linoleic acid (EeL). Table 4.12 displays the nomenclature for the various components present in a biodiesel sample.

The amount of esters in any given sample is is calculated using Equation (4.4).

$$\%Ester = 100\frac{A_E}{A_E + A_{MG} + 2A_{DG} + 3A_{TG}} \tag{4.4}$$

Where:

- A_{group} is the area of the corresponding group (E, MG, DG, TG) which is calculated using Equation (4.5).

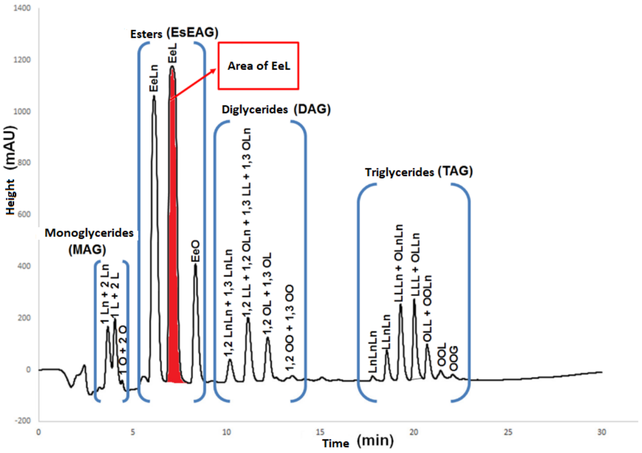


Figure 4.14: Chromatogram of a biodiesel sample with the components labeled on the corresponding peaks (Costa Junior (2017))

Table 4.12: Nomenclature and notation of components in chromatogram

Groups	Nomenclature	Notation	Double Bonds
Monoglycerols	Monolinolenin	Ln	3
	Monolinolein	L	2
	Monoolein	O	1
Esters	Ethyl Ester-Linolenic Acid	EeLn	3
	Ethyl Ester-Linoleic Acid	EeL	2
	Ethyl Ester-Oleic Acid	EeO	1
Diglycerols	Diolinolenin	LnLn	6
	Linoleoyl-Linolenoyl-Glycerol	LLn	5
	Dilinolein	LL	4
	Oleoyl-Linolenoyl-Glycerol	OLn	4
	Oleoyl-Linoleoyl-Glycerol	OL	3
	Diolein	OO	2
Triglycerols	Trininolenin	LnLnLn	9
	Dilinolenoyl-Linoleoyl-Glycerol	LLnLn	8
	Dilinoleoyl-Linolenoyl-Glycerol	LLLn	7
	Dilinolenoyl-Oleoyl-Glycerol	OLnLn	7
	Trilinolein	LLL	6
	Oleoyl-Linoleoyl-Linolenyl-Glycerol	OLLn	6
	Dilinoleoyl-Oleoyl-Glycerol	OOL	5
	Dioleoyl-Linolenoyl-Glycerol	OOLn	5
	Dioleoyl-Linoleoyl-Glycerol	OOL	4
	Triolein	OOO	3
	Dioleoyl-Gadoleoyl-Glycerol	OOG	3

$$A_{group} = \sum \frac{A_{component}}{NDB_{component}} \tag{4.5}$$

Where:

- $A_{component}$ is the area of the specific peak corresponding to the component.
- $NDB_{component}$ is the number of double bonds corresponding to the component, displayed in Table 4.12.

Chapter 5

Results and Discussion

5.1 Esterification of High FFA Content Oil

5.1.1 Experimental Results

In order to carry out base catalyzed transesterification to create biodiesel, the FFA content of the feedstock must be low otherwise the FFAs will react with the base catalyst creating soap. Large amounts of soap in the mixture decreases mass transfer efficiency and makes purification more difficult which has adverse effects on overall biodiesel yields. The recommended level of FFA content in the feedstock is less than 0.5% FFA before transesterification. WCO typically has FFA content larger than the recommended 0.5% but can be reduced using a pretreatment step of esterification with a acid catalyst. Feedstock used for esterification studies in literature have a starting FFA content as low as 2% to as high as 100% FFA. Sourcing WCO with this level of FFA content was difficult, therefore high FFA content oil was created using a mixture of oleic acid (a common FFA) and soybean oil which is chemically identical to WCO for the purposes of this study. The beginning FFA content of the oil mixture used in this study was measured at 5.9%.

The esterification experiments were conducted using the high FFA content oil mixture, ethanol, and MSA as a catalyst in a microreactor device thermally driven by a parallel process. Full description of the experimental equipment and procedures can be found in Section 4.3. The esterification experimental results are summarized in Table 5.1. Each trail run was conducted three times and the results averaged to provide more accurate final FFA value since the titration analysis can be more fallible to human bias. The signal to noise ratio is also calculated to provide another heuristic to analyze the results. Information on calculating signal to noise ratio is found in Appendix B. See Section 4.3.5 for a description of the titration method used in this study. The best results occurred with a MSA catalyst load of 5% wt-oil, a 20:1 ethanol to oil molar ratio, and a residence time of 2.5 minutes. All the experiments were conducted with at maximum temperature in which the electrical tension was set to 17.5 volts. As was discussed in Section 4.2.3, the maximum temperature of the system reaches just below the boiling point if ethanol (78 °C) in order to keep the reactants in liquid phase. The final products average temperature leaving the reactor was measured to be 56 °C, 57 °C, and 56 °C for each run respectively. In this trial run (run 9) the FFA content was decreased from 5.9% to 0.21% average over 3 runs which falls below the recommended 0.5%.

For comparison, Table 5.3 lists some esterification experimental studies in literature with the key parameters used for the best results in the study. These experimental studies were done using spinning tank reactors and unfortunately the parametric values used vary widely making comparison difficult. However, the parameters of the best results in this study fall within the outer bounds of the studies in Table 5.3 other than residence time, which is greatly reduced conducting the experiments with microreactors. In trial 9 of this study a molar ratio of 20:1 ethanol to oil was used. Both Arora et al. (2016) and Brinks et al. (2013) achieved best results using a 20:1 alcohol to oil molar ratio although Arora et al. 2016 was unable to reduce FFA below the 0.5% recommended level. Most of the studies in Table 5.3 were conducted using methanol however both Marchetti et al. (2008) and Neumann et al.(2016) conducted their studies with ethanol. In fact Marchetti et al. (2008) is a good comparison with this study as both use ethanol as the alcohol as well as a similar catalyst concentration, 5% MSA for this study and 5.1% sulfuric acid for Marchetti et al. (2008). The advantages of conducting the reaction in microreactors can be seen when comparing the residence time of Marchetti et al. (2008) and this study. Marchetti et al. (2008) reduced FFA from 10.7% to 0.5% in 240 minutes while this study showed FFA reduction from 5.9% to 0.2% in just 2.5 minutes.

The ANOVA results are shown in Table 5.2. Refer to Section 4.2.7 for a description of how the values in Table 5.2 were found.

