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Biodiesel Production form High FFA Feedstock Using a Membrane Reactor

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Biodiesel Production from High FFA Feedstock Using a Membrane Reactor

by

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Abstract

Biodiesel is a renewable source of energy typically produced in a chemical process known as transesterification. The process involves the reaction of an alcohol with vegetable oil or animal fat in the presence of a catalyst to yield mono-alkyl esters (biodiesel) and glycerol as a by-product. The biodiesel market is amongst the fastest growing renewable energy markets and there is a genuine interest in its development from industry and academia. However, there are some challenges that are facing biodiesel and hindering its commercialization. The major ones are production cost and quality. The process must be cost-effective whilst producing biodiesel that meets international standards (ASTM D6751 and EN 14214). The main objectives of this project were to investigate the use of a continuous membrane reactor for the production of biodiesel from waste vegetable oil feedstock with high free fatty acid (FFA) content and to investigate the effect of membrane pore size on the separation of soap and triglycerides in the reactor. This was achieved through the construction and operation of a lab scale continuous membrane reactor. The membrane reactor integrates many procedures such as combining the chemical reaction and the membrane-based separation in the same unit. The biodiesel was produced by base-catalyzed transesterification. Two levels of FFA in

the waste vegetable oil feedstock were studied, 4.8 and 10 mass%. Ceramic membranes were used, with membrane pore sizes ranging from 1 to 800 nm.

It was found that the free glycerol and total glycerol content in the fatty acid methyl ester (FAME or biodiesel) produced were significantly below the maximum limit of the ASTM D6751 standard. There was no trend associating changes in membrane pore size with glycerol concentration. Additionally, it was found that the water content in the FAME produced met the ASTM D6751 standard. Furthermore, the results of the soap analysis indicated that the soap dissolved in the alcohol and passed through the membrane. Thus, soap was not completely retained in the reactor. Therefore, the soap produced as a result of using high FFA feedstock in a base-catalyzed transesterification did not affect the FAME production process and the passage of mono-, di-, and tri-glycerides through the membrane. The quality of the biodiesel produced in this project met the requirements for the ASTM D6751 standard.

Résumé

Le biodiésel est une source d'énergie renouvelable typiquement produite dans un processus chimique connu sous le nom de transestérification. Le processus implique la réaction d'un alcool et de l'huile ou graisse animale ou végétale en présence d'un catalyseur pour produire des esters monoalkyliques (FAME) et le glycérol en tant que sous-produit. Le marché du biodiésel est parmi les marchés d'énergie renouvelable qui à la plus rapide croissance et il y a un intérêt véritable pour son développement industriel ainsi qu'en milieu universitaire. Cependant, plusieurs défis existent dans la production du biodiésel de qualité à un niveau commercial. Le processus doit être rentable tout en produisant le biodiésel qui répond aux normes internationales (ASTM D6751 et EN 14214). Les objectifs principaux de ce projet étaient d'étudier l'utilisation d'un réacteur à membrane en continu pour la production du biodiésel à partire de rebuts d'huile végétale ayant un contenu élevé d'acide gras libre (FFA) et pour étudier l'effet de la taille des pores de membrane sur le processus. Ceci a été réalisé par la construction et le fonctionnement d'un réacteur continu à membrane. Le réacteur de membrane intègre beaucoup de procédures telles que combiner une réaction chimique et une séparation par membrane dans la même unité. La quantité d'acides gras dans la matière première rebut

d'huile végétale a été variée de 4.8 à 10 pourcent par poids. Des membranes de céramique ont été utilisées, avec des tailles de pore de membrane s'étendant de 1 à 800 nm.

On a constaté que la glycérine libre et la glycérine totale dans l'ester monoalkylique produit étaient nettement sous la norme ASTM D6751. Il n'y avait aucune tendance associant des changements de taille de pore de membrane à la concentration en glycérol. En plus, on a constaté que la teneur en eau dans la FAME produite a répondu aux normes d'ASTM D6751. Les résultats de l'analyse des savons ont indiqués que le savon se dissous dans l'alcool et traverse la membrane. Ainsi, le savon n'a pas été retenu dans le réacteur. Par conséquent, le savon produit à la suite de l'utilisation de matières premières ayant une haute teneur en acides gras n'a pas eu d'incidence sur le passage des mono-, di-, et triglycerides au travers de la membrane. La teneur du biodiesel en tri-, di- et mono- glycerides du biodiesel produit dans ce projet a dépassé aux exigences de la norme ASTM D6751.

Statement of Contributions

I hereby declare that I am the sole author of this thesis. I performed all the practical and written work required for its completion. My supervisors Dr. Marc Dubé and Dr. André Tremblay provided scientific guidance and editorial comments.

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I would like to express my deepest gratitude to my supervisors Dr. Marc Dubé and Dr. André Tremblay. Thank you for your help and support; and for sharing your invaluable experience.

Achieving a Masters degree requires sacrifices, which are rarely made alone. I would like to thank my mum and dad who generously devoted their lives to raise me with love, care and morals. Thank you for a lifetime of unconditional love and for always being there for me. A special thanks to my brother for supporting me during my studies. I could not ask for a better brother and friend. I am thankful for the love of my friends; their motivation and friendship during the completion of my degree has been wonderful.

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Abbreviations

ASTM	American Society for Testing and Materials
DG	Diglyceride
EN	European Norm
FAME	Fatty acid methyl ester
FFA	Free fatty acid
GC	Gas chromatography
MG	Monoglyceride
n.d.	Not detected
ppm	parts per million
TG	Triglyceride

CHAPTER 1
Introduction

1.1 Motivation

Throughout the 20th century, petroleum based fuels were inexpensive and plentiful. Many oil fields around the world were discovered and the use of crude oil as the primary source of energy was unquestionable. The modern world relied almost exclusively on foreign oil reserves for the production of liquid fuels. However, the cost and politics of being fully dependent on these foreign reserves got progressively more expensive, from both a sociological and strategic stance. Moreover, during this time the world population increased and automobiles became more widespread. Consequently, pollution levels soared causing concern amongst many people, especially environmentalists. As we move into the 21st century, the energy demand continues to grow while fossil fuel reserves are being depleted. This has motivated many researchers to work on the development of alternative sources to petroleum based fuels.

