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# ***CHAPTER 1***

## ***Introduction***

Great emphasis has been placed on global warming, environmental pollution and the ever depleting fossil fuel resources. These issues have created concerns and major global issues various methods have been suggested to address the undesired effects. Energy sources, such as ethanol and biodiesel which are renewable, have lower carbon dioxide emissions and are biodegradable have been suggested as alternatives to fossil fuel sources (Kasteren et al. , 2006). Biodiesel fuel can be produced from a variety of feedstock, particularly from vegetable oils. These are converted into biodiesel through trans-esterification, which utilizes an alkaline catalyst in the presence of an alcohol (Phan et al., 2008). The process produces fatty acid methyl esters (FAME) at atmospheric pressure and temperature between 50 and 60 °C. Glycerol is produced as a by -product which can be used in the soap making industry (Marchetti et al., 2011).

The direct discharge of waste cooking oil into drainage systems can cause water and soil pollution and disturb the aquatic ecosystem, it may also be detrimental to human health. Waste cooking oil instead of being discharged into the drain, is collected and used as feedstock for biodiesel production. This is the most appropriate method of making use of waste cooking oil as recycling it further for frying purposes has been shown to enhance the chances of cancer due to the toxic contents produced when the oil is oxidized. The use of waste cooking oil as a feedstock has been favored as other feedstock are in direct competition with food crops which have increased the cost of food prices. Research has proven that biodiesel is more environmentally friendly than conventional diesel as it essentially contains traces of sulphur or aromatic compounds, whereas diesel contains about 500 ppm of sulphur and 20-40 % aromatic compounds (Marchetti et al., 2011). It is necessary to determine the quality of the biodiesel produced and to determine if the process is financially worthwhile.

### ***1.1 Project Motivation***

In view of the growing concerns over the use of vegetable oils as feedstock for biodiesel which is part of the food chain, waste cooking oil is seen as the ideal alternative feedstock as it can be sourced from restaurants, schools, industry and homes. Secondly, the price of

waste cooking oil is 2-3 times less than that of vegetable oils (Phan et al. , 2008).

*Table 1.1: World production of Biodiesel Avinash et al (2013)*

<b>Year</b>	<b>Production in millions of gallons</b>
1991	3
1992	23
1993	38
1994	75
1995	108
1996	144
1997	151
1998	155
1999	190
2000	213
2001	265
2002	383
2003	510
2004	614
2005	995
2006	1710
2007	2775
2008	4132
2009	4699
2010	4893
2011	5651
2012*(Projection)	5670

Political instability in many oil producing regions has been one of the causes of increase in the price of crude oil. This has driven the global search for alternative sources, including biodiesel. Table 1.1 shows the world biodiesel production from 1991 to 2012. The Table show a remarkable rise in biodiesel production during this period. Market share of biodiesel in South Africa was about 1 billion litres in 2007 (Avinash et al., 2013). Government subsidies and imposed legislation on the environment over the years have driven the financial feasibility of biodiesel production in South Africa.

In addition, the need to obtain biodiesel of high quality and at minimal cost has driven the idea of using membrane reactors. In this study, membrane the reactor functions as an

extractor to overcome the equilibrium limitation of biodiesel production and hence increase the conversion of waste cooking oil to free acid methyl esters. Optimization of the biodiesel production is vital to understanding the influence of parameters that affect the yield of biodiesel.

## **1.2 Project Aim**

Biodiesel production using membrane reactors is a new concept that is still being tested for optimal conditions. Therefore, opportunities exist to find the best combination between catalyst and membrane for optimal reactor performance. Design and optimization through Response surface modelling (RSM) will be required to obtain the optimal conditions for commercial small-scale production. A process is also required to simultaneously overcome the shortcomings of waste cooking oil and the use of homogenous catalysts with the aid of membrane technology and heterogeneous catalysts.

## **1.3 Project Objectives**

The objectives of the study are:

- a. To determine the effect of temperature, circulation rate and catalyst concentration on biodiesel production.
- b. To determine influence of the operating conditions above on the optimal yield of biodiesel.
- c. To determine the feasibility of using heterogeneous catalyst as a substitute for homogeneous catalyst by evaluating its recovery and reusability.
- d. To determine the efficiency of a membrane reactor by increasing the yield of biodiesel.

## **1.4 Problem statement**

- a. Biodiesel production at non-optimal conditions is not efficient.
- b. Conventional homogeneous catalysts though efficient, are costly due to further purification processes required downstream as compared to heterogeneous catalysts.
- c. Batch processes have mass transfer and equilibrium limitations.

### ***1.5 Research Questions***

1. Can biodiesel production be optimized?
2. Can heterogeneous catalyst be recovered and reused in biodiesel production?

### ***1.6 Project Scope***

This study covers the optimization of biodiesel production using response surface methodology. It also verifies whether this method is sufficient for the optimization. The study also investigates the effect of temperature, circulation rate and catalyst concentration on biodiesel production. In addition, the study examines the reusability of the heterogeneous catalyst used during the trans-esterification stage.

# **CHAPTER 2**

## **Literature review**

## **2.1. Biodiesel**

Biodiesel is a mono-alkyl ester of fatty acids derived from renewable feedstock such as vegetable oils. The prefix “bio” indicates the biological origin of biodiesel in contrast with conventional diesel. In appearance it is a clear liquid with a light to dark yellow colour, with a boiling point of 200°C, flash point between 145-175°C and a distillation range of 195-325°C. It is insoluble in water and has a soapy odour.

Various methods such as micro emulsification, pyrolysis and trans-esterification have been used in the production of biodiesel from vegetable oil. The widely used method is transesterification, which will also be used in this project. The process involves reacting alcohols and vegetable oils in the presence of a catalyst to produce biodiesel and glycerol (Araujo et al. , 2012). Methanol is the most commonly used alcohol as it is less costly and helps produce methyl esters with unique advantages over other non-renewable fuels, such as being a clean engine fuel. The factors which affect the trans-esterification process significantly are the reaction temperature and the molar ratio of alcohol to vegetable oil. Several oils such as sun flower oil, palm oil, soybean oil, rapeseed oil, jatropha seed oil and waste cooking oil can be used (Avinash et al., 2013).

## **2.2. Properties of Biodiesel**

In comparison to fossil based diesel, biodiesel is superior to fossil based diesel as it is renewable, biodegradable non-toxic, has low emissions and sulphur content, high lubricity and better flash point and ignition properties as shown in Table 2.1 (Yaakob et al., 2012).

*Table 2.1: Comparison of biodiesel and commercial fuel diesel Yaakob et al (2012)*

<b>Fuel Property</b>	<b>Units</b>	<b>Biodiesel from WCO</b>	<b>Commercial diesel fuel</b>
Kinematic Viscosity	mm <sup>2</sup> /s	5.3	1.9-4.1
Density	kg/L	0.897	0.075-0.4
Flash point	K	469	340-358
Pour point	K	262	254-260
Cetane Number		54	40-46
Ash content	%	0.004	0.008-0.01
Sulphur Content	%	0.06	0.35-0.4
Carbon residue	%	0.33	0.35-0.55
Water content	%	0.04	0.02-0.05
Higher heating value	MJ/kg	42.65	45.62-46.48
FFA	mgKOH/g	0.1	-

## **2.3. Biodiesel use**

### **2.3.1. Advantages of biodiesel**

#### **Environmental Benefits**

Biodiesel contains virtually no sulphur or aromatics according to the United States Biodiesel organization. Its use in a diesel engine results in a reduction of unburnt hydrocarbons, carbon monoxide and particulate matter. Biodiesel is a non- toxic compound, the acute oral LD<sub>50</sub> (lethal dose) is greater than 17.4g/kg body weight. Sodium chloride is almost ten times more toxic by comparison. Biodiesel degrades about 4 times faster than petroleum diesel; blending biodiesel with petroleum diesel accelerates its biodegradability (Atabani et al., 2012).

#### **Energy Security benefits**

With highly fluctuating global oil prices and agricultural commodity prices approaching record lows, a great deal can be done to enhance the energy security concerns. Biodiesel can be produced from existing industrial production facilities and used in conventional diesel engines. Particularly for countries that import substantial amount of oil such as South Africa, local production of biodiesel will result in import substitution of foreign

oil with balance of payment savings (Avinash et al., 2013).

### **Economic Benefits**

According to the United States department of Energy, by the year 2009 biodiesel was supporting more than 50000 jobs adding 4.287billion dollars to the gross domestic product (US Department of Energy., 2013). In South Africa, this industry is set to benefit the country immensely as government stepped in by introducing a 40% bio-fuels levy in 2006 and the strict legislation on fuel specifications is driving the growth of bio-fuels industry. This has resulted in the growth of the agricultural sector and created employment, particularly in the rural areas (SA Department of Energy., 2013).

### **Safety benefits**

The flash point of biodiesel is a little over 130°C which is well above the flash point of petroleum based diesel fuels of around 52°C. Research has shown that biodiesel blends have higher flash points and the flash point temperature increases with increase in the amount of biodiesel in the blend. Thus, biodiesel blends are safer to store, handle and use than the conventional petroleum based fuels (Atabani et al., 2012).

### **Lubricity benefits**

Diesel fuel injection equipment is highly dependent on diesel fuel as a lubricant. Moving parts are lubricated by the fuel itself as it moves through the pumps. Low lubricity fuel may cause high wear and scarring. Blending of diesel fuel with biodiesel eliminates the inherent variability associated with use of additives (Atabani et al., 2012).

### **2.3.2. Disadvantages of biodiesel**

- Biodiesel has a 12% lower energy content compared to mineral diesel resulting in higher fuel consumption when biodiesel is utilized. In addition biodiesel has a higher cloud point, pour point and higher nitrogen oxide emissions than diesel. It also contains lower volatilities that cause the formation of deposits in engines due to incomplete combustion characteristics (Atabani et al., 2012).
- Biodiesel has relatively a higher viscosity, than that of diesel and lower volatility than diesel and thus requires higher injector pressure.
- Oxidative stability of biodiesel is lower than that of diesel. It can be oxidized into

fatty acids in the presence of air causing corrosion of fuel tank, pipe and injector.

- Use of biodiesel in internal combustion engine may lead to engine durability problems including injector cocking, filter plugging and piston ring sticking.
- Since more than 95% biodiesel is made from edible oils; economic problems are bound to arise.
- The trans-esterification process is expensive which increases the cost of the fuel produced from vegetable oils. Furthermore separation of fatty acids from the mixture is expensive. In addition waste from the trans-esterification process poses an environmental hazard as it still has to be discharged.

## **2.4. Raw Materials**

### **2.4.1 Alcohol type**

The correct choice of alcohol used for the formation of biodiesel reaction is of prime importance. Primary and secondary monohydric aliphatic alcohols (containing 1-8 carbon atoms) are often used. However, methanol and ethanol are the most commonly used alcohols. Methanol is widely used due to its ease of affordability and high reactivity compared with ethanol (Yaakob et al., 2012). Methanol is produced from methane found in natural gas. Thus the disadvantage of using methanol is that as a petroleum based alcohol it is more detrimental to the environment (Moser et al., 2010).

Ethanol has the advantage of being produced from renewable feed sources such as sugar cane and maize. Besides in some regions the ethanol production method is cheaper than that of methanol. In addition, ethanol is more soluble in oil than methanol as it is less polar, which enhances mass transfer during the trans-esterification reaction (Moser et al., 2010). Furthermore, the base catalyzed production of fatty acid ethyl esters (FAEE) is more problematic than that of FAMES. For the methanolysis reaction, a phase, which is less rich in glycerol is formed and can easily separate when the mixture is stationary as compared to the ethanolysis reaction. In the ethanolysis reaction these emulsions are much more stable and therefore complicate biodiesel purification in the subsequent stages (Zhou et al., 2003). Biodiesel produced from ethanol has a lower pour and cloud points than that produced using methanol. This increases the storage ability of biodiesel. Butanol is completely miscible in

vegetable oils and animal fats as it is far less polar, thus the trans-esterification reaction is monophasic throughout and has no mass transfer limitations. However the drawback is that reverse reactions are more likely to occur as all materials are in close contact throughout the reaction.

#### 2.4.2 Waste Cooking oil

Since waste cooking oil is composed of various components it is important to know exactly the composition of the substances in order to verify whether a pretreatment stage is required or not. Table 2.2 shows typical physical and chemical properties of waste cooking oil. The chemical and physical properties used in this study are shown in Appendix A.