Table 5.1: Esterification of high FFA content oil results

Trial #	CC	MR	RT	%FFA				S/N
-	(%wt MSA)	(Ethanol:Oil)	(min)	R1	R2	R3	Avg	-
1	1.0	5:1	1	4.22	4.13	4.34	4.23	-12.53
2	1.0	10:1	2.5	3.83	3.29	3.67	3.60	-11.14
3	1.0	20:1	5	3.65	3.52	3.14	3.44	-10.74
4	2.5	5:1	2.5	1.47	1.50	1.44	1.47	-3.35
5	2.5	10:1	5	1.29	1.36	1.67	1.44	-3.22
6	2.5	20:1	1	2.32	2.01	1.99	2.11	-6.49
7	5.0	5:1	5	0.50	0.52	0.52	0.51	5.79
8	5.0	10:1	1	0.43	0.39	0.48	0.43	7.23
9	5.0	20:1	2.5	0.15	0.25	0.22	0.21	13.52

Table 5.2: ANOVA table for esterification experiments

Source of Variation (Factor)	Degree of Freedom f	Sum of Squares S	Variance (Mean Square) V	Variance Ratio F	Pure Sum of Squares S'	Percent Contribution P
CC	2	17.35	8.68	1332.23	17.34	96.20
MR	2	0.09	0.05	7.21	0.08	0.52
RT	2	0.46	0.23	35.47	0.45	2.56
error	20	0.13	0.01	1	0.09	0.72

Table 5.3: Esterification optimization results in literature using spinning tank reactors. Catalyst concentration in %wt-oil

Study	Key Parameters	Conversion
Arora et al., 2016	20:1 (methanol:Rice Bran Oil), 0.5% (H_2SO_4), 90 (minutes), 60 °C	12% FFA to 1.8% FFA
Berrios et al. 2007	60:1 (methanol:FFA), 5% wt-FFA(H_2SO_4), 120 (minutes), 60 °C	3.5% FFA to 0.5% FFA
Brinks et al. 2013	20:1 (methanol:rapeseed oil), 0.1% (H_2SO_4), 4 (hours), 70 °C	5% FFA to 0.2% FFA
Chai et al. 2014	40:1 (methanol:FFA), 10% wt-FFA (H_2SO_4), 120 (minutes), 65 °C	5% FFA to 0.5% FFA
Ding et al. 2012	20% vol (methanol:WCO), 0.4% vol (H_2SO_4), 5 (hours), 50 °C	34.4% FFA to 1.85% FFA
Goyal et al. 2012	6.5:1 (methanol:jatropha oil), 1.5% (H_2SO_4), 125 (minutes), 50 °C	14.6% FFA to 0.34% FFA
Hayyan et al. 2012	8:1 (methanol:crude palm oil), 1% (MSA), 30 (minutes), 60 °C	9% FFA to 0.5% FFA
Khan et al. 2010	15:1 (methanol:rubber seed/palm oil), 0.5% (H_2SO_4), 180 (minutes), 65 °C	11.9% FFA to 0.6% FFA
Kostic et al. 2016	8.5:1 (methanol:plum stone oil), 2% (H_2SO_4), 60 (minutes), 45 °C	15.8% FFA to 0.24% FFA
Marchetti et al. 2008	12.3:1 (ethanol:WCO), 5.1% (H_2SO_4), 240 (minutes), 55 °C	10.7% FFA to 0.5% FFA
Neeharika et al. 2017	20:1 (methanol:FFA), 1% wt-FFA (MSA), 270 (minutes), 60 °C	22.5% FFA to 0.5% FFA
Neumann et al. 2016	6:1 (ethanol:oleic acid), 1.5% (H_2SO_4), 120 (minutes), 74 °C	100% FFA to 15% FFA
Ouachab et al. 2012	35:1 (methanol:olive oil), 20% (H_2SO_4), 60 (minutes), 40 °C	2.3% FFA to 0.3% FFA
Pisarello et al. 2010	15:1 (ethanol:sunflower oil), 1.14% (MSA), 30(minutes), 70 °C	18% FFA to 1.5% FFA
Present Work	20:1 (ethanol:WCO), 5.0% (MSA), 2.5(minutes), 56 °C	5.9% FFA to 0.21% FFA

5.1.2 Effect of Catalyst Concentration

The catalyst concentration is important and necessary for FFA esterification at atmospheric pressure. The most common acids used in esterification of FFAs are sulfuric acid, hydrochloric acid, and MSA. Sulfuric acid is the most common acid used because of its low cost, however the catalyst used in this study was MSA and was chosen because of its safety and availability. The catalyst concentration of MSA (CH_3SO_3H) had by far the largest impact on the variance of the reduction of FFAs with a percent contribution of 96.20%, shown in Table 5.2. The means effect plot (Figure 5.1) is a graph of the average of the results in Table 5.1 at each level (described more in depth in Section 4.2.7), in this case the average of the results at each level of the catalyst concentration (1.0%, 2.5%, and 5%). With the main effect plot we have a graphical representation of the effect of the factor on the results. As can be seen from Figure 5.1 the FFA content continued to decrease with an increase in catalyst concentration. Nearly all experiments with a catalyst concentration of 5% (%wt-oil) reduced the FFA content to the recommended 0.5% FFA before alkali catalyzed transesterification regardless of the ethanol oil molar ratio or the residence time.

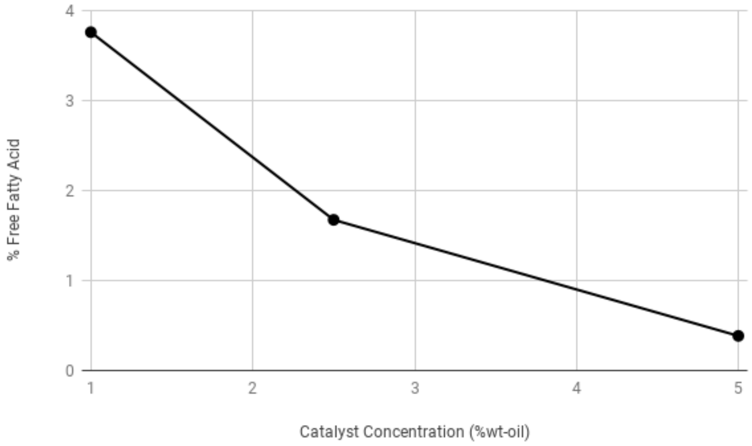


Figure 5.1: Catalyst Concentration main effect plot for esterification

The catalyst concentration of the best results in literature vary substantially. The amount of acid catalyst needed to reduce FFA content through esterification depends largely on various parameters including the properties of the acid being used, the reactor type, the alcohol being used and the amount, as well as the reaction temperature, pressure, and residence time. Most studies referenced in this study used a catalyst concentration between 1-2% wt-oil, however several studies have achieved optimal results with catalyst concentrations from 5% wt-oil and above. As can be seen in Table 5.1, a catalyst load of 1.0% (trial runs 1-3) only reduced the FFA content to 3-4% depending on the other parameters, still much larger than the

0.5% FFA we are aiming for. Raising the catalyst concentration to 2.5% made a noticeable improvement on the reduction of FFAs but the FFA (trial runs 4-6) with final FFA content in the range of 1.44-2.11%, however still larger than the 0.5% we need to do transesterification. The FFA content was reduced to below 0.5% only when the catalyst concentration was raised to 5% (trial runs 7-9).