Due to their similarities, biodiesel has emerged as a petroleum diesel substitute. Biodiesel is a fuel comprised of mono-alkyl esters of long chain fatty acids derived from

vegetable oils or animal fats (ASTM D6751 Standard, 2009). Biodiesel is an alternative and renewable source of energy with a smaller environmental impact. The feedstock materials can be grown domestically, thereby strengthening the country's economy and lessening its dependence on foreign oil.

Biodiesel is produced from the reaction of vegetable oils or animal fats with an alcohol in the presence of a catalyst, in a process called transesterification. This process yields fatty acid alkyl ester (biodiesel) and glycerol as a by-product. The alcohol used is usually methanol due to its low cost. The resulting fatty acid alkyl ester is then referred to as fatty acid methyl ester (FAME).

Biodiesel is relatively environmentally friendly. The energy content of the plant feedstock comes from the sun through photosynthesis and this energy is conserved even when plants are processed into other materials. Plant materials are available in an unlimited supply, making biodiesel a renewable source of energy. Biodiesel is potentially an ideal fuel for vehicles because it adds fewer emissions to the atmosphere than petroleum based fuels. Biodiesel is a diesel fuel substitute that is safe to handle and non-toxic. It can be used in diesel engines without any modifications to the engines. In fact, biodiesel is beneficial to diesel engines since it is a better lubricant than petro-diesel fuel and has superb solvent properties. With time, conventional diesel fuel leaves deposits inside the storage tanks and fuel delivery systems. On the other hand, biodiesel does not leave any deposits and may dissolve deposits produced from the diesel fuel (Knothe *et al.*, 2005).

Despite its numerous advantages, there are some challenges hindering the commercialization of biodiesel. The major obstacle facing biodiesel is the high manufacturing cost (Khan, 2002). The price of the feedstock accounts for approximately 75% of the total manufacturing cost (Phan & Phan, 2008). An optimal solution is a feedstock that is cheaper yet does not compromise the quality of the biodiesel.

Waste vegetable oil and animal fat are promising feedstock options that could lower the cost of biodiesel production. The price of waste vegetable oil is typically 2 to 3 times lower than virgin vegetable oil. Therefore, if waste vegetable oil is utilized, the total manufacturing cost of biodiesel can be reduced. However, the high amounts of free fatty acids (FFAs) and water in the cheaper feedstock give rise to production challenges. Using a feedstock with a high percent of FFAs causes major problems such as soap formation, water formation and lower yield. Therefore, waste vegetable oils and animal fats cannot usually be converted to biodiesel using the conventional base-catalyzed transesterification.

To overcome the problems of using a high FFA feedstock, an alternative two-step process was developed (Canakci & Van Gerpen, 2003). The first step is an esterification reaction that reduces the FFA content of the feedstock. The second step is the conventional base-catalyzed transesterification reaction. Although the two-step process avoids some issues that would result from the one-step base-catalyzed process, it is by no means ideal. The two-step process results in the release of harmful materials such as sodium sulphate into the environment, which is inconsistent with the environmental objectives of using biodiesel.

The use of membrane reactor technology is a promising solution to the above issues (Dubé *et al.*, 2007). A membrane reactor is a device where a chemical reaction and a membrane-based separation are carried out simultaneously, in the same physical enclosure. Transesterification is a standard reversible chemical reaction; therefore, when producing biodiesel via transesterification, a membrane reactor could be employed. Previous research has shown that a micro-porous inorganic membrane reactor can selectively permeate biodiesel, methanol and glycerol during the transesterification reaction (Dubé *et al.*, 2007; Cao *et al.*, 2008). This leads to the following questions. Can a membrane reactor be used to produce biodiesel from high FFA feedstock? Can a membrane reactor overcome the issues that arise from the base-catalyzed transesterification of high FFA feedstock? How do the membrane properties, such as pore size, affect the biodiesel production process and quality of the biodiesel produced? The answers to these questions outline the main objectives of this project.

1.2 Thesis Objectives

The main objectives of this project were to investigate the use of a membrane reactor for the production of biodiesel from waste vegetable oil feedstock with high FFA content and to investigate the effect of membrane pore size on the biodiesel production process. This was to be achieved through the construction and operation of a continuous membrane reactor.

1.3 Thesis Organization

This thesis is organized as follows. Chapter 2 presents background information on the biodiesel production process and reviews previous literature and related work. In Chapter 3 the methodology is presented and explained. The experimental results are then shown and discussed in detail in Chapter 4. Finally, Chapter 5 concludes this work by summarizing the main contributions, discussing their importance and suggesting some future research directions.

1.4 References

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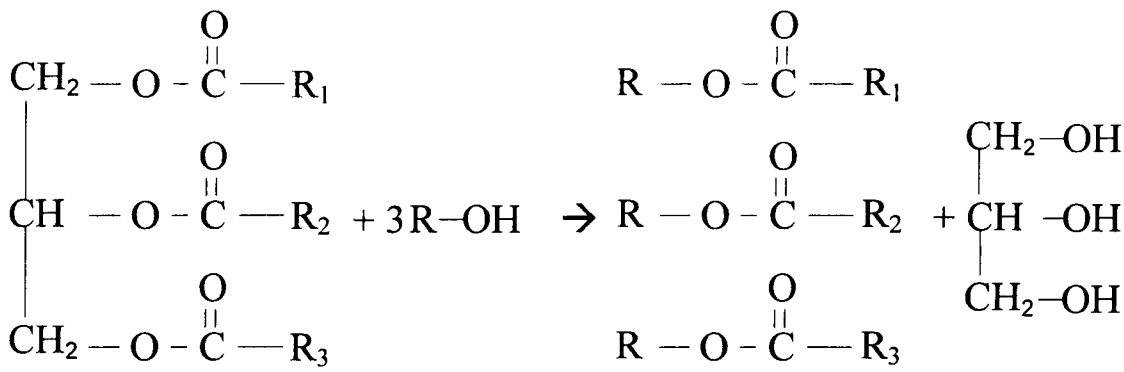
CHAPTER 2
Theoretical Background