*Table 2.2: Physical and chemical properties of Waste cooking oil (Yaakob et al., 2012)*

<b>Property</b>	<b>Units</b>	<b>Value</b>
Palmitic acid content	wt%	8.5
Stearic acid content	wt%	3.1
Oleic acid content	wt%	21.2
Linoleic acid content	wt%	55.2
Linolenic acid content	wt%	5.9
others	wt%	4.2
Water content	wt%	1.9
Density	cm <sup>3</sup> /g	0.91
Kinematic Viscosity	mm <sup>2</sup> /s	4.2
Saponification value	mgKOH/g	207
Acid value	mgKOH/g	3.6
Iodine number	gl <sup>2</sup> 100g <sup>-1</sup>	83
sodium content	mg/kg	6.9
Peroxide value	mg/kg	23.1

#### 2.5. Pretreatment of Waste Cooking Oil

Waste cooking oil (WCO) contains unwanted substances that may interfere with the trans-esterification process and high free fatty acid concentration which can lead to saponification. Various pre-treatment methods have been utilized to overcome these problems, acid

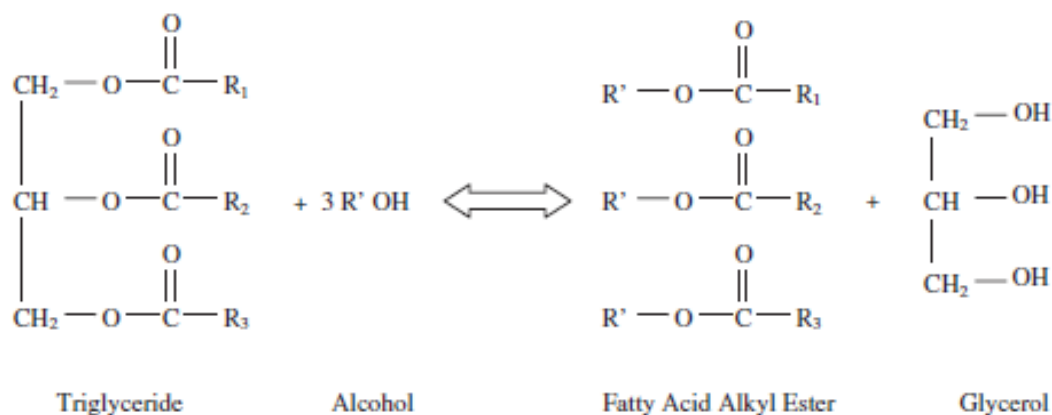
esterification with methanol and sulphuric acid, ion exchange resins, neutralization with alkalis followed by soap separation using a decanter are amongst some of the methods used (Talebein-Kiakaleiah et al., 2012). Whereas to remove water the waste cooking oil sample can be heated to a temperature where the water evaporates often a temperature above 100°C is used. Industrially vacuum distillation is the most appropriate method. Suspended solids, lipids and other impurities can be washed away with hot water or removed by centrifugation and paper filtration.

## ***2.6. Methods for Biodiesel production***

There has been worldwide effort to develop and improve vegetable oil properties in order for them to be comparable or similar to those of mineral diesel fuel. The problems that have been associated with these oils are high viscosity, low volatility and polyunsaturated characteristics. Transesterification methods are outlined below which are used to convert oils to esters which have better fuel properties.

### ***2.6.1 Trans-esterification***

In this process the glycerol in the triglycerides is replaced with a short chain alcohol. The process basically involves 3 stages of reversible reactions: initially triglycerides are converted into diglycerides, which in turn are converted into monoglycerides, then finally monoglycerides are converted to glycerol. Fig 2.1 shows the overall trans-esterification reaction (Yaakob et al., 2012).



*Figure 2.1: Reaction for formation of methyl esters (Shuit et al., 2012)*

Three esters are produced from a single triglyceride molecule. The esterification reaction can be catalyzed by either homogeneous catalysts or heterogeneous catalysts. The homogeneous catalyzed processes have been proven to require less time and have a lower cost than enzyme catalyzed processes. The role of the catalyst is to split the oil molecules and ethanol/methanol can thereafter combine with a separate ester to produce the alkyl ester (Yaakob et al., 2012). The use of alkali catalysts though is limited when there is a high content of free fatty acids as these will neutralize the catalyst. However, alkali catalyst is preferred as it results in a higher yield of biodiesel and high purity of products. As these reactions are reversible, excess alcohol is used to shift the equilibrium to the reaction producing the desired product.

### **2.6.2 Enzyme Catalyzed Trans-esterification**

Recent research has shown that enzymatic catalyst (immobilized lipase) can be successfully used for biodiesel production (Talebian-Kiakalaieh et al., 2013). The advantages of using this process are: (1) no by product is formed, (2) its products can be easily removed, (3) high reusability of the catalyst without need for separation step and (4) lower operating temperature. In addition the enzymatic reaction is insensitive to water and FFA content in waste cooking oil. The disadvantages of the process are: (1) it is expensive, (2) it takes a long reaction time for a substantial yield, (3) the low product yield in comparison to the alkaline catalyst (Shuit et al., 2012). Previous research has shown that the enzymatic process requires 24hrs for a biodiesel production of 90% yield. Besides the enzyme requires specific reaction conditions because the

denaturation of the enzyme and its deactivation as a result of the impure feedstock could decrease its efficiency (Shuit et al., 2012).

### ***2.6.3 Homogeneous Catalyzed Trans-esterification***

Base catalysts are the mostly utilized as they have higher catalytic efficiency, lower cost and lower reaction temperature and pressure. The drawback of base catalysts is that they may react with free fatty Acids (FFA) in the feedstock to form soap by a saponification reaction. Through various experiments and research these catalysts might be more suitable for waste oils with higher free fatty acid content. The disadvantage though will be that the reaction will be slower and also require excess alcohol. The catalyst loading significantly depends on the type of oil used in the trans-esterification process and type of catalyst (Talebein-Kiakaleiah et al., 2012). The optimum load of alkali catalyst, for instance NaOH is approximately 1.0wt%, whereas for acid catalysts the load can be as high as 4wt% (Phan et al., 2008).

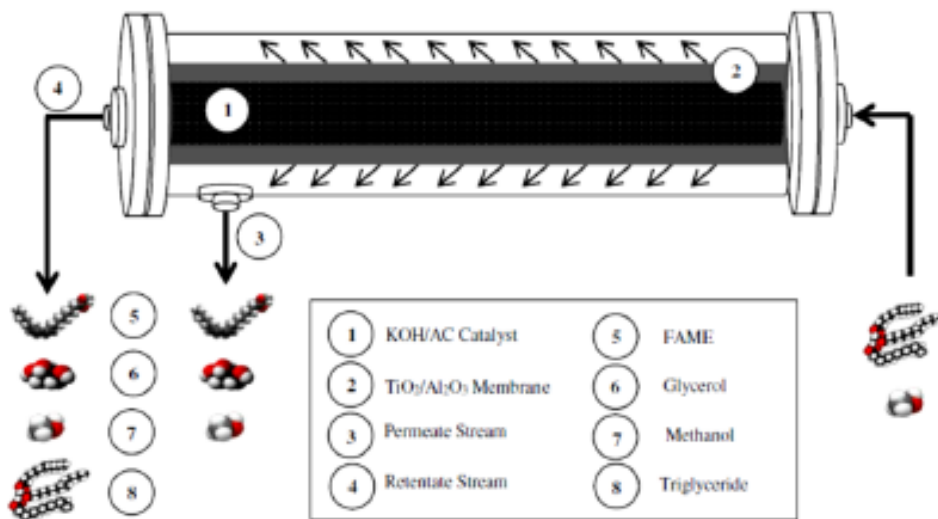
## ***2.7. Concept of Membrane reactors***

The International Union of Pure and Applied Chemistry (IUPAC) defines a membrane reactor as a device that combines reaction and separation in a single unit. Ertl et al (2008) state that a membrane reactor can be classified by the reactor design (extractor, distributor or contactor), the membrane material (inorganic, organic or porous) and whether the membrane is inert or catalytic. Membrane reactors function as an extractor to overcome equilibrium limitations in equilibrium limited reactions. In this work, the membrane reactor functions as an extractor to overcome the equilibrium limitation of biodiesel production and hence increase the conversion of WCO to fatty acid methyl esters (FAME). Membrane reactors have a high available surface area per unit volume, intensify the contact between reactants and catalyst at the same time separating products from the unreacted components (Atadashi et al., 2011).

### ***2.7.1 Application of membranes for the Production of biodiesel***

Inorganic membranes which can be metallic, ceramic, zeolite or carbon based can be used for catalytic inert membranes, in which the catalysts are either added to the reactants or packed

within the membrane (Shuit et al., 2012). These membranes are preferred as they can withstand higher temperatures, high acidic and basic conditions. This membrane type in biodiesel production is essential in selectively allowing FAMES, alcohol and glycerol to permeate as they have small molecular sizes whilst retaining the larger emulsified oil droplets as shown in Figure 2.2.



*Figure 2.2: Base trans-esterification reaction in a packed bed membrane reaction*

Thus no glycerides are found in the permeate stream. The advantage of this process is that removal of the products from the reactor will ensure that the desired reaction is favoured according to Le Chateliers principle. According to Baroutian et al (2010) the membrane is beneficial since it blocks unreacted triglyceride molecule and impurities as they have larger particle size.

### **2.7.2 Membrane life-time and fouling in biodiesel production**

Catalytic inert membranes are subject to harsh operating conditions which can be severely acidic or basic. Thus it is imperative that for these processes a membrane with high resistance to

degradation and corrosion resistance be utilized (Shuit et al., 2012). Dube et al (2008) state that carbon and ceramic membranes are effective in resisting such harsh conditions and even after 10 months of operation they will still be functional without any noticeable damage.

Fouling is a major challenge in membrane processes. This is due to accumulation and deposition of solutes or particles in the feed onto the membrane surface and into the membrane pores (Shuit et al., 2012). A high alcohol content results in the formation of small glycerol particles which can lead to fouling.

### ***2.7.3 Advantages of catalytic membrane reactors in biodiesel production***

#### ***Environmentally friendly process***

The use of catalytic membranes for biodiesel production requires low energy consumption which makes it an environmentally friendly process. The operating conditions are not severe as the highest temperature reported is 70°C, which is similar to the conventional homogeneous transesterification process, but significantly lower than that of heterogeneous and supercritical transesterification (Shuit et al., 2012). In addition, the catalytic membrane reactor could curtail the amount of chemicals required for the process which could be harmful to the environment. Lower catalyst concentrations give substantial biodiesel yield in catalytic membrane reactors as compared to other methods. The amount of catalysts in the catalytic membrane reactor is 0.05% lower for the basic catalyst and 2% lower for the acid catalyst (Dube et al., 2007).

#### ***Lower investment cost***

In the catalytic membrane reactor the catalytic and separation process are combined unlike in the conventional homogeneous process. The integration of the two processes reduces the number of operating units as well as the process stages thus leading to reduction in size and complexity of the plant (Dittmeyer et al., 2004). Besides, a catalytic membrane reactor has the advantage of not requiring a decantation stage to separate the two phases obtained after the reaction. Furthermore the catalytic membrane process does not require the inter stage temperature and pressure changes required in biodiesel production such as in the supercritical technology in which the mixture needs to be cooled before separation. This entails that the energy and number of heat exchangers required for the process can be reduced (Shuit et al., 2012).

## ***2.7.4 Influence of contaminants on biodiesel production***

### ***Water***

Water is a major source of fuel contamination and has two major problems. Water causes corrosion in the engine fuel system, the major direct form of corrosion is rust. The other major problem is that it contributes to microbial growth. Bacteria can grow between the interface of the biodiesel and water phases. Water can be removed from the biodiesel produced by a vacuum flash process, decanting or evaporation (Van Gerpen et al., 1996).

### ***Glycerol***

Glycerol is produced as a by-product during the esterification process. Glycerol is detrimental as it causes deposit formation in the engine (Van Gerpen et al., 1996).