5.1.3 Effect of Molar Ratio

The stoichiometric ratio for esterification of FFA is a 1:1 ratio, a alcohol molecule reacts with a FFA molecule to create a ester and a water molecule. Because the reaction is reversible the alcohol content is increased to drive the reaction towards ester production. The most common alcohol used in esterification is methanol however ethanol is also used often. For this study ethanol was used mainly because of its safety and availability. The ethanol to oil molar ratio had the smallest effect on the variance with a percent contribution of just 0.52%, shown in Table 5.2. From the main effect plot in Figure 5.2 a small reduction in the FFA content can be observed when the ethanol to oil molar ratio was raised from 5:1 to 10:1. The average FFA content was found to be slightly higher for the experiments conducted with an ethanol to oil molar ratio of 20:1, but the difference is minimal and can be considered equal to the results with a ethanol to oil molar ratio of 10:1.

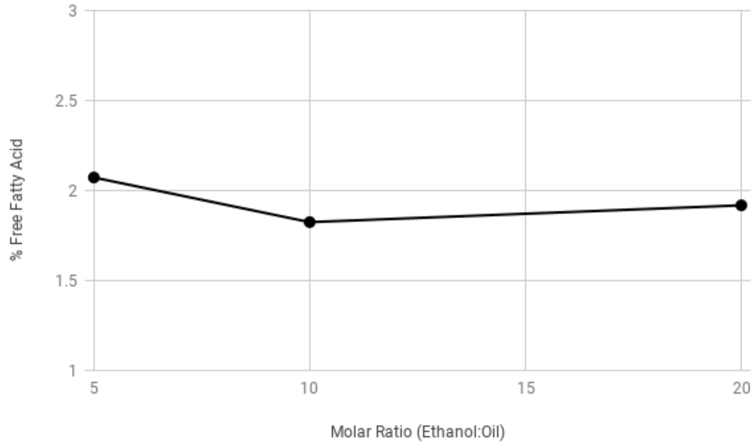


Figure 5.2: Molar Ratio main effect plot for esterification

None of the trail runs using a ethanol to oil molar ratio of 5:1 (trial runs 1, 4, and 7 in Table 5.1) reduced the FFA content to below 0.5% wt-oil. Raising the molar ratio to 10:1 ethanol to oil (trial runs 2, 5, and 8) improved the results but only trail run 8 with catalyst concentration of 5% wt-oil MSA was the FFA content reduced below the desired 0.5%. An ethanol to oil molar ratio of 20:1 was used for trial runs 3, 6, and 9. The best results in this study were achieved using a ethanol to oil molar ratio of 20:1 in trail 9. In practice, the minimum amount of alcohol to achieve the desired results is preferred. This is to save money and minimize transesterification to suppress the presence of the intermediary species for purification. Most studies use batch processes where the reactants are constantly stirred for several hours and a lower amount of alcohol and catalyst can be used successfully. In continuous processes, the mass transfer of the reactants must be considered when analyzing. The reactor used in this study uses a simple Y-mixer to mix the reactants, the oil is better dispersed with a alcohol molar ratio of 20:1. In addition, many of the referenced studies used methanol which typically converts FFA at lower molar ratios than ethanol.

5.1.4 Effect of Residence Time

The residence time of the reaction also had a minimal effect on the variance of the results with a 2.56% contribution, see Table 5.2. In the main effect plot of Figure 5.3 a reduction in the FFA content is observed when the residence time is increased from 1 to 2.5 minutes. No significant difference was observed when the residence time was increased from 2.5 to 5 minutes. This shows that the reactants were in equilibrium at 2.5 minutes.

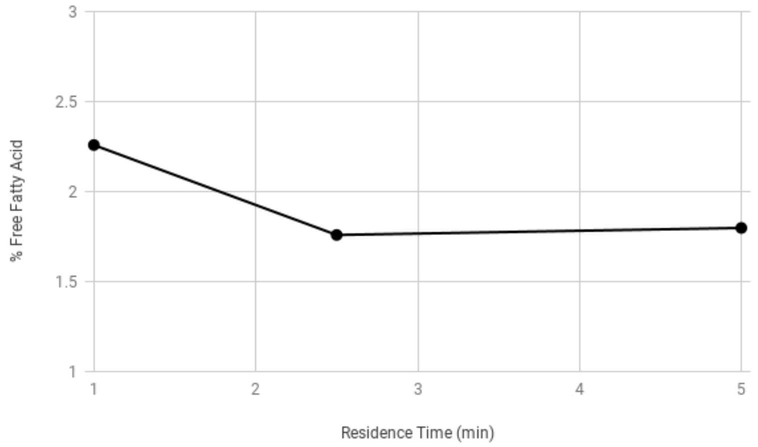


Figure 5.3: Residence Time main effect plot for esterification

A residence time of 1 minute was used in trail runs 1, 6, and 8 in Table 5.1. Because the results largely correlate with the catalyst concentration, trial run 8 with a catalyst concentration of 5% wt-oil reduced the FFA content below the targeted 0.5%. Trial runs 2, 4, and 9 were conducted using a residence time of 2.5 minutes. The highest reduction of FFA occurred during trail 9 with a residence time of 2.5 minutes. Trials 3, 5, and 7 were done using a residence time of 5 minutes. None of these runs with the residence time of 5 minutes achieved the desired level of

FFA reduction. The improvement in shortened residence times is where the major advantage of microreactors is observed. The residence times for batch reactors are typically 30 minutes to 2 hours. The time saved using microreactors make this technology attractive to industrial producers looking to reduce costs.

5.1.5 Problem With Emulsions

One limiting factor discovered during the esterification is the problem of emulsions of the oil during purification steps, shown in Figure 5.4 the top layer emulsified oil and the bottom layer wash water. The reactions taking place in the reactor during the experiment are the esterification reaction, Equation 5.1, acid catalyzed transesterification, Equations 5.2, and because of the presence of water from esterification, hydrolysis reactions, Equations 5.3.

$$FFA + C_2H_6O \xrightleftharpoons{catalyst} E + H_2O \tag{5.1}$$

$$TG + C_2H_6O \xrightleftharpoons{catalyst} DG + E \tag{5.2a}$$

$$DG + C_2H_6O \xrightleftharpoons{catalyst} MG + E \tag{5.2b}$$

$$MG + C_2H_6O \xrightleftharpoons{catalyst} G + E \tag{5.2c}$$

$$TG + H_2O \xrightleftharpoons{catalyst} DG + FFA \tag{5.3a}$$

$$DG + H_2O \xrightleftharpoons{catalyst} MG + FFA \tag{5.3b}$$

$$MG + H_2O \xrightleftharpoons{catalyst} G + FFA \tag{5.3c}$$

In order to convert a large percentage of triglycerides to biodiesel through transesterification of triglycerides using an acid catalyst, large residence times are required. The residence times used in this study are not long enough to convert the triglycerides to esters but some of the intermediary species (diglycerides, monoglycerides) will be created. This is a situation where the efficiency of microreactors can create large amount of certain species that are unwanted. Diglycerides and monoglycerides are excellent emulsifiers and large amounts of them in the mixture will create emulsions during water washing. In addition, the use of ethanol as the alcohol makes the mixture more susceptible to emulsions.