2.1 Transesterification

Most commercially produced biodiesel is derived from vegetable oil. Vegetable oil is not used directly in engines because it could induce many problems. Such problems include injector fouling as a result of coking forming on the injector, ring sticking, carbon deposits and varnish build-up on the cylinder wall. Most of the problems related to the use of vegetable oils can be credited to their high viscosity and to the reactivity of their polyunsaturated fatty acid components. Therefore, pure vegetable oils are rarely used as a diesel substitute (Ma & Hanna, 1999). However, due to recent interest in a vegetable oil-derived fuel, four potential solutions to the problem of high viscosity were looked into: transesterification, dilution, pyrolysis and micro-emulsification (Schwab et al., 1987). Biodiesel is typically produced by transesterification, a feasible method to overcome the viscosity problems (Ma & Hanna, 1999).

Oils and fats are mainly composed of triglcyerides (TG), esters of glycerol (monoglycerides (MG) and diglycerides (DG)) and fatty acids (carboxylic acids).

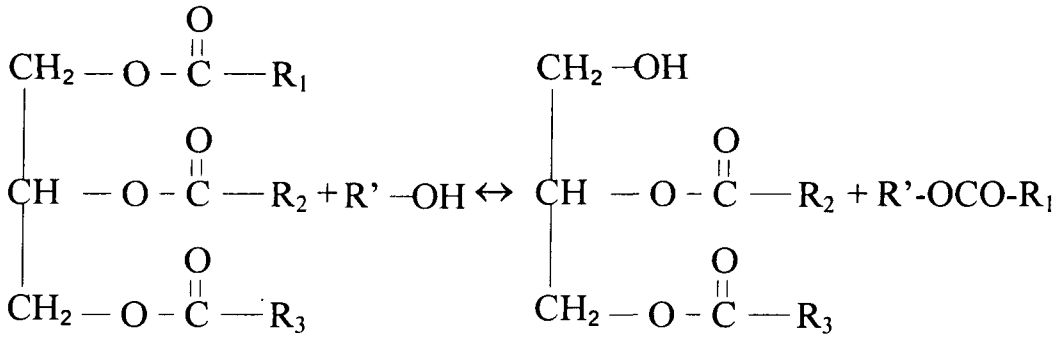
Transesterification involves the conversion of triglycerides into fatty acid alkyl esters. These fatty acid alkyl esters are known as biodiesel. The process involves the reaction of the lipid feedstock (such as vegetable oil) with an alcohol (such as methanol), in the presence of a catalyst (such as sodium methoxide), to yield the corresponding fatty acid alkyl esters and glycerol as a by-product. Figure 2.1 shows the overall transesterification reaction, where R_1, R_2 and R_3 represent long chain hydrocarbons and R represents an alcohol hydrocarbon (e.g., CH_3 if methanol is used).



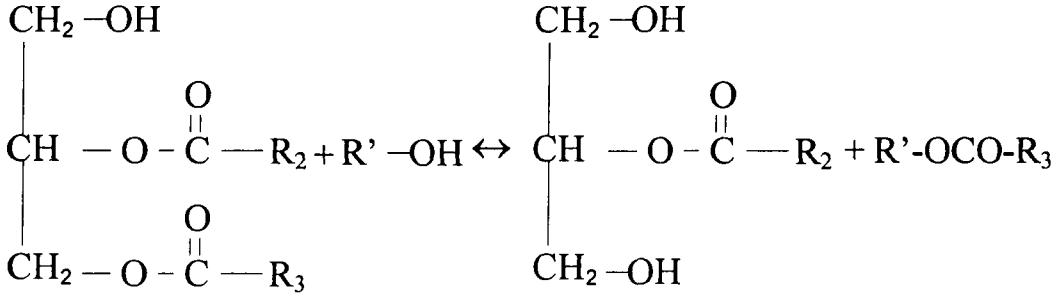
triglyceride alcohol fatty acid alkyl esters glycerol

Figure 2.1: Overall reaction for the transesterification of triglycerides

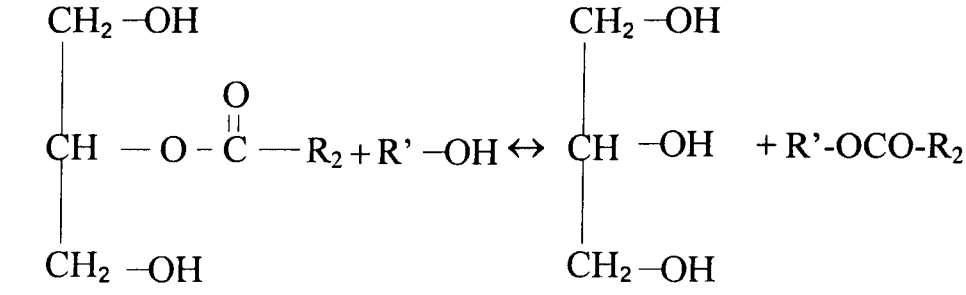
The transesterification reaction occurs in three reversible steps, as shown in Figure 2.2, where R_1, R_2 and R_3 represent long chain hydrocarbons and R' represents an alcohol hydrocarbon. The TG reacts with an alcohol molecule to produce DG. The DG then reacts with another alcohol molecule to produce MG and finally the MG reacts with a third alcohol molecule to produce the by-product, glycerol, and fatty acid alkyl ester.



triglyceride alcohol diglyceride alkyl ester



diglyceride alcohol monoglyceride alkyl ester



monoglyceride alcohol glycerol alkyl ester

Figure 2.2: Reaction steps for the transesterification of triglycerides

Converting triglyceride to methyl ester by means of transesterification decreases the molecular weight to one-third of that of oil. It also reduces the viscosity by a factor of eight (Ma & Hanna, 1999). There are several factors that influence the rate of the transesterification reaction; the most significant ones are temperature, catalyst, alcohol to oil ratio, concentration of free fatty acids and water content. Section 2.4 provides more details on the effect of each of those variables on the reaction rate.