## ***2.8. The Effect of Reaction parameters in Biodiesel production***

### ***2.8.1 Alcohol to oil ratio***

The alcohol/ oil ratio is particularly important in ensuring that the system maintains a two phase system. At high alcohol/oil ratios it takes more time for the mixture to be a homogeneous liquid phase. The stoichiometry of the reaction requires 3 moles of alcohol and 1 mole of triglycerides to form 3 moles of fatty acid ester and 1 mole of glycerol. To achieve better results a higher molar content of alcohol is used in order to shift the equilibrium to the desired product. Trans-esterification is low at the ratios of methanol/oils below 5:1 (Shuit et al., 2012). A volume ratio of 1:1 is usually used. The ratio is also subject to the type of catalysts that are to be used. For instance the optimal ratio for a waste cooking oil feedstock is 4.8 in the presence of NaOH catalyst while it may be up to 250 in the presence of acidic catalysts. Increasing the ratio has also shown to aid the settling process. According to Phan et al (2008) the settling time took only 30mins for the molar ratios of 7:1 and 8:1.

### ***2.8.2 Reaction Temperature***

The transesterification reaction is endothermic and according to Le Chateliers principle it will be favored by a high temperature. According to Baroutian et al (2010) the most desirable range of temperature is between 50-70°C. Besides, higher temperatures increase solubility of unwanted materials in the product stream resulting in challenges in the separation process. In

addition, as a result of mass transfer limitations this reaction temperature should not exceed the boiling point of methanol of 64.5°C. The two phase system between the reactants, oil and methanol is necessary within the membrane to obtain a desirable yield. According to Yaakob et al (2012) the ideal reaction temperature is often near the boiling point of alcohol. Besides, the reaction temperature is also dependent on the chemical and physical properties of the type of oil that is used. Based on the aforementioned, a temperature range of 49-65°C was chosen for this work.

### **2.8.3 Concentration of catalyst**

The catalyst concentration speeds up the conversion of oil to fatty acid methyl ester (FAME), an increase in catalyst concentration favours the conversion of triglycerides to FAMES. It was demonstrated that the membrane reactor could drive the reversible trans-esterification toward the (FAME) product, even at very low catalyst concentration of 0.05 wt% (Cheng et al., 2012). When high methanol oil ratios are used the emulsion of oil in the methanol layer leads to mass transfer limitations (Shuit et al., 2012). A high catalyst concentration will be necessary to attain complete conversion of oil (Dube et al., 2007). Optimum catalyst loading for alkali catalysts is approximately 1wt% (Yaakob et al., 2012). Considering data from literature reviews the concentration of KOH which is utilized for high biodiesel yields is in the range of 0.5-1.5 wt% (Phan et al., 2008). Therefore a range of 0.5-1.5wt% of catalyst concentration was investigated in this study based on previous research findings.

### **Circulation flow rate**

Baroutian et al (2011) and Dube et al (2007) obtained a significant increase in conversion of oil to fatty acid methyl ester when the flow rate of reactants was increased which in this study is referred to as the circulation flow rate. According to Shuit et al (2012) there has been no detailed study on the effect of the reactant flow rate on biodiesel production in membrane reactors. Circulation of the reactants is essential in enhancing the transesterification reaction due to the increased mixing intensity of oil and methanol (Kumar et al., 2010). In addition the circulation flow rate allows more efficient permeability through the membranes (Shuit et al., 2012). For this study the chosen range for the circulation flow rate was limited by the maximum speed of the peristaltic pump that was available for use.

## **2.9 Analysis and Purification methods**

### **2.9.1 Purification of biodiesel**

The products of the transesterification reaction are not pure and thus have to be processed in order to meet international or desired standards. The crude esters consist of excess alcohol, unreacted oil, catalyst residue, soap and glycerol. The purification stage is very crucial and various methods have been developed to achieve this. These include gravitational settling, centrifugation, decantation and funneling (Atadashi et al., 2011). The washing process is often carried out 3 times at 50 °C in separate funnels until washings are neutral. Finally a dry washing process can be utilized with magnesium sulphate or molecular sieves and then filtered under vacuum. Other methods which can be used are dry washing with silica gel to remove traces of water and wet washing (Marta et al., 2011).

### **2.9.2 Analysis of Biodiesel produced from Waste Cooking Oil**

Several analytical methods have been used to determine the quality of the biodiesel produced from WCO. These include gas chromatography, high performance liquid chromatography (HPLC) thin layer chromatography (TLC) and proton nuclear magnetic resonance (Yaakob et al., 2012). Gas chromatography is the widely used method with either nitrogen or helium is used as the carrier gas. The peaks obtained from the GC are compared with those from the pure standard product to determine the weight and composition of the various elements in the produced biodiesel (Diyauddeen et al., 2012).

# **CHAPTER 3**

## **Experimental**

### 3.1. Catalyst Preparation

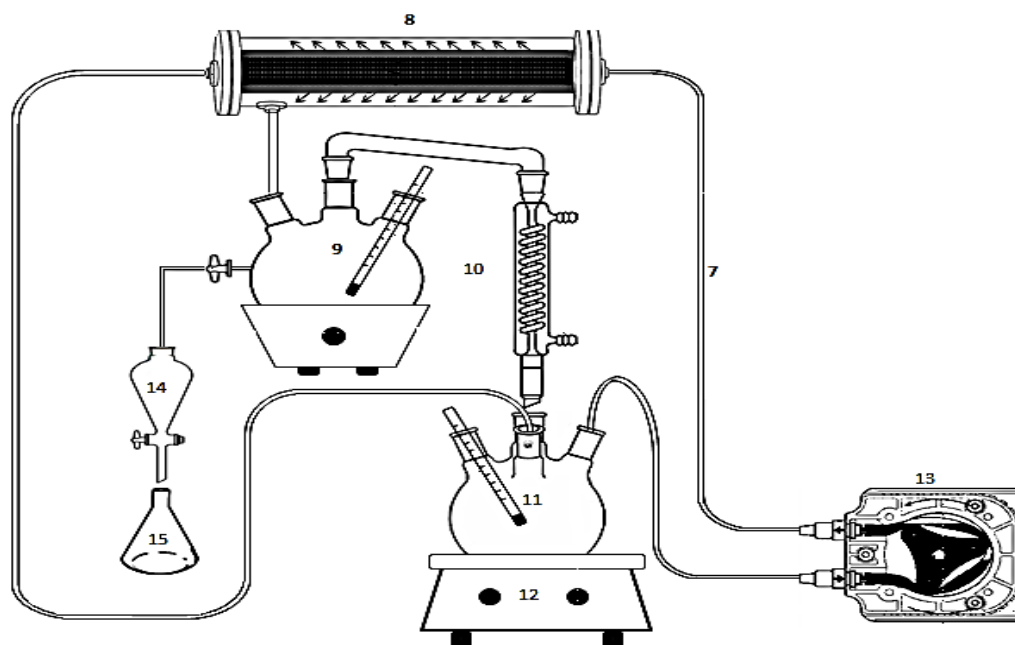
Zirconium oxy-chloride  $ZrOCl_2 \cdot 8H_2O$  and Ammonium sulphate  $(NH_4)_2SO_4$  were used for the preparation of the catalyst, sulphated zirconia  $NH_4SO_4$  which is used for the pretreatment stage. A solvent free method as described in Sun et al (2004) was utilized.  $ZrOCl_2 \cdot 8H_2O$  and  $(NH_4)_2SO_4$  with a molar ratio of 1:6 were ground in a mortar for 20 minutes at room temperature. After placement for 18 hours at room temperature, the mixture was calcined for 5 hours at  $600^\circ C$ . According to Sun et al (2004), the resulting zirconia has a high surface area ( $165-193 \text{ m}^2/\text{g}$ ) and exhibits uniform pore distribution aggregated by zirconia nanoparticles. These particles exhibit much higher activity than conventional sulfated zirconia. For the transesterification stage, activated carbon was sieved to a size range of 550 to  $810 \mu\text{m}$ . Thereafter it was washed with deionized water to remove fines and dirt, oven dried at  $100^\circ C$  for a day, then allowed to cool. A solution of KOH was prepared by dissolving KOH in distilled water. This solution was mixed with activated carbon, then agitated at ambient temperature for 24 hours. The amount of KOH adsorbed was measured by gravitational method. Table A4 in Appendix A shows the loading content of the potassium hydroxide on the activated carbon based on the initial weight of activated carbon which is 34 wt%.

*Table 3.1: Equipment used in the experiment, numbered as shown in the diagram below*

Apparatus	
7. Chemical Resistant pipe	11. 3 neck round bottom flask
8. Membrane Reactor	12. Magnetic heater
9. Round neck bottom flask	13. Peristaltic pump
10. Liebig Condenser	14. Decanter
	15. Volumetric flask

### 3.2 Experimental Setup

Reactants for the trans-esterification reaction were prepared in a four neck round bottom flask (12) placed on a magnetic stirrer. A  $\text{TiO}_2/\text{Al}_2\text{O}_3$  tubular membrane enclosed in PVC housing (from Atech Innovations GmbH Germany) was used as the membrane reactor. The KOH packed catalyst was maintained within the membrane by incorporating sieve plates ( $150\mu\text{m}$ ) at the inlet and outlet of the membrane. Reactor design shown in figure 3.1 below was adapted from Baroutian et al (2010). The specifications for the reactor are as follows; length 40cm inner diameter 1.6cm, outer diameter 2.54cm, filtration surface area  $0.0201\text{m}^2$ . A pore size of  $0.05\mu\text{m}$  was selected to ensure the retention of oil molecules within the membrane.



*Figure 3.1: Experimental setup adapted from Baroutian et al (2010)*

### **3.3 Procedure**

#### **Free fatty acid content test**

Titration solutions and pH indicator were prepared for the FFA titration test. The pH indicator was made by adding 0.05g of phenolphthalein to 50ml of 95% pure ethanol and diluting it to a 100ml solution with distilled water. Thereafter the titration solution was made by adding 1g of

the NaOH powder to one litre of distilled water. The titrate was loaded into a burette and held at in place at eye level, using a clamp and retort stand.

The test procedure required the addition of 1ml of sample to the beaker filled with 10ml of 99% pure isopropyl alcohol. Thereafter two drops of the pH indicator were added to the beaker. Measured amounts of titrate were added to the sample beaker while continuously stirring until a colour change to pink/purple was observed. The recorded volume of KOH solution required to neutralize the sample was used in equation 3.0 below to calculate the acid value and subsequently the %FFA (Ding et al., 2012).

$$\text{Acid value} = \frac{kxVxC}{M} \quad (\text{Equation 3.0})$$

Where,

K= 56.1 which is an acid value constant for cooking oil

V= Volume of titrate required to neutralize the sample (ml)

C= Concentration of the titrate solution (g/ml)

M= mass of sample used (g)

Two runs were done for each set of conditions thereafter the packed catalyst was replaced after removing it and flushing the system for 30 minutes with pure methanol. Appendix E shows the quantities of oil, methanol and biodiesel used for each run.



*Figure 1.2: FFA test strips*

Each of the strips has four bars as shown in Figure 3.2, which can be used to evaluate the colour response to FFA concentration. The sample was warmed to 40°C which the functional temperature for the usage of the test strips. Using a tong, one test strip was removed before resealing the container. The strip was then placed in the sample for ten seconds while ensuring that all four bars were covered. The strips were given an hour to infuse after which the number of bars that changed to a yellow colour were recorded.

The waste cooking oil was treated using sulphated zirconia. FFA content of the raw waste cooking oil (RWCO) and treated WCO were tested, the results of which are shown in Appendix B. Prior to use, the membrane system was flushed with methanol to clean the system and ensure there will be no contamination. The activated carbon, loaded with KOH was packed inside the ceramic membrane and held in place using stainless steel attached to the feed and outlet of the tubing. The treated WCO was fed via a peristaltic pump (13) and chemical resistant tubing into reactor. The temperature was limited to a maximum of 65°C due to the boiling point of methanol: methanol bubbles inhibit mass transfer at the interface. Lower temperatures were avoided as they do not favour reaction kinetics (Zabeti et al., 2009). Baroutian et al (2010) chose a reaction time of 60 minutes for the trans-esterification reaction using similar reactants and conditions. Similarly, in this particular work a reaction time of 60 minutes was chosen. The retentate stream consisting of unreacted WCO was recycled to the three neck round bottom flask. The permeate stream was collected in an additional three neck round bottom flask.