Emulsified oil makes the purification steps more time consuming and laborious. Sometimes the emulsions will settle out given enough time, however waiting for the

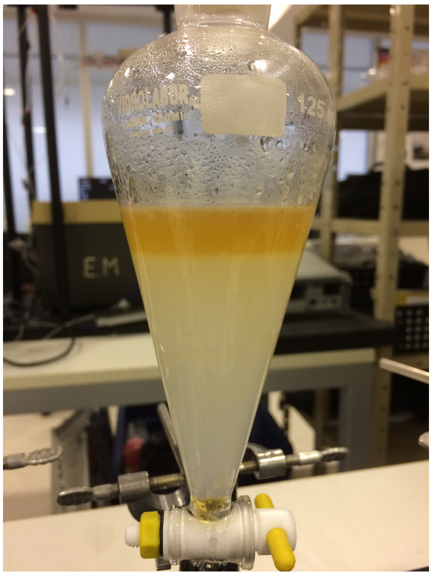


Figure 5.4: Emulsified oil after esterification reaction.

emulsions to settle out can take several days and even then they may not fully decant. Washing with salt water was another method incorporated in this study to remove emulsions. At times the oil needed to be washed up to seven times over several days for the wastewater to have a neutral pH. To test for the amount of mono and diglycerides present in the esterified oil, the oil was tested using HPLC. The chromatogram shown in Figure 5.5 displays a large amount of mono and diglycerides present in the oil.

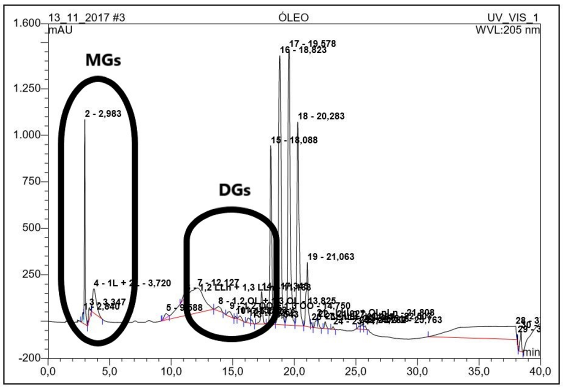


Figure 5.5: Chromatogram of esterified oil

5.2 Transesterification of WCO

5.2.1 Experimental Results

Transesterification of WCO was conducted using a microreactor device of 10 microchannel reactors in parallel with 11 micro-heat exchangers using a parallel thermal process to heat the system, described in detail in Section 4.3.2, reacting ethanol with the oil facilitated with a KOH catalyst. Ethanol was chosen because of its safety and availability, and KOH was chosen because it is shown to be better than NaOH for transesterification of WCO according to literature. The WCO preparation is described in Section 4.4.2 and the composition of the WCO is summarized in Table 4.11. Experimental procedures for the transesterification experiments are described in detail in Section 4.4.4. The results of the transesterification experiments are summarized in Table A.1. The best ester conversion occurred in trial 19 where a ester conversion of 90% was achieved with a KOH concentration of 1.25%, ethanol to WCO molar ratio of 25:1 with a residence time of 2 minutes. The system temperature was placed at its maximum in which the the electrical tension of the heat exchanger described in Section 4.3.3 is set to 17.5V which places the reactants just below the boiling point of ethanol (78 °C).

For comparison Table 5.6 displays some of the best conversions of experimental studies in literature using spinning tank reactors, along with the parameters used for the best results in the studies. Abd Rabu (2012), Al-Hamamre (2013), Felizardo (2015), Leung (2006), and Uzan (2012) converted WCO to esters with Al-Hamamre (2013), Filizardo (2015), and Uzan (2012) achieving conversions above the government mandated 96% ester conversion for use in industry. Leung (2006) shows a slight decrease in ester conversion, from 93.5% to 88.8%, when soybean oil is replaced with WCO. Anastopoulos (2009), Encinar (2002), Encinar (2007), and Tippayawang (2005) used ethanol as the reacting alcohol used in transesterification however none of the studies achieved an ester conversion above 94.5%. Two different studies by the same author, Encinar (2007) and Encinar (2002), demonstrate how the use of WCO (2007) in place of a refined oil (2002) can decrease overall conversions as in the 2002 study cynara oil was reacted with ethanol for an ester conversion of 94.5% and the 2007 study using ethanol and WCO had a ester conversion of just 72.5%. The results from this study compare very favorably with the studies in Table 5.6. The ester conversion of 90% from Table A.1, trial 19, is larger than any of the studies using ethanol and WCO in Table 5.6. In addition, when comparing the residence times the present study is far superior as the ester conversion of 90% was achieved in a just 2 minute residence time while the studies in Table 5.6 achieved their results with residence times from 30 minutes to 2.5 hours. Compared to other studies, a molar ratio of 25:1 is quite large. This can be attributed to the reactor design and the fact that ethanol was used in this study as the working alcohol.

The best ester conversions from studies using microreactors along with the parameters used is summarized in Table 5.7 for comparison. Al-Dhubabian (2005), Sun (2008), Wen (2009), Dai (2014), and Sun (2010) used methanol in their studies with Wen (2009), Dai (2014), and Sun (2010) achieving nearly total conversion in residence times of 28, 14.9, and 17 seconds respectively. Arias (2012), Santana (2016), Chen (2013), and Costa Junior (2017) used ethanol in their studies with Santana (2016) and Costa Junior (2017) achieving near total conversion with residence times of 12 and 34 seconds respectively. While results in this study shown in Table A.1 are do not match the quality of much of the results in Table 5.7 however all the studies in Table 5.7 converted refined vegetable oil as compared to the WCO used in this study. Vegetable oil degrades when used for cooking with water from the food driving hydrolysis of the triglycerides creating FFAs and particles and water from the food becoming suspended within the oil which must be removed before transesterification. Refined oil is free of these impurities while inefficiencies in the purification of the WCO will inevitably leave higher levels of FFAs, food particles, and water in WCO. These impurities have a negative effect on mass transfer of the reactants ultimately decreasing ester conversions.

Table 5.4: Transesterification of WCO experimental results

Trial # -	Catalyst Load (%wt KOH)	Molar Ratio (Ethanol:Oil)	Residence Time (min)	Tension (V)	%Ester -
1	0.50	10:1	1	6	22
2	0.50	15:1	2	9	39
3	0.50	20:1	3	12	46
4	0.50	25:1	4	15	47
5	0.50	30:1	5	17.5	53
6	0.75	10:1	2	12	45
7	0.75	15:1	3	15	47
8	0.75	20:1	4	17.5	59
9	0.75	25:1	5	6	37
10	0.75	30:1	1	9	46
11	1.00	10:1	3	17.5	50
12	1.00	15:1	4	6	55
13	1.00	20:1	5	9	46
14	1.00	25:1	1	12	56
15	1.00	30:1	2	15	62
16	1.25	10:1	4	9	62
17	1.25	15:1	5	12	68
18	1.25	20:1	1	15	88
19	1.25	25:1	2	17.5	90
20	1.25	30:1	3	6	59
21	1.50	10:1	5	15	70
22	1.50	15:1	1	17.5	84
23	1.50	20:1	2	6	69
24	1.50	25:1	3	9	81
25	1.50	30:1	4	12	88

Table 5.5: ANOVA table for transesterification of WCO experiments

Source of Variation (Factor)	Degree of Freedom f	Sum of Squares S	Variance (Mean Square) V	Variance Ratio F	Pure Sum of Squares S'	Percent Contribution P
CC	4	5345.36	1336.34	34.14	5188.80	71.69
MR	4	541.36	135.34	3.46	384.80	7.26
RT	4	186.96	46.74	1.19	30.40	2.51
T	4	1069.76	267.44	6.83	913.20	14.35
error	8	313.12	39.14	1	939.36	4.20