2.2 Biodiesel Standards

Biodiesel can be significantly contaminated with unseparated glycerols, unreacted MG, DG, TG, alcohol and water. Theses contaminants can lead to major problems to both the environment and engines (e.g., filter clogging or engine deposits). The determination of biodiesel fuel quality is crucial to its successful commercialization. Therefore, standards such as the ASTM D6571 in the United States and EN 14214 in Europe were developed to provide limits on the levels of these compounds in biodiesel fuel.

In the United States, biodiesel is standardized by the American Society for Testing and Materials. The standard is ASTM D6751 which consists of the specifications for biodiesel (B100) blend stock for distillate fuels. Table 2.1 presents this standard. In Europe, the biodiesel standard is EN 14214 which describes the minimum requirements for biodiesel, as shown in Table 2.2. This was agreed upon by countries that are members of the European Committee for Standardization (CEN).

Table 2.1: ASTM D6571 biodiesel standard

Property	Test method	Limits	Unit
Flash point (closed cup)	D 93	130.0 min	°C
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity, 40°C	D 445	1.9 – 6.0	mm^2/s
Sulphated ash	D 874	0.020 max	% mass
Sulphur	D 5453	0.0015 max	% mass
Copper strip corrosion	D 130	No. 3 max	-
Cetane number	D 613	47 min	-
Cloud point	D 2500	Report	°C
Carbon residue (100% sample)	D 4530	0.050 max	% mass
Acid number	D 664	0.80 max	mg KOH/g
Free glycerol	D 6584	0.020 max	% mass
Total glycerol	D 6584	0.240 max	% mass
Phosphorous content	D 4951	0.001 max	% mass
Distillation temperature, atmospheric equivalent, 90% recovered	D 1160	360 max	°C

Table 2.2: EN 14214 biodiesel standard

Property	Test Method	Limits		Unit
		Min	Max	
Ester Content	EN 14103	96.5	-	% (m/m)
Density, 15°C	EN ISO 3675 EN ISO 12185	860	900	kg/m^3
Viscosity, 40°C	EN ISO 3104 EN ISO 3105	3.5	5.0	mm^2/s
Flash Point	EN ISO 3679	120	-	°C
Sulphur Content	EN ISO 20846 EN ISO 20884	-	10	mg/kg
Carbon Residue, 10% bottoms	EN ISO 10370	-	0.30	% (m/m)
Cetane Number	EN ISO 5165	51	-	-
Sulphated Ash	EN ISO 3987	-	0.02	% (m/m)
Water Content	EN ISO 12937	-	500	mg/kg
Total Contamination	EN 12662	-	24	mg/kg
Copper Strip Corrosion (3h at 50°C)	EN ISO 2160	1	1	-
Oxidation Stability, 110°C	EN 14112	6 .0	-	hours
Acid Value	EN 14104	-	0.5	mg /g
Iodine Value	EN 14111	-	120	-
Linolenic acid content	EN 14103	-	12	% (m/m)
Polyunsaturated methyl esters	-	-	1	% (m/m)
Methanol Content	EN 14110	-	0.20	% (m/m)
Monoglyceride Content	EN 14105	-	0.80	% (m/m)
Diglyceride Content	EN 14105	-	0.20	% (m/m)
Triglyceride Content	EN 14105	-	0.20	% (m/m)
Free glycerol	EN 14105 EN 14106	-	0.02	% (m/m)
Total glycerol	EN 14105	-	0.25	% (m/m)
Alkali Metals (Na + K)	EN 14108 EN 14109	-	5.0	mg/kg
Earth Alkali Metals (Ca + Mg)	prEN 14538	-	5.0	mg/kg
Phosphorus Content	EN 14107	-	10.0	mg/kg

Over the past few years, various methods to analyze the biodiesel quality have been investigated. Chromatographic and spectroscopic methods are the most common analytical techniques used (Knothe *et al.*, 2005). Chromatographic methods include gas chromatography (GC) and high performance liquid chromatography (HPLC). Spectroscopic methods include near infrared spectroscopy (NIR) and nuclear magnetic resonance (NMR). It is necessary that the technique used is reliable, accurate and relatively quick. GC analysis is the most commonly used method due to its simplicity and high level of accuracy in quantifying minor components (Khan, 2002). Another analytical technique is Karl Fischer coulometric titration, used to quantitatively determine the biodiesel's water content.

2.3 Advantages and Challenges of Biodiesel

The world's reserves of non-renewable energy (coal, oil and gas) will eventually deplete. Therefore, biodiesel provides an alternative and renewable source of energy (Sharma & Singh, 2008). Biodiesel is produced domestically; therefore, its production provides more jobs and stimulates economic growth. Additionally, it is expected to lessen the dependence on oil importing countries and thereby bring along geopolitical stability (Demirbas, 2008).

In its life cycle, biodiesel yields 3.2 units of fuel energy for every unit of fossil energy consumed in its production (Sheehan *et al.*, 1998). Furthermore, biodiesel is relatively environmentally friendly. It is potentially an ideal fuel for vehicles because it adds fewer emissions to the atmosphere than petroleum based fuels. The presence of

oxygen in biodiesel (11 wt.%) brings about complete combustion in the engine. This results in lower exhaust emissions compared to diesel fuel: 20% less carbon monoxide emissions, 30% less hydrocarbon emissions, 50% less soot emissions, and 40% less particulate matter emissions. It also has 99% less sulphur oxide (SO_x) emissions than diesel fuel because it is sulphur-free (Tat, 2003). It is approximately carbon dioxide neutral because any carbon dioxide released during reaction or production or distribution was absorbed by the plant feedstock when it was alive. Toxicity tests reveal that biodiesel is considerably less toxic than diesel fuel (Knothe *et al.*, 2005). Moreover, biodiesel provides a higher lubricity than diesel fuel, hence reducing engine wear (Graboski & McCormick, 1998). Another advantage of biodiesel is that it could be used directly in diesel engines without the need for engine modifications.