Upon completion of the trans-esterification residual reaction mixture of biodiesel, glycerol and methanol was placed in a beaker to allow for the phases to separate. This was crucial to recover

methanol which could be reused in the trans-esterification reaction and biodiesel which had not been separated by the membrane reactor. The biodiesel recovered was not discarded but washed as described in section 3.4 and contributed towards the overall biodiesel yield. It took approximately 20 minutes for the glycerol, biodiesel and methanol phases to separate. This was as a result of the formation of a homogeneous liquid system during the reaction process and methanol contains a polar hydroxyl group which can make the separation process difficult. The WCO: methanol molar ratio of 1:23 ensured that the trans-esterification reaction was favoured as there was excess number of moles of methanol.

### ***3.4 Separation of biodiesel produced***

The residual products were transferred into a decanter where biodiesel is separated from the glycerol by product. After two runs the system was drained and the mixture was poured into a separating funnel (Phan et al., 2008). The ester located in the upper layer was separated by gravity and located in the upper layer. The glycerol, extra methanol and undesired products were in the lower layer and were decanted. The ester layer was there after washed 3 times with a small amount of hot distilled water to ensure the washings were neutral. It was then dried over sodium sulphate and filtered. The conversion of biodiesel was determined as follows

$$conversion (\%) = \frac{m_{ester}}{3x \frac{m_{oil}}{MW_{oil}} x MW_{ester}} x 100 \quad (Equation 3.1)$$

Where  $m_{ester}$  = weight of ester collected (g);  $m_{oil}$  = weight of the oil sample (g);  $MW_{oil}$  = averaged molecular weight of oil sample (Phan et al., 2008).

$$MW_{oil} = 3x \sum_i^j (MW_i x \%m_i) + 38 \quad (Equation 3.2)$$

$MW_i$  = Molecular Weight of fatty acid;  $\%m_i$  = percentage of fatty acid in the raw material;  $MW_{ester}$  = averaged molecular weight of fatty acid ester (Phan et al., 2008).

The yield of biodiesel was determined as follows

$$Biodiesel Yield (mol\%) = \frac{\text{overall moles of esters formed}}{\text{moles of ester that would have been formed if there were no side reactions}}$$

$$Yield (mol\%) = \frac{n_{ester}}{3x \frac{m_{oil}}{MW_{oil}}} \times 100 \quad (\text{Equation 3.3})$$

Equation 3.3 is derived from equation 3.1 which considered the biodiesel in the permeate and that in the retentate.

### ***HPLC test***

The purity of biodiesel was tested using the high performance liquid chromatogram to ensure that what was produced was indeed biodiesel. A mixture of FAMES was purchased from Sigma Aldrich which was used as the standard as well as methanol Chromasolv HPLC  $\geq 99.9\%$  which was used as the solvent. The standard sample was dissolved in methanol to a concentration of 100mg/mL. A Calibration standard of 10 mg/mL was made using the standard sample. Similarly the biodiesel samples were dissolve in methanol to a concentration of 10mg/mL to ensure consistency.

The samples were run in the HPLC for 30 minutes and thereafter the peaks were identified by comparing the retention times to that of the FAMES standards as the components are known. There were similar peaks that were large for the standard and biodiesel samples and other peaks were very small. This was indicative of the high quality biodiesel produced.

## ***3.5 Data analysis***

### ***Response surface methodology***

It is impeccable in science and engineering to be able to link inputs and outputs, the process is generally difficult to comprehend and describe using elemental mathematical models. Tools have been developed which enable more complex modelling and can be used to describe the influence of each variable in the system and also antagonistic relationships between variables in the system. Response surface methodology is one such tool, which basically aims to create empirical models which are able to deduce useful statistical relationships between all the variables in a system based on experimental design. In response surface methodology inputs are called factors or variables and the outputs represent responses that are generated, under connecting action of the factors or variables Myers & Montgomery (2002).

A series of experiments were done in which the input variables are changed to investigate their effect on the output response. The central composite design method was utilized for the experimental design. This design can be used for fitting a 2<sup>nd</sup> order model which significantly improves the optimization process. Whereas, a 1<sup>st</sup> order model is ineffective due to a lack of fit because of interaction between variables and surface curvature. The general second order model is defined as

$$y = \beta_0 + \sum_{j=1}^k \beta_j x_j + \sum_{j=1}^k \beta_{jj} x_j^2 + \sum \sum_{i < j=2}^k \beta_{ij} x_i x_j + \varepsilon \quad (\text{Equation 3.4})$$

Where:  $y$  – Predicted response

$\beta_0$  – Coefficient of intercept

$\beta_i$  – Coefficient of linear effect

$\beta_{jj}$  – Coefficient of quadratic effect

$\beta_{ij}$  – Coefficient of interaction effect

$\varepsilon$  – Term that represents other sources of variability not accounted for by the response function

$x_i$  &  $x_j$  – Coded independent variables

The central composite design was used to fit the second order design, as this method requires less experimental runs compared to the full factorial design method which would require  $3^N$  points where  $N$  is the number of variables. In addition the CCD is effective in describing steady state responses Simate et al (2009). The central composite design CCD consists of  $2k$  factorial points, where  $k$  is the number of factors being studied,  $n_f$  coded as ( $\pm 1$  rotation)  $n_a$  axial points  $[\pm a, 0, 0, \dots, 0], (0, \pm a, 0, \dots, 0), (0, 0, \pm a, \dots, 0), \dots, (0, 0, \dots, \pm a)$  and  $n_c$  central point's  $[0, 0, 0, \dots, 0]$ . A CCD can be made to be rotatable by selecting the appropriate value of  $\alpha$  and for a rotatable CCD,  $\alpha = \pm \sqrt[4]{n_f}$  Myers & Montgomery (2002).

$$n_c \approx 0.8385 \left( 2^{k/2} + 2 \right)^2 - 2^k - 2k \quad (\text{Equation 3.5})$$

Where:  $n_c$  – Replication points

$k$  – Number of factors studied

$$n_f = l^k$$

In this study, the

No. of factors (k) =3 and no of levels (l) =2

Therefore  $n_f = l^k = 2^3 = 8$

$n_a$  = No. of axial points =  $2 \times k = 2 \times 3 = 6$

$n_c$  = No. of central point's = 6

There Z = Total number of design points or total number of runs required =  $n_f + n_a + n_c = 8 + 6 + 6 = 20$

The value of  $\alpha$  shown in table 3.2 is calculated as follows  $\alpha = \pm \sqrt[4]{n_f} = \pm \sqrt[4]{8} = \pm 1.682$

**Table 3.2: Relationship between coded and actual values of the variable (Napier-Munn et al., 2000)**

Code	Actual value of Factor
$-\alpha$	$x_{min}$
-1	$\frac{x_{max} + x_{min}}{2} - \frac{x_{max} - x_{min}}{2\alpha}$
0	$\frac{x_{max} + x_{min}}{2}$
+1	$\frac{x_{max} + x_{min}}{2} + \frac{x_{max} - x_{min}}{2\alpha}$
$+\alpha$	$x_{max}$

$x_{min}$  and  $x_{max}$  are the minimum and maximum values of the actual variable respectively. Table 3.2 shows the five levels of each factor shown in their real and coded values. Thus each parameter being investigated had 5 levels. The choice of real values utilized in this study is explained in section 2.8.

**Table 3.3: Experimental layout and runs for the central composite rotatable design**

Run	Temperature (C)	Catalyst Conc wt( %)	Circulation flow rate (ml/min)	X <sub>T</sub>	X <sub>C</sub>	X <sub>F</sub>	Y <sub>O</sub> (%)
1	49	0.7	14	-1	-1	-1	78.7000
2	61	0.7	14	1	-1	-1	80.8441
3	49	1.3	14	-1	1	-1	83.2404
4	61	1.3	26	1	1	-1	82.3575
5	49	0.7	26	-1	-1	1	80.8441
6	61	0.7	14	1	-1	1	84.6277
7	49	1.3	26	-1	1	1	86.5195
8	61	1.3	26	1	1	1	92.6995
<b>Axial points</b>							
9	45	1	20	-1.682	0	0	78.8261
10	65	1	20	1.682	0	0	92.1950
11	55	0.5	20	0	-1.682	0	81.6008
12	55	1.5	20	0	1.682	0	83.3665
13	55	1	10	0	0	-1.682	80.9702
14	55	1	30	0	0	1.682	91.8167
<b>Centre Points</b>							
15	55	1	20	0	0	0	90.0510
16	55	1	20	0	0	0	90.6816
17	55	1	20	0	0	0	91.6905
18	55	1	20	0	0	0	90.9338
19	55	1	20	0	0	0	91.0600
20	55	1	20	0	0	0	90.3032

Table 3.3 shows the values derived from the relationship shown in table 3.2, with 8 factorial points, 6 axial points and 6 centre points as desired for the central composite method with 3 variables. X<sub>T</sub>=coded Temperature value, X<sub>C</sub> –coded catalyst concentration value, X<sub>F</sub>- coded circulation flow rate value, Y<sub>O</sub>-coded biodiesel yield value.

Previous research on biodiesel production has showed that temperature, catalyst concentration and the WCO/methanol affect the yield of biodiesel. Thus Response Surface Methodology (RSM) and central composite rotatable design have been used in this study to obtain the optimal conditions for the above named parameters.

The coefficients of the regression model were estimated by fitting the experimental results in Appendix E using Mat Lab 2012 software.

## Statistical analysis

RSM is used to fit the regression model to data from a designed experiment. It is important to obtain two or more observations on the output at the same conditions of the independent variables. In this study the experiment was repeated at the same conditions to obtain two observations.

The quadratic model given as equation (3.4) is written in matrix notation (Myers et al., 2009).

$$Y = X\beta + \varepsilon \quad (\text{Equation 3.6})$$

where

$$Y = \begin{bmatrix} y_1 \\ y_2 \\ \vdots \\ y_n \end{bmatrix}, X = \begin{bmatrix} 1 & x_{11} & x_{12} & \dots & x_{1k} \\ 1 & x_{21} & x_{22} & \dots & x_{2k} \\ \vdots & \vdots & \vdots & & \vdots \\ 1 & x_{n1} & x_{n2} & \dots & x_{nk} \end{bmatrix}, \beta = \begin{bmatrix} \beta_0 \\ \beta_1 \\ \vdots \\ \beta_k \end{bmatrix}, \text{ and } \varepsilon = \begin{bmatrix} \varepsilon_0 \\ \varepsilon_1 \\ \vdots \\ \varepsilon_k \end{bmatrix}$$

In general, Y is an  $n \times 1$  vector of the observation is, X an  $n \times 1$  model matrix consisting of the levels of the independent variables expended to model form,  $\beta$  is a  $p \times 1$  vector of the regression coefficients, and  $\varepsilon$  is an  $n \times 1$  vector of random errors.

The equations given above were solved using the method of least squares which is a multiple regression technique. The difference between the observed and the fitted values for the  $i$ th observation  $\varepsilon_i = y_{i,exp} - y_{i,cal}$  is called the residual and is an estimate of the corresponding  $\varepsilon_i$ , where  $\varepsilon_i$  is the residual,  $y_{i,exp}$  is the observed value, and  $y_{i,cal}$  is the predicted value (Simate, 2009).

The criterion for choosing the regression coefficient estimates ( $\beta_i$ ) is that they should minimise the sum of the squares of the residuals, which is often called the sum of squares of the errors ( $SS_E$ ). The  $SS_E$  function by Bas & Bayaci (2007):

$$SS_E = \sum_{i=1}^N \varepsilon_i^2 = \sum_{i=1}^N (y_{i,exp} - y_{i,cal})^2 \quad (\text{Equation 3.7})$$

The residuals may be written as  $\varepsilon = y - X\beta$ , see Equation (3.4). Therefore, the least squares estimated of the elements of  $\beta$  in Equation (3.6) are given by Bas & Boyaci (2007); Myers et al (2009):

$$\beta = (X'X)^{-1}X'Y \quad (\text{Equation 3.8})$$

Where  $X'$  is the transpose matrix of  $X$  and  $(X'X)^{-1}$  is the inverse matrix of  $(X'X)$ . After, the regression coefficients have been calculated, the estimated response equation can be obtained by substituting the coefficients into Equation (3.4).