Table 5.6: Transesterification experimental results in literature using spinning tank reactors. Catalyst concentration in %wt-oil

Study	Key Parameters	Ester Conversion
Abd Rabu 2012	12:1 (methanol:WCO), 1% (NaOH), 120 (minutes), 70 °C	95%
Al-Hamamre 2013	9.5:1 (methanol:WCO), 1% (KOH), 40 (minutes), 50 °C	98%
Anastopoulos 2009	12:1 (ethanol:sunflower oil), 1% (NaOH), 2.5 (hours), 80 °C	81.4%
Atapour 2014	9:1 (methanol:WCO), 0.72% (NaOH), 45 (minutes), 65 °C	92.05%
Encinar 2007	12:1 (ethanol:WCO), 1% (KOH), 2 (hours), 78 °C	72.5%
Encinar 2002	12:1 (ethanol:cynara oil), 1% (NaOH), 2 (hours), 75 °C	94.5%
Felizardo 2005	4.8:1 (methanol:WCO), 0.6% (NaOH), 60 (minutes), 65 °C	99%
Keera 2011	6:1 (methanol:soybean oil), 1% (NaOH), 60 (minutes), 60 °C	91%
Leung 2006	6:1 (methanol:soybean oil), 1% (NaOH), 60 (minutes), 45 °C	93.5%
Leung 2006	7:1 (methanol:WCO), 1.1% (NaOH), 60 (minutes), 60 °C	88.8%
Tippayawang 2005	10.5:1 (ethanol:soybean oil), 1% (NaOH), 120 (minutes), 70 °C	93%
Uzan 2012	7.5:1 (methanol:WCO), 0.5% (NaOH), 30 (minutes), 50 °C	97%

5.2.2 Effect of Catalyst Concentration

The KOH concentration contributed the most to the variance with a percent contribution of 71.69%, shown in Table 5.5. From the main effect plot in Figure 5.6 that amount of ethyl esters created continued to increase with an increase in KOH concentration. From 0.5% to 1.0% (%wt-oil) catalyst concentration a steady

Table 5.7: Transesterification experimental results in literature using microreactors. Catalyst concentration in %wt-oil

Study	Key Parameters	Ester Conversion
Al-Dhubabian 2005	7.2:1 (methanol:soybean oil), 1% (NaOH), 10 (minutes), 25 °C	91%
Sun 2008	6:1 (methanol:rapeseed oil), 1% (NaOH), 6 (minutes), 60 °C	98.8%
Wen 2009	9:1 (methanol:soybean oil), 1.2% (NaOH), 28 (seconds), 56 °C	99.5%
Dai 2014	8.5:1 (methanol:soybean oil), 1.2% (KOH), 14.9 (seconds), 59 °C	99.5%
Sun 2010	8:1 (methanol:cottonseed oil), 1% (KOH), 17 (seconds), 70 °C	99.5%
Arias 2012	25:1 (ethanol:castor oil), 1% (NaOH), 10 (minutes), 50 °C	96.7%
Santana 2016	9:1 (ethanol:sunflower), 1% (NaOH), 12 (seconds), 50 °C	99.53%
Chen 2013	12.7:1 (ethanol:soybean oil), 1% (NaOH), 5.6 (minutes), 60 °C	81%
Costa Junior 2017	20:1 (ethanol:soybean oil), 1% (NaOH), 34 (seconds), 52 °C	99.5%
Present Work	25:1 (ethanol:WCO), 1.9% (KOH), 2 (minutes), 56 °C	98%

increase was observed. A large jump in the conversion % is seen with a catalyst concentration jump from 1.0% to 1.25%, then another steady increase is seen from 1.25% to 1.50% catalyst concentration.

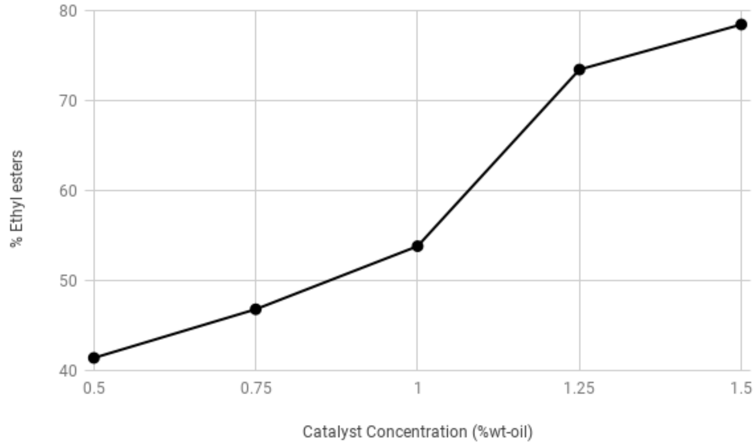


Figure 5.6: Catalyst Concentration main effect plot for transesterification

A catalyst concentration of 0.50% wt-oil was used for trial runs 1-5, displayed in Table A.1. The results from experiments run with this catalyst load are poor, with a ethyl ester conversion range of 22%-53%. When the KOH concentration was increased to 0.75% wt-oil (trials 6-10 in Table A.1) the results improved slightly, but were still poor, with ethyl ester conversions in the range of 37%-59%. Trial runs 11-15 in Table A.1 were conducted using a catalyst concentration of 1.0% wt-oil and resulted in an ester conversion range of 46%-62%. The best result (trial 19) in Table A.1 was achieved using a catalyst concentration of 1.25% wt-oil (trial runs 16-20). The lowest ethyl ester conversion using this amount of catalyst was 59% while the best result was 90% conversion. Good conversions also occurred when the KOH concentration was increased to 1.50% wt-oil (trial runs 21-25 in Table A.1 with a ester conversion range of 69% to 88%.

From the main effect plot, Figure 5.6 we can see that the ester conversion still has a positive slope at our highest level, 1.5%. This suggests that the conversion can still increase if the catalyst concentration is increased. In order to discover if this is indeed the case, we take the best results of the MR, RT, and voltage controlling the temperature and run experiments steadily increasing the catalyst concentration from 1.5%. Experiments were run for 1.6%, 1.7%, 1.8%, 1.9%, and 2.0%. The results are summarized in Table 5.8. The ester conversion on WCO was increased up to 98% with 1.9% KOH the conversion then decreased to 90% when KOH concentration was increased to 2.0% suggesting the best catalyst concentration for our system is in fact 1.9%.

Table 5.8: Transesterification of WCO experimental results

Catalyst Load (%wt KOH)	Molar Ratio (Ethanol:Oil)	Residence Time (min)	Tension (V)	%Ester -
1.60	25:1	2	17.5	92
1.70	25:1	2	17.5	93
1.80	25:1	2	17.5	97
1.90	25:1	2	17.5	98
2.00	25:1	2	17.5	90

5.2.3 Effect of Molar Ratio

The ethanol to WCO molar ratio had a percent contribution to the variance of 7.26%, shown in Table 5.5. From the main effect plot, Figure 5.7, a large jump in the conversion was observed with a increase in the molar ratio from 10:1 to 15:1. Another slight increase in the conversion was observed with an increase in the molar ration from 15:1 to 20:1. From 20:1 to 30:1 no significant increase in ethyl ester conversion is observed from the means effect plot in Figure 5.7.