Despite its numerous advantages, there are some challenges facing biodiesel. The major obstacle in the commercialization of biodiesel is the high cost of production (Khan, 2002). The price of the feedstock accounts for approximately 75% of the total manufacturing cost (Phan & Phan, 2008). Using a less expensive feedstock, such as waste cooking oils, could reduce the overall production cost. Furthermore, the glycerol by-product could be recovered and used in other industrial processes, to help make the process more cost-effective.

2.4 Variables Affecting Transesterification

2.4.1 Temperature

Transesterification can take place at different temperatures. In order to increase the rate of reaction, biodiesel production should be performed at a high temperature and pressure (Phan & Phan, 2008). The boiling point of methanol is 64.7°C. Thus, the transesterification reaction could be carried out from room temperature up to 65°C since temperatures higher than this will boil off the alcohol and result in a much lesser yield (Sharma & Singh, 2008).

2.4.2 Catalyst

An acid or base catalyst could be used in the transesterification reaction. Common acid catalysts include sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4) and hydrochloric acid (HCl). Common base catalysts include sodium hydroxide (NaOH), sodium methoxide (CH_3ONa), potassium hydroxide (KOH) and potassium methoxide (CH_3OK) (Van Gerpen *et al.*, 2006). Using a base catalyst leads to a much faster reaction than an acid catalyst. Nowadays, base-catalyzed transesterification is the most widely used method for biodiesel production.

Van Gerpen *et al.* (2006) compared the results of four different base catalysts in terms of biodiesel yield and soap formation, at different catalyst concentrations. The four catalysts used were NaOH, CH_3ONa, KOH and CH_3OK. It was found that the methoxide catalysts produced higher yields than the corresponding hydroxide catalyst. Furthermore,

the potassium-based catalysts produced higher yields than the sodium-based catalysts. However, potassium-based catalysts resulted in a higher soap formation than the sodium-based catalysts.

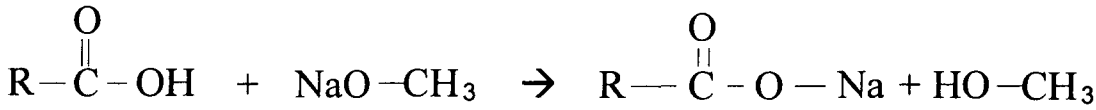
2.4.3 Alcohol to Oil Ratio

The transesterification reaction is reversible; thus, using an excess of reactant (i.e., alcohol) or removing the products as they form can help move the reaction forward. The stoichiometric ratio for transesterification requires 3 moles of alcohol and 1 mole of triglyceride to yield 3 moles of fatty acid alkyl ester and 1 mole of glycerol. However, transesterification is usually carried out with an extra amount of alcohol in order to shift the equilibrium to the desired biodiesel product. Usual commercial practice is to use excess alcohol, i.e., an alcohol:oil ratio of at least 6:1, instead of the molar stoichiometric ratio of 3:1. As a result, more biodiesel is formed in a shorter period of time. This results in a decrease in residence time and an increase in reactor capacity (Allen & Prateepchaikul, 2006). Nevertheless, this comes at the expense of operating cost.

Increasing the alcohol to oil ratio beyond the stoichiometric ratio of 3:1 is advantageous because it enhances the settling process of the products. If a ratio below 7:1 is used, several hours are required for the completion of the settling process. On the other hand, the settling process takes approximately 30 min for ratios of 7:1 and 8:1 (Phan & Phan, 2008).

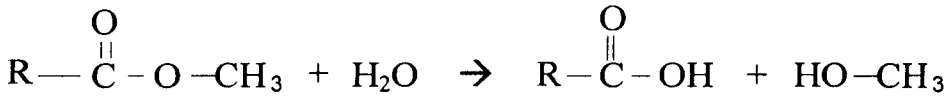
2.4.4 Free Fatty Acids and Water Content

The presence of water and free fatty acids (FFAs) affect the transesterification reaction. In a base-catalyzed transesterification, the FFAs in the feedstock are converted to soap rather than biodiesel. Figure 2.3 shows the reaction of a FFA molecule with a base to produce soap and water. Additionally, the water in the feedstock reacts with the biodiesel to produce FFA and methanol, as shown in Figure 2.4.



fatty acid sodium methoxide soap methanol

Figure 2.3: Formation of soap and methanol



biodiesel water fatty acid methanol

Figure 2.4: Formation of fatty acid and methanol

The presence of soap causes problems such as an increase in viscosity, formation of gels, lower biodiesel yield, difficulty in separating the glycerol from the

biodiesel and the formation of water (Freedman *et al.*, 1984). On the other hand, if an acid-catalyzed transesterification is used to avoid soap formation, a much longer reaction time is observed.

2.5 Feedstocks

2.5.1 Types of Feedstocks

The different feedstock materials that could be used to produce biodiesel are: vegetable oil, animal fat, waste vegetable oil and other, mostly non-edible, materials. Vegetable oils, such as canola oil, soybean oil, rapeseed oil, sunflower oil and palm oil, are the most common feedstocks. Animal fats, such as beef tallow and yellow grease, are also occasionally used. Other less common feedstock materials include oils from coconut, fish, karanja, microalgae, *Jatropha curcas*, laurel, *Lesquerella fendleri*, oat, rubber seed, sorghum and wheat (Demirbas, 2008).

Different countries use different materials as the primary feedstock, depending on their availability. In Canada, canola oil (which is produced from modified rapeseed with the erucic acid removed) was developed in the 1970s, and it is the main feedstock for biodiesel production. Rapeseed oil is more commonly used in Europe. Soybean oil is usually used in the United States, while coconut oil and palm oil are used in Malaysia and Indonesia (Demirbas, 2008). In India and Southeast Asia, biodiesel research projects are conducted using *Jatropha curcas* and karanja oil.