The difference resulting in the output allows for testing of lack of fit. The test procedure involves partitioning the residual sum of squares ( $SS_E$ ) into two components

$$SS_E = SS_{PE} + SS_{LOF} \quad (\text{Equation 3.9})$$

Where  $SS_{PE}$  is the sum of squares due to pure error and  $SS_{LOF}$  is the sum of squares due to lack of fit. The  $SS_E$  was obtained using analysis of variance ANOVA method (Khuri & Cornell, 1987). This technique was basically used to determine the adequacy of the models. ANOVA is a statistical method that can be used to quantify the significant differences between factors and levels. It compares the magnitude of the estimated effects of factors with the magnitude of experimental error (Keller et al., 2001). The solver technique was used to obtain the optimal parameters for the maximum yield of biodiesel using the quadratic model.

# **CHAPTER 4**

## **Results and Discussion**

A standard titration test was done on the waste cooking oil (WCO) to determine the free fatty acid (FFA) content, as the catalyst is sensitive to FFA content. The FFA content ranged from 0.2-0.56% as shown in Table B1 in Appendix B. According to Charoanenchaitrakool and Thienmethangkoon (2011), the FFA content should be less than 0.5% in the feed material to avoid saponification. Thus the pretreatment stage was necessary for two of the 9 samples tested. The pretreatment process was however conducted for all the samples for consistency. The pretreatment stage was successful in reducing the FFA content to less than 0.5% as shown in table B2 in Appendix B. A thin layer of glycerol was observed upon completion of the esterification process which showed that most of the FFA content had been converted into biodiesel rather than glycerol. There was a higher reduction in the FFA for samples that initially had a high amount of the FFA content as compared to ones with less FFA content. Sample 1 of WCO shown in Table B2, had its FFA content reduced by 0.187% whereas sample 3 with the lowest FFA content had a reduction of 0.057%. This was due to the fact that, for the WCO with higher concentration of FFA, there was a high chance of the reactant molecules colliding, reacting and thus favouring the conversion of the FFA content to glycerol and biodiesel.

The reduction in the FFA content was confirmed using a pH meter. The test results indicate that the pretreatment stage using sulphated zirconia was effective in reducing the FFA content to a value below 0.5%. This stage was essential as the transesterification process was more efficient as it minimized the chances of the saponification side reaction from occurring and consuming of the alkaline catalyst, which would have meant that a higher catalyst concentration would have been required and resulted in difficulty in separating the products.

The distillation process was efficient in the recovery of methanol during the trans-esterification process, unlike conventional methods which lack this step. It was essential as the amount of methanol was kept high to ensure that the trans-esterification reaction was being favoured and this was economical as this meant that no additional methanol was required as the recovered methanol could also be reused for other reactions.

The experimental results obtained indicate that the catalyst concentration, circulation flow rate and temperature all have a positive effect on biodiesel production. These observations confirm the findings of previous research done in this field. Circulation flow rate was the parameter with the major effect on the biodiesel production. A high temperature favoured the reaction and was essential in reducing the reaction time as it speeded up the reaction. It also ensured that a two phase liquid phase system was maintained as transesterification was believed to occur at the surfaces of oil droplets suspended in methanol (Shuit et al., 2012). It took an average of 30 minutes for the separation of the phases in which higher temperatures were utilized, as compared to 15 minutes when lower temperatures were used. This could have been due to the increase in solubility of glycerol and methanol with the esters at higher temperatures. Besides this drawback, the high biodiesel yield at higher temperatures entails that operating at higher temperatures is more sensible. The high yield of biodiesel at higher temperatures is as expected as the transesterification reaction is endothermic and according to Le Chateliers principle high temperatures will favour the production of biodiesel. It was also observed that at higher temperatures the flow of the mixture in the system was easier as there was less fluctuations in the flow rate this could have been as a result of the viscosity of the reduced substances, particularly glycerol which has a high viscosity and will tend to affect the flow once formed.

There was a significant increase in the conversion to FAMES when the circulation flow rate of the mixture was increased. This was evident in all the instances when the flow rate was increased. An increase in the circulation flow rate resulted in increased mixing intensity. Mixing is imperative in the trans-esterification process as oil is immiscible in methanol. Without mixing the trans-esterification reaction will only occur at the interface of the methanol and oil phases which would result in low conversion. As the circulation flow rate was increased the total permeate collected also increased. According to Shuit et al (2012) concentration polarization is a common problem in membrane separation which is due to accumulation of retained solute on the interface. This acts as a barrier and thus the permeate flux is significantly reduced. Thus increasing the circulation flow rate is important for the trans-esterification reaction as the resulting flow will reduce the boundary layer of solute formed.

Upon physical inspection, it was observed that there were no suspended solids nor settled particles and no visible layers in the homogenous phase of biodiesel. This observation confirms that micro porous membranes are effective in separating residual impurities such as glycerol, catalyst, methanol and unreacted waste cooking oil from the desired fatty acid methyl esters. The utilized process has a potential to be effective in integrating reaction and separation which reduces production costs if the process is used on a commercial scale. In addition, the efficiency of the membrane was not compromised since high biodiesel yields were obtained in subsequent experiments. This shows the ceramic membrane is either resistant to the conditions which it is subjected, that is, alkaline and high temperature, or the high temperature was effective in countering any fouling since increased temperatures reduces solution viscosity (Phan et al., 2008).

Appendix E shows the experimental data for all the experiments conducted. Upon repeating the experiment using the same experiment conditions and reusing the catalyst the data shows that the biodiesel yield did not change significantly. This attests that the heterogeneous catalyst can be recycled and reused. The reusability of catalyst has huge implications on the reduction of costs for biodiesel production. In addition, the resulting waste is less as the catalyst is retained in the membrane and this reduces disposal costs.

Table 4.1 shows coefficients of the fitted model obtained. The experimental data used to validate the model is shown in appendix E Whereas the Mat Lab code used to obtain the equation is shown in Appendix C.

***Table 4.1: Coefficients of estimated response equation***

<b><math>\beta</math> terms</b>	<b>Values</b>
0	90.8094
1	2.4683
2	1.6673
3	2.7671
4	2.0138
5	3.0840
6	-1.7017
7	-0.0788
8	1.0878
9	-0.9617

The fitted second order model obtained was

$$: y = 90.8094 + 2.4683x_1 + 1.6673x_2 + 2.7671x_3 - 2.0138x_1^2 - 3.0840x_2^2 + \\ -1.7017x_3^2 - 0.0788x_1x_2 + 1.0878x_1x_3 - 0.9617x_2 \quad \text{Equation 4.1}$$

where:  $x_1$  – is the coded value for temperature

$x_2$  – is the coded value for circulation flow rate

$x_3$  – is the coded value for catalyst concentration

$y$  – is the response (biodiesel yield)

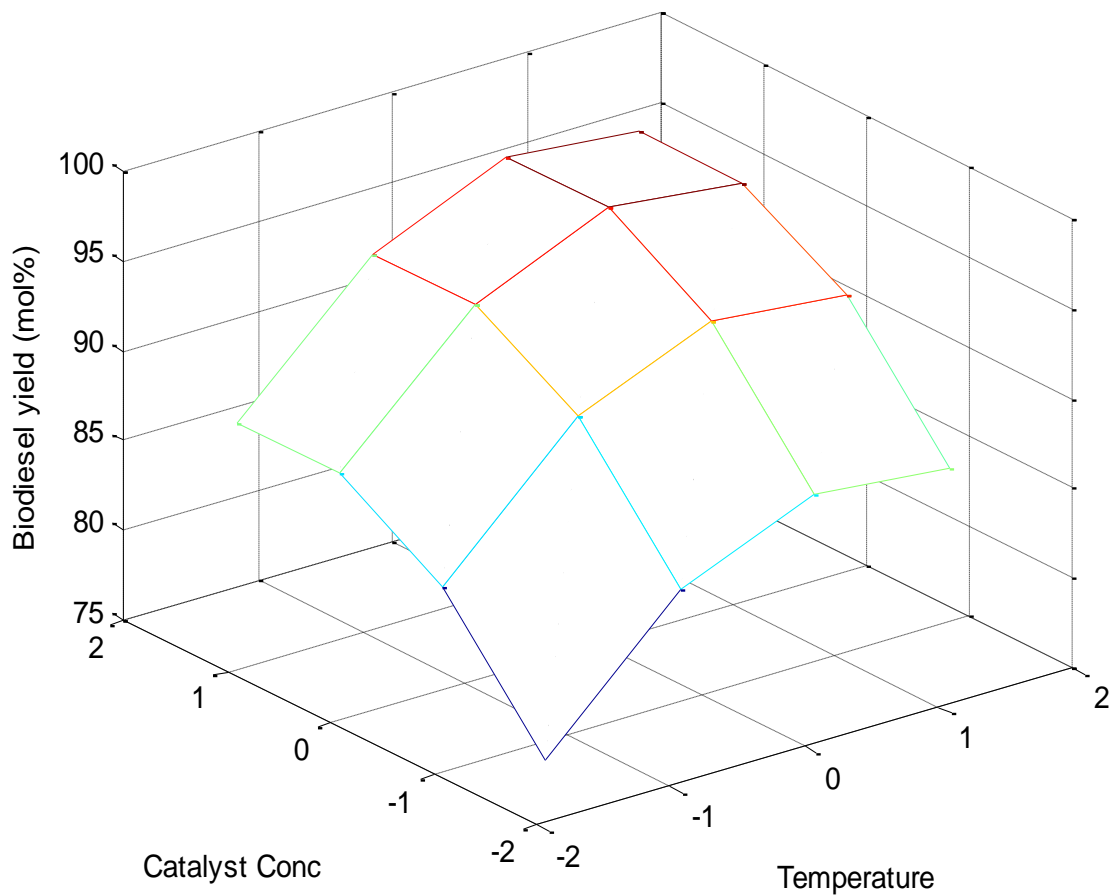
As one of the objectives of this research was to obtain the optimal operating conditions. Equation 4.1 was used to determine the optimal conditions in excel using the Solver optimization method. The response was set at maximum, whilst an iteration of the three parameters was conducted to obtain the desired optimal operating conditions. The optimal conditions are shown in Table 4.2. The reaction time was kept constant at 60 minutes whilst the methanol to oil molar ratio was also kept constant at 23:1.

**Table 4.2: Derived optimal operating conditions**

<b>Variable</b>	<b>Optimal conditions</b>
Temperature ( °C )	58.5
Circulation flow rate (ml/min)	18.78
Catalyst concentration (wt %)	1.24
<b>Biodiesel yield (mol %)</b>	<b>94.03</b>

Three dimensional surface plots of the biodiesel yield were obtained, using the coded values of the parameters and the biodiesel yield. The surface plots show that temperature, reactant flow rate and catalyst concentration have positive effects on the yield of biodiesel. These results are consistent with those obtained by Baroutian et al (2010). According to Yaakob et al (2012) a temperature of 50-70°C is the best temperature range to obtain highest biodiesel yield. The optimal temperature of 58.5°C falls within this range. Furthermore, a catalyst concentration of