An ethanol to WCO molar ratio of 10:1 was used for trial runs 1, 6, 11, 16, and 21, shown in Table A.1. An ethyl ester conversion range of 22%-70% was found when the ethanol to WCO molar ratio was set to 10:1. When the ethanol to WCO molar

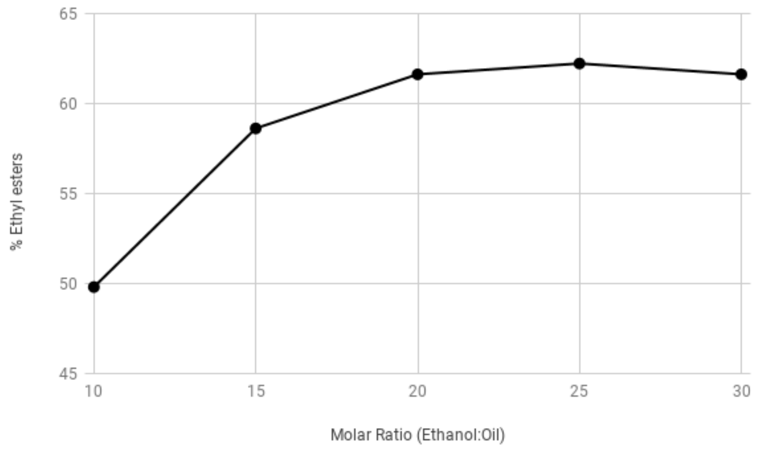


Figure 5.7: Molar Ratio main effect plot for transesterification

ratio was increased to 15:1 (trials 2, 7, 12, 17, and 22 in Table A.1) an increase in ester conversion is observed with a range from 39% to 84%. Trial runs 3, 8, 13, 18, and 23 were conducted using a ethanol to WCO molar ratio of 20:1. The ethyl ester conversion continued to increase with a range from 46% to 88%. The best results were obtained when the ethanol to WCO molar ratio was 25:1 (trials 4, 9, 14, 19, and 24 in Table A.1) with ethyl ester conversions from 37% to 90%. An ethanol to WCO molar ratio of 30:1 was used in trial runs 5, 10, 15, 20, and 25 with the low end conversion being 46% to the high end ethyl ester conversion of 88%.

5.2.4 Effect of Residence Time

A residence time of 1 minute was used for trail runs 1, 10, 14, 18, and 22 shown in Table A.1 with an ethyl ester conversion range of 22% to 88%. A residence time of 2 minutes was used for runs 2, 6, 15, 19, and 23 with ester conversions between 39%-90%. Trial runs 3, 7, 11, 20, and 24 were done using a residence time of three minutes with ethyl ester conversions in the range of 46% to 81%. A residence time of 4 minutes was used for trail runs 4, 8, 12, 16, and 25 with ester conversions ranging from 47% to 88% during these experiments. Trial runs 5, 9, 13, 17, and 21 were conducted with a residence time of 5 minutes with ethyl ester conversions between 37% to 70%.

The residence time of the reaction had the lowest effect on the variance with a percent contribution of 2.51%, shown in Table 5.5. Average results from each level of the factor is plotted in the mean effects plot, Figure 5.8. From the main effect plot, a small rise in ethyl ester conversion can be seen raising the residence time from 1 minute to 2 minutes. A slight decrease in ethyl esters occurred increasing the residence times from 2 to 3 minutes. Then the ethyl ester conversion increased slightly when the residence time was 4 minutes and then slightly decreased when the residence time was 5 minutes.

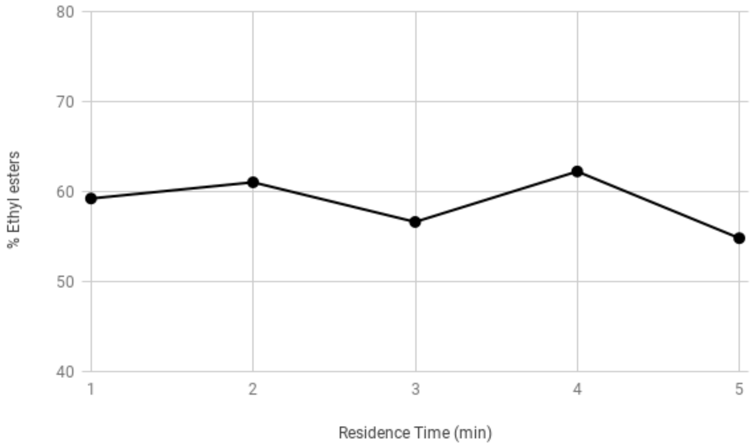


Figure 5.8: Residence Time main effect plot for transesterification

The reactions that are taking place in the reactor are transesterification, Equation 5.4, saponification, Equation 5.5, and hydrolysis, Equation 5.6. Both the saponification and hydrolysis equations are usually ignored when using pure, refined vegetable oil. When using WCO can have a noticeable effect on the conversion and can explain some of the difference within average of the different residence times. The fact that a partial factorial experimental design was used also explains some of the difference from the expected results. Overall, the effect of residence time did not have much of a contribution at all on the variance of the response so it can be concluded that the reaction is in equilibrium after 1-2 minutes residence time.

$$TG + C_2H_6O \xrightleftharpoons{catalyst} DG + E \tag{5.4a}$$

$$DG + C_2H_6O \xrightleftharpoons{catalyst} MG + E \tag{5.4b}$$

$$MG + C_2H_6O \xrightleftharpoons{catalyst} G + E \tag{5.4c}$$

$$FFA + KOH \xrightleftharpoons{catalyst} Soap + H_2O \tag{5.5}$$

$$TG + H_2O \xrightleftharpoons{catalyst} DG + FFA \tag{5.6a}$$

$$DG + H_2O \xrightleftharpoons{catalyst} MG + FFA \tag{5.6b}$$

$$MG + H_2O \xrightleftharpoons{catalyst} G + FFA \tag{5.6c}$$

5.2.5 Effect of Temperature

The measured temperatures of the products that are exiting the reactor during the experiments is displayed in Table 5.9 along with the corresponding electrical tension the heat exchange system was set to for the experiment. This gives a tangible sense of how temperature varied during for the various levels used. The lowest temperature setting used in this study was 6V for trial runs 1, 9, 12, 20, and 23 (Table A.1) in which the ethyl ester conversion was between 22% to 69%. The higher setting for level 2 (9V) was used for trial runs 2, 10, 13, 16, and 24. The range of ethyl ester conversion was 39% to 81%. For a setting of 12V (trials 3, 6, 14, 17, and 25 in Table A.1) the ethyl ester conversion varied between 46% to 88%. Results improved for a setting of 15V which was used for trial runs 4, 7, 15, 18, and 21. The ester conversion for this setting was between 47% to 88%. The best results were found using the level 5 setting of 17.5V (trials 5, 8, 11, 19, and 22) with ethyl ester conversion from 50% to 90%.

Table 5.9: Electrical tension levels and their corresponding measured temperatures of the products leaving the reactor.