Argentina, Malaysia, Indonesia, Brazil and the Philippines are the major exporters of vegetable oils. The major importers are China, United Kingdom and Italy. A small number of countries are exporters and importers of vegetable oils; for example Germany, United States, Netherlands and Singapore (Demirbas, 2008).

The high cost and limited availability of the feedstock are key issues in biodiesel production. Typically, the feedstock component accounts for approximately 75% of the total manufacturing cost (Phan & Phan, 2008). Thus, an ideal choice would be a feedstock that is cheaper yet does not compromise the quality of the biodiesel. Waste vegetable oils and animal fats are promising feedstock options that could lower the cost of biodiesel production. The price of waste vegetable oil is around 2 to 3 times lower than virgin vegetable oil. Therefore, if waste vegetable oil is utilized, the total manufacturing cost of biodiesel can be reduced.

A large amount of waste vegetable oil and animal fat is produced each year. European Union countries produce between 700,000 to 1,000,000 tonnes per year (Chhetri *et al.*, 2008). The Energy Information Administration in the United States estimated that the average waste cooking oil was 4 kg per year per capita (Chhetri *et al.*, 2008). The population of Canada is estimated to be 34 million (Statistics Canada, 2010). Assuming the per capita waste cooking oil in Canada is comparable to that of the United States, the total waste cooking oil produced in Canada is approximately 150 million litres per year.

Generally, waste management of used cooking oils and fats poses a significant concern because of the potential disposal problems (Phan & Phan, 2008). Therefore,

using waste vegetable oils as a feedstock is beneficial because it will reduce the environmental impacts caused by disposal and it will decrease biodiesel production costs.

When used in cooking, vegetable oil is heated to high temperatures. This causes chemical reactions, such as polymerization, oxidation and hydrolysis, to occur. As a result, changes occur in the physical and chemical properties of the vegetable oil. Extensive research has been performed to characterize these changes in physical and chemical properties. Polymerization results in the formation of higher molecular weight compounds and thus an increase in viscosity. Furthermore, the acid value, specific gravity and saponification value of the vegetable oil increases, while the iodine value decreases (Mittelbach *et al.*, 1992). The percent of FFAs increases due to the hydrolysis of TG in the presence of food moisture and oxidation (Canakci, 2005). FFAs present in fats, oils and greases are saturated or unsaturated carboxylic acids. As the quantity of FFA increases, the acid value increases.

The waste cooking oil is characterized by the amount of FFA present. If the FFA level is less than 15% then it is referred to as yellow grease. Yellow grease is made of vegetable oil or animal fat that has been used for cooking food such as meat, fish or vegetables. If the FFA level is greater than 15%, it is referred to as brown grease.

2.5.2 High FFA Feedstock Challenges

Although waste vegetable oils and animal fats are appealing feedstock options due to their lower costs, their conversion to biodiesel is substantially more difficult compared to that of high quality virgin oils. Waste vegetable oils contain high amounts of

FFA and water that cannot usually be converted to biodiesel using conventional base-catalyzed transesterification. When waste vegetable oil is used as a feedstock, an additional amount of base catalyst is used to neutralize the FFAs. Hence the total amount of base used in waste vegetable oil is greater than in virgin vegetable oil. Using oil feedstock with a high percent FFA causes major problems such as: soap formation, water formation and lower yield.

When a base catalyst is used, the FFAs in the waste vegetable oil predominantly react with the base to form soap and water, as shown in Figure 2.3 above. Thus the FFAs in the feedstock are converted to soap, as opposed to the desired fatty acid alkyl esters. This results in a lower product yield and quality. Furthermore, the presence of soap causes difficulties in separating the fatty acid alkyl ester phase from the glycerol phase. Soap formation also increases the viscosity and causes gel formation (Canakci & Sanli, 2008).

In order for the base-catalyzed transesterification to effectively take place, the amount of FFA in the waste vegetable oil should not exceed a certain limit. If exceeded, the yield will be notably low or the reaction may not take place at all (Sharma & Singh, 2008). Table 2.3 provides recommendations for the maximum FFA limit in which the base-catalyzed transesterification reaction could effectively occur.

Table 2.3: Maximum recommended %FFA for base-catalyzed transesterification

Author	FFA (mass %)
Zhang *et al.*	< 0.5
Ma and Hanna	< 1
Freedman *et al.*	< 1
Tiwari *et al.*	< 1
Sahoo *et al.*	≤ 2
Ramadhas *et al.*	≤ 2
Canakci and Van Gerpen	< 3

Another method that could be used is acid-catalyzed transesterification. Soap formation is not a major concern and the process does not require a pre-treatment step to reduce the FFAs. However, acid-catalyzed transesterification requires more alcohol and consequently larger reactors. Furthermore, stainless steel materials must be utilized due to the corrosive nature of the acid catalyst. These aspects result in higher equipment costs (Canakci & Sanli, 2008). As a result, not many commercial biodiesel plants use the acid-catalyzed process (Zhang *et al.*, 2003).

2.5.3 Two-step Process

A two-step process was developed to produce biodiesel from high FFA feedstock (Canakci & Van Gerpen, 2003). The first step is an esterification reaction that reduces the FFA content of the feedstock. The second step is a base-catalyzed transesterification that yields the desired biodiesel product. The purpose of the first step of the process is to lower the acid value (and hence FFA content) of the feedstock to less than 2 mg KOH/g (Canakci, 2005). This step is referred to as the pre-treatment reaction. This is achieved by an acid-catalyzed esterification reaction, where the FFAs are converted to monoesters. It involves the reaction of the FFA with an alcohol, in the presence of an acid catalyst, to produce monoesters and water, as shown in Figure 2.5. The catalyst amount and molar alcohol ratio used in the pre-treatment reaction are calculated based on the initial FFA content of the feedstock (Canakci & Sanli, 2008). The formation of water is the main problem of the pre-treatment step because water inhibits the conversion of FFAs to esters (Freedman *et al.*, 1984).

fatty acid alcohol monoester water

Figure 2.5: Pre-treatment process (acid-catalyzed esterification reaction)

After the pre-treatment process, the second step proceeds. The second step is a base-catalyzed transesterification reaction where the TG reacts with an alcohol, in the presence of a base catalyst, to produce biodiesel and glycerol.