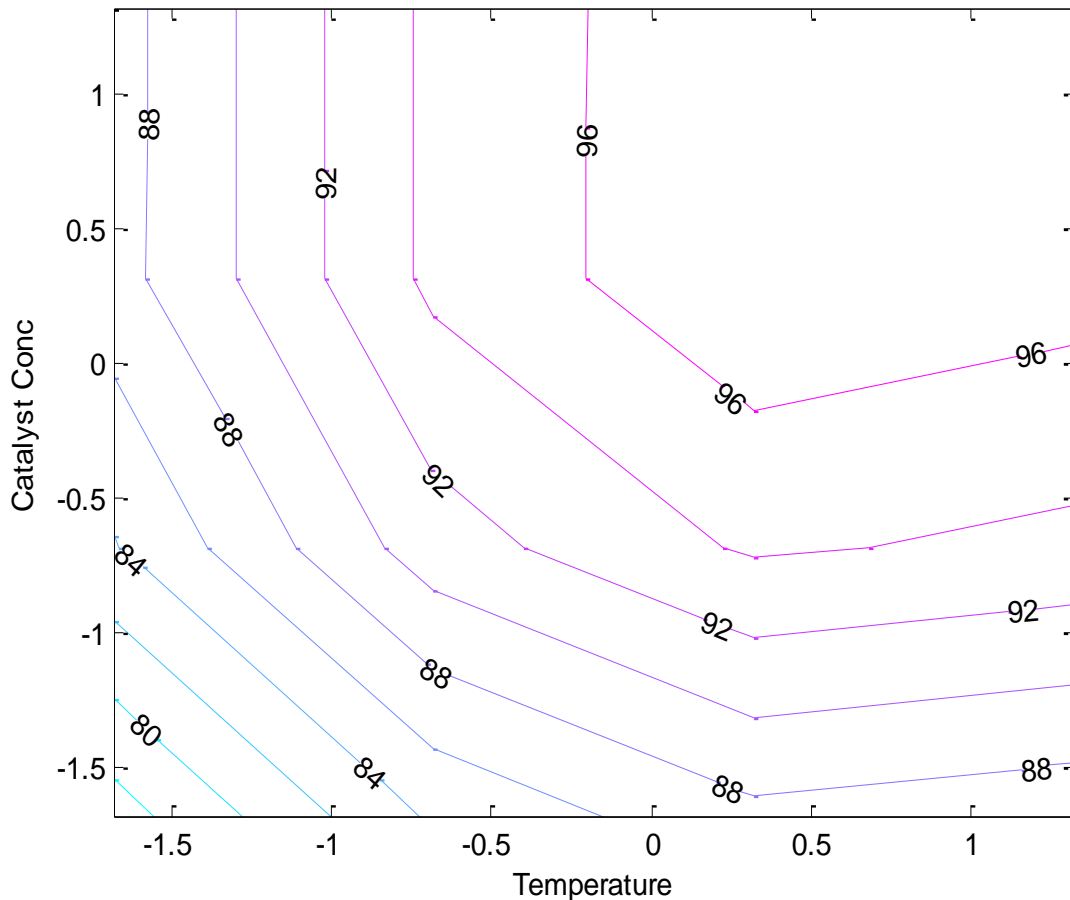
approximately 1wt% has been determined to be the optimal KOH catalyst concentration. A catalyst concentration of 1.24% was obtained in this study this may be higher than that obtained in Yaakob et al (2012). As the optimal catalyst concentration will also depend on the type of oil used in this case, waste cooking oil was used which contains free fatty acids although pre-treated traces of free fatty acid may result in a higher requirement of catalyst.



*Figure 4.1: Response surface plot of biodiesel yield against catalyst concentration and temperature*

Figure 4.1 shows the effect of catalyst concentration and temperature interactions on the yield of biodiesel at constant circulation flow rate. As the temperature increased the biodiesel yield

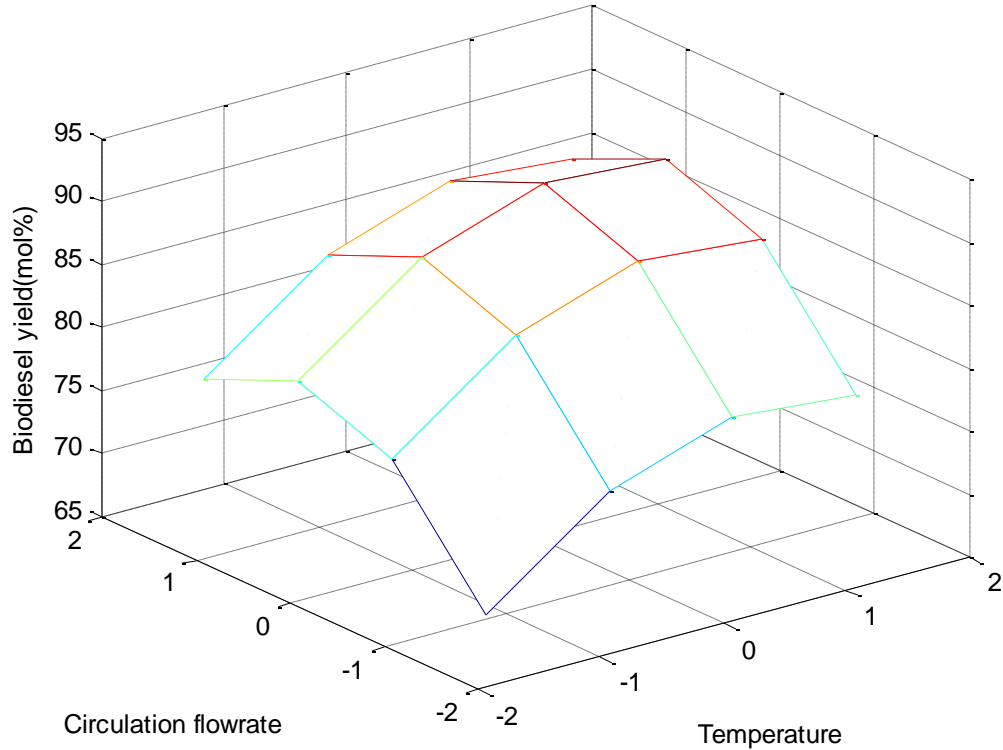
increased significantly this could be due to the fact that the trans-esterification reaction is endothermic and a higher temperature would favour the yield of biodiesel. Similarly an increase in concentration the catalyst resulted in an increase in biodiesel yield, this could be due to the fact that there are more catalyst particles available to speed up the reaction.



*Figure 4.2: Contour plot of biodiesel yield against catalyst concentration and temperature*

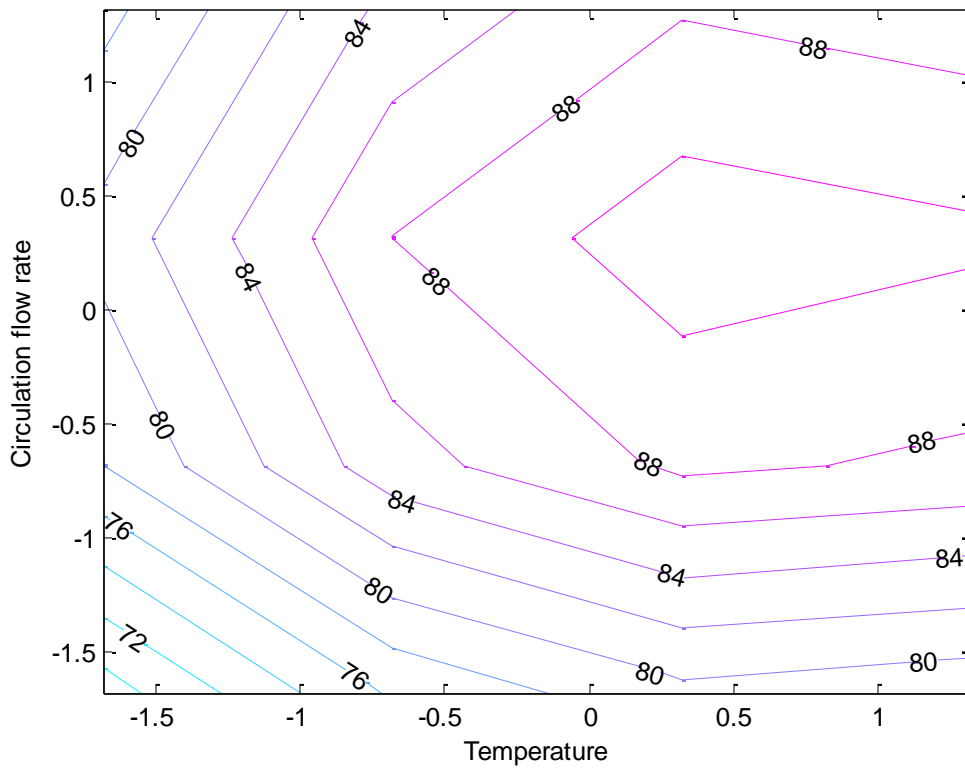
Figure 4.2 shows that the contour lines are not complete concentric ellipses which suggests that there is flexibility in the choice of temperature as additional experimentation can warrant consideration although this would not be possible due to the limitation of the boiling point of methanol which is 64.5°C thus the maximum reaction temperature was set at 65°C, at this

temperature only a small amount of methanol evaporated due to the mixing effect with waste cooking oil.



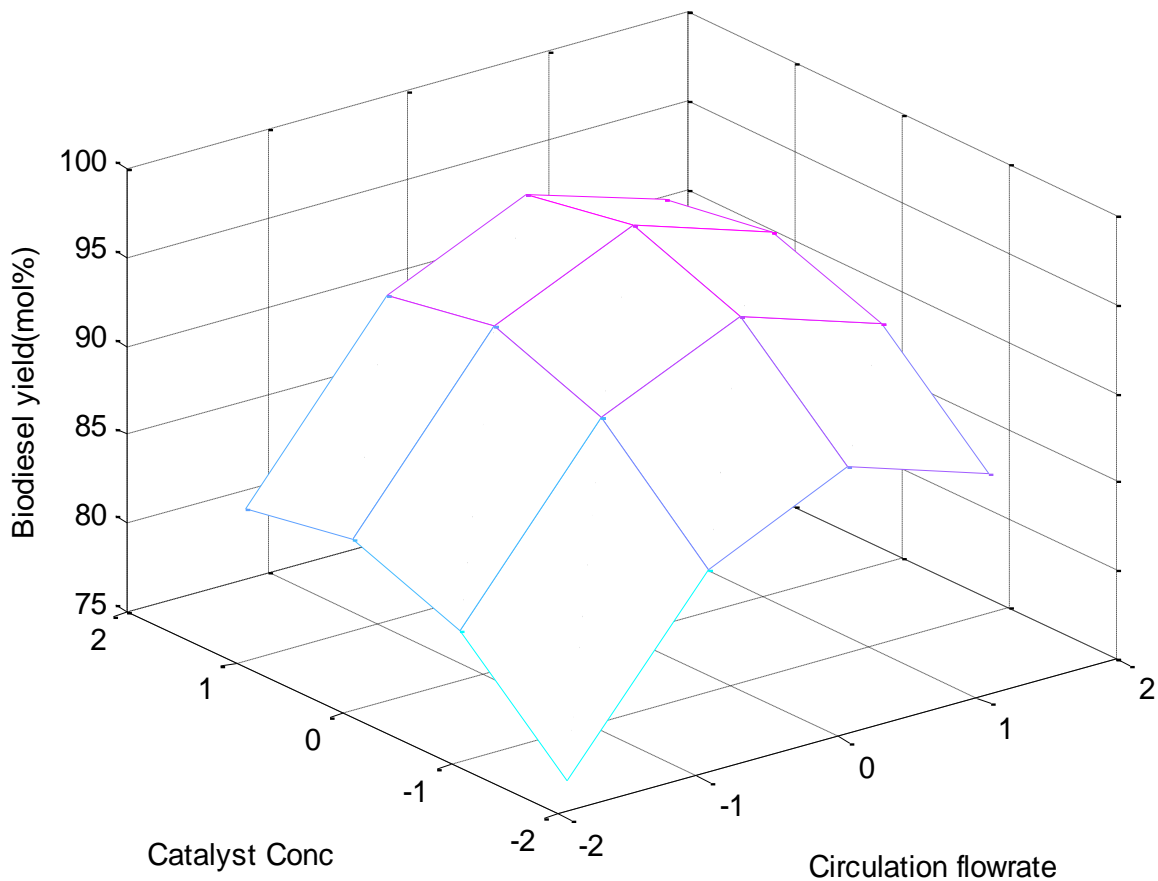
*Figure 4.3: Response surface plot biodiesel yield against temperature and circulation flow rate*

Figure 4.3 shows the effect of circulation flow rate and temperature at a constant catalyst concentration on the yield of biodiesel. Both parameters had a positive effect on the biodiesel yield but the increase in the yield is not as substantial compared to that in Figure 4.1 and 4.5. The catalyst concentration had the greatest effect on the yield of biodiesel ethanol as it can be seen that when catalyst concentration was kept constant at its centre level and temperature and circulation flow rate were varied the result in the lowest production of biodiesel as can be seen from the contour plot in Figure 4.4.