Level	Voltage (V)	Product Temp (°C)
1	6	35±4
2	9	40±4
3	12	45±4
4	15	50±4
5	17.5	55±4

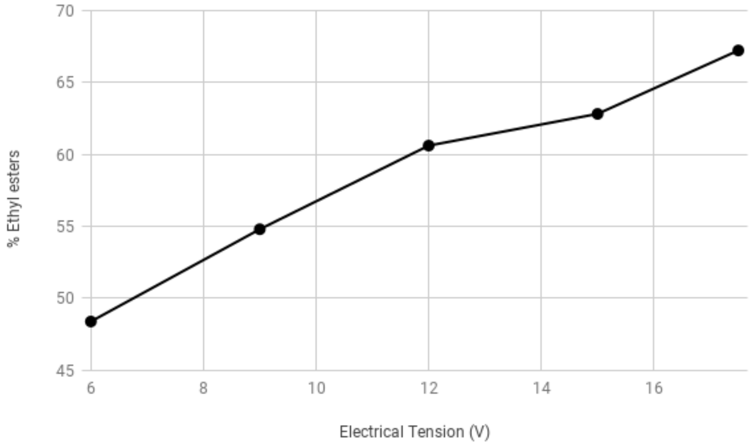


Figure 5.9: Temperature main effect plot for transesterification

The temperature of the reaction had the second largest percent contribution to the variance of 14.35%. Average results from each level of the factor is plotted in the main effect plot, Figure 5.9. From the mean effects plot it is observed that the conversion of triglycerides to ethyl esters increased steadily as the electrical tension was increased thus increasing the temperature. These results match well with the literature of biodiesel synthesis with ethanol. The ester conversion is greatest when the temperature is just below the boiling point of ethanol, which is the maximum temperature while keeping the mixture in liquid phase.

Chapter 6

Conclusions and Future Work

6.1 Conclusions

6.1.1 Esterification of High FFA Content Oil

High content FFA oil was made using oleic acid and refined soybean oil. This oil had a FFA content of 5.9% and is a chemically good simulation of lower quality used oil which generally has a FFA content of 2-7%. Using a microdevice with 10 microreactors in parallel with 11 micro heat-exchangers, the feasibility of the esterification of the high FFA content oil was carried out with ethanol as the working alcohol and MSA as the acid catalyst using a partial factorial Taguchi experimental plan. The reaction was heated using a parallel thermal process of passing water through a heat exchanger heated with electrical resistance.

The variance of the results was effected most by the catalyst concentration. The best results of a 0.2% FFA were achieved using 5% catalyst with a 20:1 ethanol to oil molar ratio and a residence time of 2.5 minutes (trial 9 in Table 5.1). In fact, all the runs with a catalyst concentration of 5% achieved a reduction of FFA to roughly the 0.5% that is recommended for alkali catalyst transesterification.

Although the FFA content was reduced to an appropriate amount for transesterification, the use of this method on an industrial scale would be unlikely because of the difficulty of purification. A way to make purification less laborious is to switch the use of ethanol with methanol. As described in Section 3.4.4, the properties of methanol make the final product easier to purify. The use of microreactors increases the efficiency of the all chemical reactions taking place which include esterification of FFAs as well as transesterification of triglycerides. Transesterification using an acid catalyst will take much longer to complete than transesterification with an alkali catalyst, but the large amount of alcohol as well as the increase in efficiency of microreactors created a large amount of monoglycerides and diglycerides. Both mono and diglycerides are excellent emulsifiers and made the purification steps much more labor intensive and time consuming.

6.1.2 Transesterification of WCO

WCO was obtained from a local restaurant and had a FFA content of 1.0%. The oil was first filtered and dried and then taken through an esterification process to reduce the FFA content to 0.5% before transesterification (described in depth in Section 4.4.2. After these pretreatments, a partial factorial Taguchi experimental plan was carried out using ethanol and a KOH catalyst incorporating the same heating method and microdevice used during the esterification experiments.

The best result of 90% ester conversion was achieved with 1.25% KOH, an ethanol to oil molar ratio of 25:1, a residence time of 2 minutes, and the electrical tension was set to 17.5V which is the maximum temperature used in the experiments (trial 19 in Table A.1). Extra experiments were run increasing the catalyst concentration from the highest set value in our original analysis. An ester conversion of 98% was achieved when the catalyst concentration was increased to 1.9% keeping the other parameters constant from our previous best result. Overall, the results achieved with these experiments are very promising for potential biodiesel production with WCO using microreactors in the future. The increase in conversion efficiency and versatility of production quantity make microreactor chemical synthesis an attractive option for biodiesel production. Advances in manufacturing will continue to make microreactor systems cheaper and more widespread.

6.2 Future Work

6.2.1 Esterification of High FFA Content Oil

The purpose of this research was to test the feasibility of reacting WCO and ethanol with microreactors in order to reduce the cost of biodiesel production. The difficulty of the purification steps during the esterification experiments make widespread use of the esterification process used in this study unlikely. The following modifications are proposed as possible solutions to the emulsion problem:

- Use methanol as the reacting alcohol as oil purification is easier when methanol is used and less emulsions are formed.
- Modify the microreactor design to better mix the reactants before entering the reaction. The simple Y-mixer used requires large molar ratios of alcohol to oil for the oil to completely disperse and react. With better initial mixing, either a different mixer design or perhaps a short pre-mixing stage, less alcohol would be needed for the reduction of FFAs and therefore there would be less

alcohol for transesterification that is occurring simultaneously. The repressed transesterification reaction would leave less mono and diglycerides which are the main cause of the emulsions.

6.2.2 Transesterification of WCO

Conversion of WCO with a FFA content of 0.5% was effective and the technology of microreactors shown great promise for future biodiesel production studies. However, in order to produce fuel grade biodiesel using WCO and microreactors the following is proposed:

- Create a system to augment the quantity of biodiesel produced in order to synthesize a sufficient amount to test the biodiesel according to governmental regulated test standards such as the United States ASTM D6751 standard or the European EN 14214 standard.
- React the WCO with methanol instead of ethanol to see if any improvements in conversion or purification can be realized.
- Experiment with dry washing techniques (described in Section 3.6) to reduce the purification time.

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Appendix A

Intermediary Species - Transesterification

Table A.1: Transesterification of WCO intermediary species results

Trial #	%MG	%DG	%TG	%Ester
1	4	30	44	22
2	4	18	39	39
3	5	4	45	46
4	7	6	40	47
5	15	9	23	53
6	5	10	40	45
7	8	8	37	47
8	5	10	26	59
9	4	26	33	37
10	4	14	36	46
11	9	11	30	50
12	11	10	24	55
13	8	16	30	46
14	13	6	25	56
15	5	19	14	62
16	8	8	22	62
17	12	5	15	68
18	8	2	2	88
19	5	2	3	90
20	4	3	34	59
21	4	5	21	70
22	7	2	7	84
23	15	3	13	69
24	10	2	7	81
25	8	1	3	88

Appendix B

ANOVA Calculations

Table B.1: ANOVA quantities and notation

V	mean square (variance)	P	percent influence
S	sum of squares	T	total (of results)
S'	pure sum of squares	n	number of experiments
f	degrees of freedom	$C.F.$	correction factor
e	error (experimental)	f_T	total degrees of freedom
F	variance ratio	Y	result of trial run