To sum up, the current research findings suggest that two paths could be followed, and the choice depends on the FFA content in the feedstock. This is illustrated in Figure 2.6.

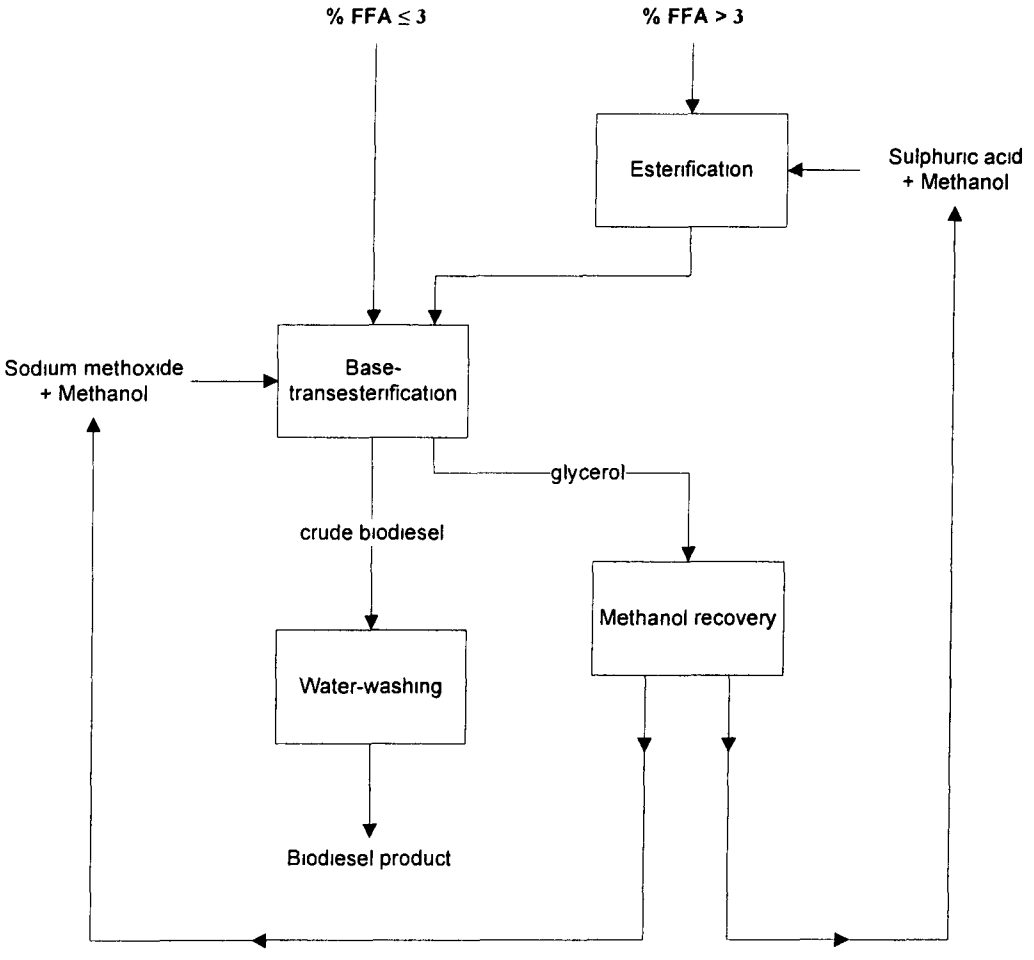


Figure 2.6: Flow diagram of biodiesel production process, depending on initial %FFA in the feedstock

Although the two-step process avoids some issues that would result from a one-step process, it is by no means ideal. The main purpose of using waste vegetable oils is to reduce the biodiesel production cost. However, in the two-step process, the addition of a pre-treatment unit to reduce the FFAs adds extra cost to the process. Some findings indicate that the two-step process does not necessarily reduce the unit price of biodiesel (Canakci & Sanli, 2008). Furthermore, the two-step process results in the release of harmful materials into the environment. The sulphate ion from the first step reacts with the base cation during the second step to form sulphates. For example, if CH_3ONa is the base catalyst, then sodium sulphate is produced. The sodium sulphate is soluble in water and is removed in the water-wash.

2.6 Membrane Reactor for Biodiesel Production

2.6.1 Membrane Reactor

By definition, a membrane reactor is a "device for simultaneously carrying out a reaction and membrane-based separation in the same physical enclosure" (IUPAC, 1996). The concept of a membrane reactor dates back to the 1960s (Julbe *et al.*, 2001). During the last two decades extensive research was performed and numerous papers published in this area (Hsieh, 1996). Membrane reactors play an important role in many chemical processes. They have several advantages over conventional chemical reactors. A membrane reactor where simultaneous reaction and separation occur could surpass a conventional reactor. This is because the continuous and selective separation of product

allows the equilibrium limited reaction to be released from its limitation (Michaels, 1968).

Transesterification is a standard reversible chemical reaction; therefore, when producing biodiesel via transesterification, a membrane reactor could be employed. The membrane can play different roles in a membrane reactor. It can selectively remove the reaction product and thus increase the yield of equilibrium limited reactions; or it can enable short contact times and thus increase the selectivity in fast consecutive reactions (Cao, 2008). Separative membrane reactors can selectively remove the products or by-products from the reaction mixture. This increases the conversion in equilibrium-limited reactions. Furthermore, they can limit excessive by-product formation by the selective permeation of the reactants. All these characteristics of separative membrane reactors can be utilized in the production of biodiesel by transesterification.