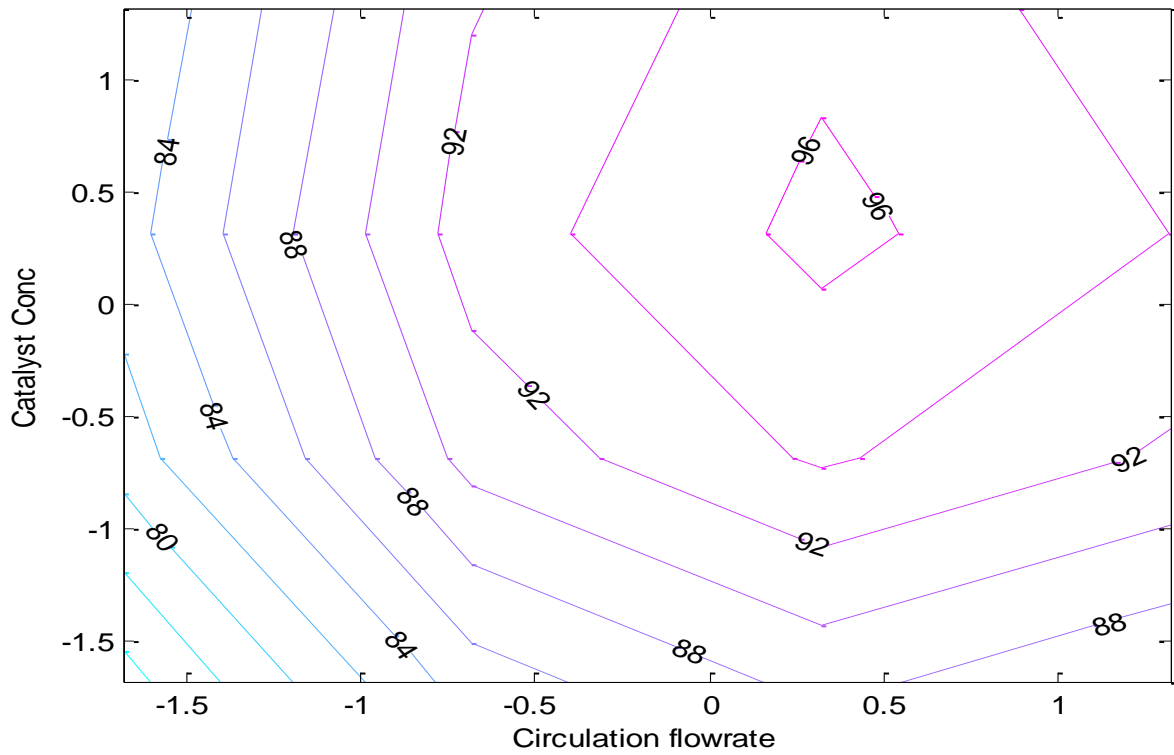
*Figure 4.4: Contour plot biodiesel yield against temperature and circulation flow rate*

Figure 4.4 shows a sizeable change in the distance between the contour lines as the parameters are maximized which shows that the temperature and reactant flow rate interaction had a substantial positive effect on the biodiesel yield at lower conditions than at higher conditions.



*Figure 4.5: Biodiesel yield against catalyst concentration and circulation flow rate*

Figure 4.5 shows that the catalyst concentration and circulation flow rate interaction had a similar effect as the temperature and catalyst concentration interaction. There is a significant increase in the biodiesel yield due to the interaction of the catalyst concentration and circulation flow rate. A high circulation flow rate overcomes the mass transfer limitations and ensures a high mixing intensity between the reactants. Whereas a high catalyst concentration ensures there is sufficient particles to speed up the trans-esterification reaction.



*Figure 4.6: Contour plot of biodiesel yield against circulation flowrate and catalyst concentration*

Figure 4.6 clearly shows the region within which the stationary point can be obtained is the elliptically shaped region with a biodiesel yield of 96%. In this region the optimal operating conditions for the circulation flow rate and catalyst concentration can be found at the centre point of temperature.

*Table 4.2: Tests on the individual Variables quadratic model*

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>
Intercept	48.690	7.470	6.518	9.71942E-06
Temperature	0.377	0.121	3.128	0.007
circulation flow rate	0.407	0.121	3.359	0.004
catalyst concentration	3.372	2.451	1.375	0.190

Table 4.2 shows t-test results on each individual variable. All t values are large enough to show that there is no non- significant variable for the obtained model thus no variable can be dropped to have a reduced quadratic model. The p values are very small indicating that the results did not occur randomly.

*Table 4.3: Analysis of variance*

ANOVA for fitted model

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>
Regression	4	382.152	95.538	13.506
Residual	15	K2106.107	7.074	
Lack of fit	10	104.408	10.441	30.720
Pure Error	5	1.700	0.340	
Total	19	488.259		

Table 4.3 shows the analysis of variance  $F_o$  calculated value of 30.72 which is less than the standard table value. This shows that there is no lack of fit in the model. Thus the model is appropriate and there is no need to try and find a more appropriate model.

---

## CHAPTER 5

### Conclusion and Recommendations

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#### 5.1 Conclusions

WCO is an important feedstock for the production of biodiesel as well as edible and non-edible feedstock as it is abundant and less costly. The pretreatment of the WCO using sulphated zirconia is effective in removing solid material, reducing the FFA content and water content. Heterogeneous trans-esterification using a packed bed membrane reactor is a worthwhile method of producing biodiesel as high yields of biodiesel were obtained. The separation of the biodiesel using the membrane reactor is not sufficient as partial separation occurred, this can be coupled with the decantation of the biodiesel, glycerol and methanol mixture after reaction to obtain the biodiesel which has not separated, which is washed to further purify it. The heterogeneous catalyst can be reused as there wasn't a significant change in the yield of biodiesel upon reusing the catalyst for the second run. Response surface methodology was effective in obtaining the optimal conditions of the parameters that were under investigation; that is temperature, catalyst concentration and circulation flow rate. All the parameters had a positive effect on the biodiesel yield with catalyst concentration having the greatest effect. The optimal conditions were a temperature of 58.5 °C, circulation flow rate of 18.78 ml/min and catalyst concentration of 1.24 wt%. At these conditions a biodiesel yield of 94.03 mol% was obtained.

#### 5.2 Recommendations

The circulation flow rate was limited by the peristaltic pump which was being utilized, which had a maximum speed of 60 rpm. As the circulation flow rate had a positive effect on the biodiesel yield, using a pump with a higher speed can possibly result in a higher biodiesel yield. Considering the purification process of biodiesel with water it was effective due to the similarity in polarity of water and glycerol, but the challenge was the loss of product due to water retention and the disposal of the waste water after the treatment. A liquid-liquid extraction method using

glycerol due to the residual glycerol from the biodiesel production can be used after basic treatment of the biodiesel as suggested by M Berrios et al (2011). According to Yaakob et al (2012) dry washing with silica gel to remove traces of water and wet washing using 5% phosphoric acid are another useful method of purification which can reduce product loss. Methanol was used for the trans-esterification process due to its wide availability and low cost, but ethanol is more soluble in oil and could counter the mass transfer limitations associated with using methanol. Thus a mixture of ethanol and methanol could be used to combine the advantages of both alcohols and an optimal ratio of the two alcohols can be deduced through experimentation. It is suggested to investigate the reusability of the catalyst further as only two runs did not show a significant change in the yield of biodiesel. In addition the chemical characteristics of the biodiesel should be determined to ensure that they satisfy the ASTM standards. Lastly the performance of the membrane reactor to that of a fixed bed reactor operated at similar conditions should be compared to verify whether there is a need of using a membrane reactor instead of conventional reactors.

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## Appendix A

### *Chemical requirements and physical properties*

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*Table A1: Properties of waste cooking oil*

<b>WCO properties</b>	
Density of WCO(g/m <sup>3</sup> )	920000
Molecular weight (g/mol)	856
Mass of WCO for 1L(g)	920
Moles of WCO for 1L (mol)	1.0748

*Table A2: Methanol properties*

<b>Methanol properties</b>	
Density (g/m <sup>3</sup> )	791800
Molecular weight (g/mol)	32.04

*Table A3: Acid catalyst requirements*

<b>Acid test chemical requirements</b>				
Chemical	Molecular weight (g/mol)	Mass (g)	Moles(mol)	Mass of sulphated zirconia obtained
ZrOCl <sub>2</sub> .8H <sub>2</sub> O	322.2526	150	0.47	65g
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	132.1402	270	2.04	
ZrO <sub>2</sub> SO <sub>2</sub>	187.2866	65	0.35	

*Table A4: Alkaline catalyst chemical requirements*

<b>Alkaline test chemical requirements</b>		
Chemical	Molecular weight (g/mol)	Mass (g)
Activated carbon	12.01	701
KOH	56.11	213.05
AC/KOH	68.12	815

Activated Carbon (g)	80
Pottasium Hydroxide(g)	200
Distilled Water (ml)	2000
Concentration of KOH solution	0.1
AC/KOH	121
Adsorbed KOH using gravitational analysis (g)	41
Adsorbed KOH on AC (%)	33.88

---

## Appendix B

### *Titration*

---

*Table B1: Free fatty acid titration test runs for waste cooking oil*

**Waste cooking oil**

Sample	Titration value (ml KOH)	Acid value (mg KOH/g oil)	%FFA
1	1.1	1.20	0.56
2	0.7	0.76	0.35
3	0.45	0.49	0.23
4	0.8	0.87	0.4
5	0.4	0.43	0.2
6	1.1	1.20	0.56
7	0.7	0.76	0.35
8	0.45	0.49	0.23
9	0.8	0.87	0.4

*Table B2: Free fatty acid titration test runs for treated waste cooking oil*

**Treated Waste cooking oil**

Sample	Titration value (ml KOH)	Acid value (mg KOH/g oil)	%FFA
1	0.76	0.83	0.37
2	0.30	0.33	0.15
3	0.34	0.37	0.17
4	0.71	0.77	0.35
5	0.35	0.38	0.18
6	0.74	0.80	0.37
7	0.75	0.76	0.34
8	0.34	0.37	0.17
9	0.41	0.45	0.21

*Table B3: Methanol recovered from pretreatment process*

<b>Sample</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>
<b>Duration (hr)</b>	2	2	2	2	2	2	2	2	2
<b>Temp ( °C)</b>	60	60	60	60	60	60	60	60	60
<b>WCO (ml)</b>	1000	1000	1000	1000	1000	1000	1000	1000	1000
<b>Methanol (ml)</b>	392	392	392	392	392	392	392	392	392
<b>catalyst</b>	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2	9.2
<b>Methanol recovered</b>	242	250	255	240	256	262	251	260	254
<b>%methanol recovered</b>	61.73	63.78	65.05	61.22	65.31	66.84	64.03	66.33	64.80

---

## APPENDIX C

### *Mat Lab Programs*

---

```
X= [1 -1 -1 -1 1 1 1 1 1 1];  
  
1 1 -1 -1 1 1 1 -1 -1 1;  
1 -1 1 -1 1 1 1 -1 1 -1;  
1 1 1 -1 1 1 1 1 -1 -1;  
1 -1 -1 1 1 1 1 1 -1 -1;  
1 1 -1 1 1 1 1 -1 1 -1;  
1 -1 1 1 1 1 1 -1 -1 1;  
1 1 1 1 1 1 1 1 1 1;  
1 -2^(3/4) 0 0 2^(3/2) 0 0 0 0 0;  
1 2^(3/4) 0 0 2^(3/2) 0 0 0 0 0;  
1 0 -2^(3/4) 0 0 2^(3/2) 0 0 0 0;  
1 0 2^(3/4) 0 0 2^(3/2) 0 0 0 0;  
1 0 0 -2^(3/4) 0 0 2^(3/2) 0 0 0;  
1 0 0 2^(3/4) 0 0 2^(3/2) 0 0 0;  
1 0 0 0 0 0 0 0 0 0;  
1 0 0 0 0 0 0 0 0 0;  
1 0 0 0 0 0 0 0 0 0;  
1 0 0 0 0 0 0 0 0 0;  
1 0 0 0 0 0 0 0 0 0;  
1 0 0 0 0 0 0 0 0 0];  
O=[1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1];  
I=eye(10);
```

```
Y=[78.70000;80.84406;83.24038;82.35752;80.84406;84.62772;86.51954;92.69951;78.82611;92.19502;81.60079;83.36650;80.970184;91.816656;90.05095;90.68156;91.69053;90.93380;91.05992;90.30320];
```

```
N=20;p=10;n=6;
```

```
T=(X'*X)
```

```
U=(X'*Y)
```

```
V=(inv(X'*X))
```

```
B= ((X'*X)\(X'*Y))
```

### **Programme for plotting response surfaces and contours**

#### **Response surface and contour at constant Sugar concentration**

##### RESPONSE SURFACE

```
[x,y]=meshgrid(-1.682:1:1.682,-1.682:1:1.682);  
z=90.8094+2.4683*x+2.7671*y-2.0138*(x.^2)-1.7017*(y.^2)+1.0878*x*y;  
mesh(x,y,z)  
xlabel('Temperature'),ylabel('Catalyst Conc'),zlabel('Biodiesel yield (mol%)')
```