In an experiment designed to determine the effect of factor A on response Y, factor A is to be tested at L levels. Assume n_1 repetitions of each trial that includes A_1. Similarly, at level A_2 the trial is to be repeated n_2 times. The total number of trials is the sum of the number of trials at each level, that is,

$$n = n_1 + n_2 + ... + n_L \tag{B.1}$$

DOF is a measure of the amount of information that can be uniquely determined from a given set of data. DOF for data concerning a factor equals one less than the number of levels. This is because data for a factor at a particular level can be compared to data of the other factor levels, but not itself. Thus, an experiment with r repetitions of each trial n, the DOF becomes:

$$f_T = n * r - 1 \tag{B.2}$$

Similarly, the DOF for a sum of squares term, f_i, is equal to the number of terms used to compute the sum of squares, and the DOF of the error term, f_e, is given by:

$$f_e = f_T - \sum_{i=1}^{L} f_i \tag{B.3}$$

The sum of squares is a measure of the deviation of the experimental data from the mean value of the data. Summing each squared deviation emphasizes the total deviation. Thus,

$$S_T = \sum_{i=1}^{n} (Y_i - \overline{Y})^2 \tag{B.4}$$

Where $\overline{Y}$ is the average of the response Y_i. We define the total of the results:

$$T = \sum_{i=1}^{n} Y_i \tag{B.5}$$

The correction factor is defined as:

$$C.F. = \frac{T^2}{n} \tag{B.6}$$

Therefore S_T becomes:

$$S_T = \sum_{i=1}^{n} Y_i^2 - C.F. \tag{B.7}$$

To calculate S for a given factor A,

$$S_A = \sum_{k=1}^{L} \frac{1}{n_k} [\sum_{i=1}^{n_i} A_{ik}]^2 - C.F. \tag{B.8}$$

Where L is the number of levels and n_i and n_k are the numbers of test samples at A_i and A_{ik} respectively.

To calculate the sum of squares of the error term:

$$S_e = S_T - (S_1 + S_2 + ... + S_L) \tag{B.9}$$

The variance of each factor is determined by the sum of the square of each trial sum result involving the factor, divided by the degrees of freedom of the factor. Thus:

$$V_i = \frac{S_i}{f_i} \tag{B.10}$$

Where the degrees of freedom for a factor f is equal to one less than the number of levels.

The variance for the error term is calculated:

$$V_e = \frac{S_e}{f_e} \tag{B.11}$$

The variance ratio is the ratio of variance due to the effect of a factor and variance due to the error term. This ratio is used to measure the significance of the factor under investigation with respect to the variance of all of the factors included in the error term. :

$$F_i = \frac{V_i}{V_e} \tag{B.12}$$

The pure sum of squares is the sum minus the degrees of freedom times the error variance:

$$S'_i = S_i - f_i V_e \tag{B.13}$$

The percent influence of each factor is the ratio of the factor sum to the total, expressed in percent:

$$P_i = S'_i \frac{100}{S_T} \tag{B.14}$$

Multiple runs of the esterification allow us to calculate the signal to noise ratio of the response. The change in the quality characteristics of a product under investigation in response to a factor introduced in the experimental design is the signal of the desired effect. However, when an experiment is conducted, there are numerous external and internal factors not designed into the experiment that influence the outcome. These uncontrollable factors are called the noise factors, and their effect on the outcome of the quality characteristic under test is termed noise". Therefore, the aim of any experiment is always to determine the highest possible S/N ratio for the result. First the mean square deviation of the set is computed. For smaller is better:

$$MSD = (Y_1^2 + Y_2^2 + ... + Y_{n_i}^2)/n_i \tag{B.15}$$

The signal to noise ratio can be calculated using the following:

$$S/N = -10log_{10}(MSD) \tag{B.16}$$

For an example we take the esterification experimental results in Table B.2.

A_1, A_2, and A_3 would be CC, MR, and RT respectively. We perform 3 trials for each level according to our matrix, therefore n_1, n_2, and n_3 are all equal to 3. So our total n is:

$$n = 3 + 3 + 3 = 9 \tag{B.17}$$

The degrees of freedom are one less than the number of levels:

$$f_1 = f_2 = f_3 = 2 \tag{B.18}$$

Table B.2: Esterification of high FFA content oil results

Trial #	CC	MR	RT	%FFA				S/N
-	(%wt MSA)	(Ethanol:Oil)	(min)	R1	R2	R3	Avg	-
1	1.0	5:1	1	4.22	4.13	4.34	4.23	-12.53
2	1.0	10:1	2.5	3.83	3.29	3.67	3.60	-11.14
3	1.0	20:1	5	3.65	3.52	3.14	3.44	-10.74
4	2.5	5:1	2.5	1.47	1.50	1.44	1.47	-3.35
5	2.5	10:1	5	1.29	1.36	1.67	1.44	-3.22
6	2.5	20:1	1	2.32	2.01	1.99	2.11	-6.49
7	5.0	5:1	5	0.50	0.52	0.52	0.51	5.79
8	5.0	10:1	1	0.43	0.39	0.48	0.43	7.23
9	5.0	20:1	2.5	0.15	0.25	0.22	0.21	13.52

Each trial was repeated 3 times ($r = 3$). The total degrees of freedom becomes:

$$f_T = 9 * 3 - 1 = 26 \tag{B.19}$$

We can then calculate the error degrees of freedom:

$$f_e = f_T - (f_1 + f_2 + f_3) = 26 - (2 + 2 + 2) = 20 \tag{B.20}$$

For the total T we simply add the average results:

$$T = 4.23 + 3.60 + 3.44 + 1.47 + 1.44 + 2.11 + 0.51 + 0.43 + 0.21 = 17.43 \tag{B.21}$$

And solve for the $C.F.$:

$$C.F. = T^2/n = 17.43^2/9 = 33.77 \tag{B.22}$$

The total sum of squares calculation is straight forward:

$$S_T = (4.23^2+3.60^2+3.44^2+1.47^2+1.44^2+2.11^2+0.51^2+0.43^2+0.21^2)-33.77 = 18.04 \tag{B.23}$$

For the sum of squares of factor CC or A_1. A_{11} corresponds to the results of the first level of factor A_1 which is 1.0%. A_{12} corresponds to the second level of factor A_1 which is 2.5% etc.:

$$A_{11} = 4.23 + 3.60 + 3.44 = 11.26 \tag{B.24}$$

$$A_{12} = 1.47 + 1.44 + 2.11 = 5.02 \tag{B.25}$$

$$A_{13} = 0.51 + 0.43 + 0.21 = 1.15 \tag{B.26}$$

Therefore the sum of squares for CC is:

$$S_{A_1} = 11.26^2/3 + 5.02^2/3 + 1.15^2/3 - 33.77 = 17.35 \tag{B.27}$$

We set S_{A_1} equal to S_1 to simplify the notation. Carried out for the other factors the sum of squares of the error can be solved:

$$S_e = S_T - (S_1 + S_2 + S_3) = 18.04 - (17.35 + 0.09 + 0.46) = 0.13 \tag{B.28}$$

The variance calculation for CC is straight forward:

$$V_1 = S_1/f_1 = 17.35/2 = 8.68 \tag{B.29}$$

And is carried out for the other factors as well. Same for the variance of error term:

$$V_e = S_e/f_e = 0.13/20 = 0.0065 \tag{B.30}$$

The pure sum of squares for CC:

$$S_1' = S_1 - f_1 V_e = 17.35 - 2(0.0065) = 17.34 \tag{B.31}$$

And then the percent contribution to the variance can be calculated:

$$P_1 = S_1'(100/S_T) = 17.34(100/18.04) = 96.20 \tag{B.32}$$