##### CONTOUR PLOT

```
[x,y]=meshgrid(-1.682:1:1.682,-1.682:1:1.682);  
z=90.8094+2.4683*x+2.7671*y-2.0138*(x.^2)-1.7017*(y.^2)+1.0878*x*y;  
[C,h]=contour(x,y,z);  
xlabel('Temperature'),ylabel('Catalyst Conc'),zlabel('Biodiesel yield (mol%)')  
set(h,'ShowText','on','TextStep',get(h,'LevelStep')*2)  
colormap cool
```

#### **Response surface and contour at constant yeast concentration**

##### RESPONSE SURFACE

```
[x,y]=meshgrid(-1.682:1:1.682,-1.682:1:1.682);  
z=90.8094+2.4683*x+1.6673*y-2.0138*(x.^2)-3.0840*(y.^2)-0.0788*x*y;  
mesh(x,y,z)  
xlabel('Temperature'),ylabel('Circulation flowrate'),zlabel('Biodiesel yield(mol%)')
```

##### CONTOUR PLOT

```
[x,y]=meshgrid(-1.682:1:1.682,-1.682:1:1.682);
z=90.8094+2.4683*x+1.6673*y-2.0138*(x.^2)-3.0840*(y.^2)-0.0788*x*y;
[C,h]=contour(x,y,z);
xlabel('Temperature'),ylabel('Circulation flow rate'),zlabel('Biodiesel yield(mol%)')
set(h,'ShowText','on','TextStep',get(h,'LevelStep')*2)
colormap cool
```

## **Response surface and contour at constant Temperature**

### RESPONSE SURFACE

```
[x,y]=meshgrid(-1.682:1:1.682,-1.682:1:1.682);
z=90.8094+2.4683*x+1.6673*y-3.0840*(x.^2)-1.7017*(y.^2)+0.9617*x*y;
mesh(x,y,z)
xlabel('Circulation flowrate'),ylabel('Catalyst Conc'),zlabel('Biodiesel yield(mol%)')
```

### CONTOUR PLOT

```
[x,y]=meshgrid(-1.682:1:1.682,-1.682:1:1.682);
z=90.8094+2.4683*x+1.6673*y-3.0840*(x.^2)-1.7017*(y.^2)+0.9617*x*y;
[C,h]=contour(x,y,z);
xlabel('Circulation flowrate'),ylabel('Catalyst Conc'),zlabel('Biodiesel yield(mol%)')
set(h,'ShowText','on','TextStep',get(h,'LevelStep')*2)
colormap cool.
```

**APPENDIX D**  
**RISK ASSESSMENT**

	Hazard Identification	What is the cause of the hazard	What are the consequences	Assessment Before Controls				
				What is the impact of the hazard on the following items			PROBABILITY	RISK RANKING
	A hazard is anything that is likely to lead to an event which has an adverse effect on your objective	Event or situation leading directly to the hazard	Immediate physical or practical event as a result of the hazard	Safety	Health	Environment		
1.	Fragility of glass making up the equipment can collapse violently	Occurs due to buildup of pressure in the equipment and falling accidentally	Injury due to cutting of one's hand or any other part of the body	1	1	1	3	Low(4)
2.	Short circuit of electrical equipment	Exposed wiring /liquid dropped on elements/poor incorrect connections	Electric Fire, burning of WCO or biodiesel leading to chemical fire.	2	1	1	2	Low(6)
3.	Contact of chemicals with eyes/skin	Mishandling of chemicals	Irritation to eyes and skin, chemical burns	2	1	1	3	Low(6)
4.	Inhalation or ingestion methanol	Spillage of chemicals and incorrect labeling of bottles	Inhalation may impact the central nervous system.	1	3	1	2	Low(6)
5.	Slippery floor	Spillages of liquid substances	Fractured bones, head injuries	3	1	1	3	Medium (9)
6.	Leakage of chemicals into drainage	Negligence, accidental spillage, incorrectly labeled	Contamination of water	1	1	2	2	Low(4)

	Controls		What is the impact of the hazard on the following items		PROBABILITY	RISK RANKING	Monitoring Mechanisms	
	Preventative Controls Controls taken to eliminate hazards or reduce the likelihood of the hazard occurring	Reactive Controls Controls taken to reduce the immediate impact of the hazard occurring	Safety	Health	Environment			How we know if we are succeeding. Include comments on effectiveness.
1.	Glass ware must be handled with caution to prevent damage it is advisable to check for the flaws such as cracks, cracked glassware should be disposed or repaired if possible	All damaged glassware should be disposed in the appropriate bins immediately upon identification, injured personnel must receive first aid treatment immediately	2	1	1	2	Low(4)	In the event of breakage the glass must be discarded in the appropriate waste disposal bin. Monitoring of the process and abiding to safety precautions can reduce further accidents.

2.	Keep the apparatus away from sinks or other water sources. The electric elements in any device should be enclosed to prevent and electric shocks or short circuiting. In the event of wires becoming worn out or damaged the device should either be discarded or replaced.	Turn off power supply ,put out fire with suitable extinguisher	3	1	1	1	Low(3)	Monitor the functionality of all electrical equipment on a regular basis.
3.	Wear safety glasses, Latex gloves and white cotton lab coat	Rinse with water, consult MSDS.	2	1	1	2	Low(4)	Monitor the use of proper PPE
4.	Label all containers to avoid improper usage of chemicals, Keep methanol containers sealed at all times. Wear face mask.	Ensure adequate ventilation, consult MSDS and report to medical practitioner.	1	3	1	1	Low(3)	Monitor use of chemical substances.

5.	Wear appropriate footwear and keep floor clean and dry	Obtain assistance from first aider or medical practitioner	3	1	1	1	Low(3)	Monitor lab to ensure it is clean all the time
6.	Label all containers correctly and dispose chemicals appropriately and not into drainage.	Remove source of contamination immediately, report to a safety officer.	1	1	2	1	Low(2)	Monitor use of chemicals

## APPENDIX E

### EXPERIMENTAL DATA

Experiment	Reaction time (min)	Reaction Temperature	Circulation flowrate (ml/min)	Catalyst concentration (wt%)	Methanol(ml)	Methanol(g)	Methanol (mol)	Treated WCO (ml)	Treated WCO (g)	Treated WCO (mol)	Mass of Packed Catalyst in membrane (g)	Biodiesel (ml)	Biodiesel (g)	Biodiesel (mol)	Biodiesel Yield (mol)	Biodiesel Yield Avg(mol%)
1	90	49	14	0.7	400	316.72	9.885143571	400	368	0.429906542	4.79304	310	272.8	1.008502773	0.781955048	78.69999196
2	90	49	14	0.7	400	316.72	9.885143571	400	368	0.429906542	4.79304	314	276.32	1.021515712	0.792044791	
3	90	61	14	0.7	400	316.72	9.885143571	400	368	0.429906542	4.79304	322	283.36	1.04754159	0.812224276	80.84406226
4	90	61	14	0.7	400	316.72	9.885143571	400	368	0.429906542	4.79304	319	280.72	1.037781885	0.804656969	
5	90	49	26	0.7	400	316.72	9.885143571	400	368	0.429906542	4.79304	333	293.04	1.083327172	0.839971068	83.24037612
6	90	49	26	0.7	400	316.72	9.885143571	400	368	0.429906542	4.79304	327	287.76	1.063807763	0.824836454	
7	90	61	26	0.7	400	316.72	9.885143571	400	368	0.429906542	4.79304	324	285.12	1.054048059	0.817269147	82.35752364
8	90	61	26	0.7	400	316.72	9.885143571	400	368	0.429906542	4.79304	329	289.52	1.070314233	0.829881326	
9	90	49	14	1.3	400	316.72	9.885143571	400	368	0.429906542	8.90136	317	278.96	1.031275416	0.799612098	80.84406226
10	90	49	14	1.3	400	316.72	9.885143571	400	368	0.429906542	8.90136	324	285.12	1.054048059	0.817269147	
11	90	61	14	1.3	400	316.72	9.885143571	400	368	0.429906542	8.90136	334	293.92	1.086580407	0.842493504	84.62771572
12	90	61	14	1.3	400	316.72	9.885143571	400	368	0.429906542	8.90136	337	296.56	1.096340111	0.850060811	
13	90	49	26	1.3	400	316.72	9.885143571	400	368	0.429906542	8.90136	341	300.08	1.10935305	0.860150553	86.51954245
14	90	49	26	1.3	400	316.72	9.885143571	400	368	0.429906542	8.90136	345	303.6	1.122365989	0.870240296	
15	90	61	26	1.3	400	316.72	9.885143571	400	368	0.429906542	8.90136	370	325.6	1.203696858	0.933301187	92.69950976
16	90	61	26	1.3	400	316.72	9.885143571	400	368	0.429906542	8.90136	365	321.2	1.187430684	0.920689009	
17	90	45	20	1	400	316.72	9.885143571	400	368	0.429906542	6.8472	309	271.92	1.005249538	0.779432613	78.82611375
18	90	45	20	1	400	316.72	9.885143571	400	368	0.429906542	6.8472	316	278.08	1.028022181	0.797089662	
19	90	65	20	1	400	316.72	9.885143571	400	368	0.429906542	6.8472	368	323.84	1.197190388	0.928256315	92.19502264
20	90	65	20	1	400	316.72	9.885143571	400	368	0.429906542	6.8472	363	319.44	1.180924214	0.915644137	
21	90	55	20	0.5	400	316.72	9.885143571	400	368	0.429906542	3.4236	326	286.88	1.060554529	0.822314019	81.60079295
22	90	55	20	0.5	400	316.72	9.885143571	400	368	0.429906542	3.4236	321	282.48	1.044288355	0.80970184	
23	90	55	20	1.5	400	316.72	9.885143571	400	368	0.429906542	10.2708	327	287.76	1.063807763	0.824836454	83.3664979
24	90	55	20	1.5	400	316.72	9.885143571	400	368	0.429906542	10.2708	334	293.92	1.086580407	0.842493504	
25	90	55	10	1	400	316.72	9.885143571	400	368	0.429906542	6.8472	316	278.08	1.028022181	0.797089662	80.97018404
26	90	55	10	1	400	316.72	9.885143571	400	368	0.429906542	4.79304	326	286.88	1.060554529	0.822314019	
27	90	55	30	1	400	316.72	9.885143571	400	368	0.429906542	6.8472	367	322.96	1.193937153	0.92573388	91.81665729
28	90	55	30	1	400	316.72	9.885143571	400	368	0.429906542	6.8472	361	317.68	1.174417745	0.910599266	
29	90	55	20	1	400	316.72	9.885143571	400	368	0.429906542	4.79304	355	312.4	1.154898336	0.895464652	90.05095234
30	90	55	20	1	400	316.72	9.885143571	400	368	0.429906542	6.8472	359	315.92	1.167911275	0.905554395	
31	90	55	20	1	400	316.72	9.885143571	400	368	0.429906542	6.8472	357	314.16	1.161404806	0.900509523	90.68156125
32	90	55	20	1	400	316.72	9.885143571	400	368	0.429906542	6.8472	362	318.56	1.17767098	0.913121702	
33	90	55	20	1	400	316.72	9.885143571	400	368	0.429906542	6.8472	368	323.84	1.197190388	0.928256315	91.69053551
34	90	55	20	1	400	316.72	9.885143571	400	368	0.429906542	6.8472	359	315.92	1.167911275	0.905554395	
35	90	55	20	1	400	316.72	9.885143571	400	368	0.429906542	6.8472	363	319.44	1.180924214	0.915644137	90.93380482
36	90	55	20	1	400	316.72	9.885143571	400	368	0.429906542	6.8472	358	315.04	1.164658041	0.903031959	
37	90	55	20	1	400	316.72	9.885143571	400	368	0.429906542	6.8472	356	313.28	1.158151571	0.897987088	91.0599266
38	90	55	20	1	400	316.72	9.885143571	400	368	0.429906542	6.8472	366	322.08	1.190683919	0.923211444	
39	90	55	20	1	400	316.72	9.885143571	400	368	0.429906542	6.8472	359	315.92	1.167911275	0.905554395	90.30319591
40	90	55	20	1	400	316.72	9.885143571	400	368	0.429906542	6.8472	357	314.16	1.161404806	0.900509523	