2.6.2 Membrane Material and Module

The harsh conditions required for biodiesel production necessitates the use of inorganic, rather than organic, membranes. If organic membranes are used, they will not withstand the thermal and corrosive conditions under which the transesterification reaction is performed. On the other hand, inorganic membranes can endure such harsh conditions due to their relative chemical, thermal and mechanical stability.

For the membrane reactor, the inorganic membrane can be made of ceramic, carbon, glass or metal. It can be inert or catalytically active; dense or porous. Furthermore, the inorganic membrane composition can be consistent or composite, with a

homogeneous or asymmetric porous structure. It can be supported on materials such as porous glass, sintered metal, granular carbon or ceramics (such as alumina). There are several membrane shapes that could be used. These include flat discs, tubes, hollow fibres, or monolithic multi-channel elements for ceramic membranes; foils, spirals or helixes for metallic membranes (Hsieh, 1996).

To ensure that the best possible membrane is chosen for biodiesel production, several things must be considered. The membrane material and pore size are of key importance to its operation. Ideally, the membrane should provide precise control of pore size, with a high permeance and low pressure drop. Furthermore, it should have a narrow pore size distribution to meet separation and quality control requirements.

The use of ceramic membranes for industrial applications is rising and this is attributed to their distinctive properties. Ceramic membranes have a great thermal stability, chemical stability, high porosity, narrow pore size distribution, high flux, long service life and are mechanically stable even under high pressures (Van Gestel *et al.*, 2006). Moreover, the thermal, chemical and mechanical stability of ceramic membranes allows them to be thoroughly cleaned. This is necessary when waste vegetable oil feedstock is used, which is the case in this project. The main drawback of ceramic membranes is their relatively high cost.

There are several membrane shapes that could be used for ceramic membranes. These include flat discs, tubes, hollow fibres, or monolithic multi-channel elements. A monolithic multi-channel shaped ceramic membrane provides a larger filtration area per unit volume than a single tube or sheet (Cao, 2008). A single tube is often used in

laboratory applications. Relatively large tube diameters allow high cross-flow velocities. Consequently, turbulent flow is observed, with reasonable permeate and retentate fluxes.

2.6.3 Biodiesel Membrane Reactor System

A micro-porous inorganic membrane reactor can selectively permeate biodiesel, methanol and glycerol during the transesterification reaction (Dubé *et al.*, 2007). The immiscibility of the oil feedstock in alcohol and the miscibility of the biodiesel in alcohol are the basis of the membrane reactor operation (Cao *et al.*, 2008). It results in an easy separation of the products from the reactant. The principle is illustrated in Figure 2.7. The oil feedstock is immiscible in alcohol; therefore, the oil molecules are trapped in oil droplets resulting in the formation of an emulsion. When the emulsion flows along the surface of the membrane, the droplets with a diameter smaller than the membrane pore size pass through the membrane while the ones with a larger diameter are retained. Transesterification occurs at the surface of the oil droplets suspended in alcohol (Ataya *et al.*, 2006). The products of transesterification (biodiesel and glycerol) and the catalyst are soluble in the alcohol while the oil feedstock is not. As the biodiesel is produced it forms a layer on the oil droplet surface; as the layer grows the biodiesel diffuses into the alcohol phase. Then, as a result of the pressure difference across the membrane, it passes through the membrane together with the glycerol and catalyst.

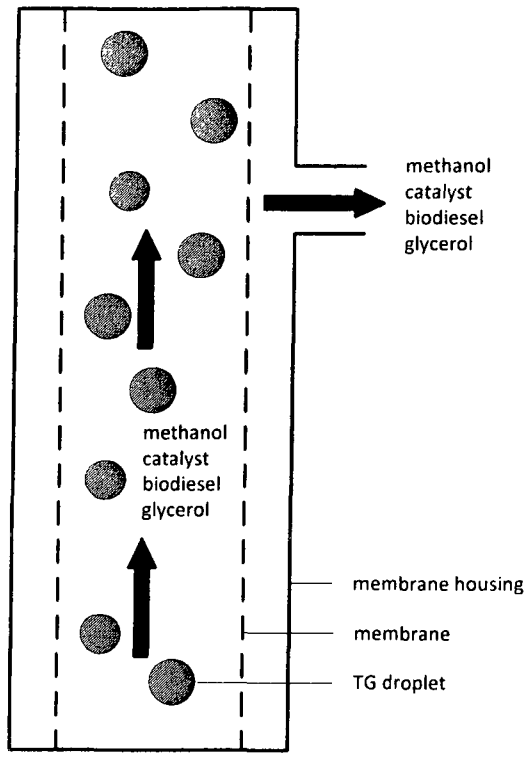


Figure 2.7: Schematic diagram of membrane cross section. Diagram not to scale.

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CHAPTER 3
Materials and Methods

3.1 Materials

The feedstock was waste vegetable oil (Bitroleum Renewable Energy Corporation, Ottawa, ON, Canada) collected from local restaurants. The alcohol used was methanol, 99.9% purity (CH_3OH, Fisher Scientific, Nepean, ON, Canada). The catalyst used was sodium methoxide, 25 wt.% in methanol solution (CH_3ONa, Sigma-Aldrich, Oakville, ON, Canada). Oleic acid, technical grade 90% ($CH_3(CH_2)_7CH=CH(CH_2)_7COOH$, Sigma-Aldrich, Oakville, ON, Canada) was used to vary the FFA content. Hydrochloric acid, reagent grade 37% (HCl, Fisher Scientific, Nepean, ON, Canada) was also used.

The tubular membrane module consisted of a ceramic membrane placed inside a stainless steel housing. The membranes used in this project were purchased from Inopor (Inopor, Veilsdorf, Germany). The specifications of the membranes are presented in Table 3.1. The support material of the ceramic membranes was aluminium oxide (Al_2O_3) and the selective layer was titanium dioxide (TiO_2). Seven different pore sizes were used

ranging from 1 nm to 800 nm. The 1 nm membrane is classified as nanofiltration; the 3 nm, 5 nm and 30 nm as ultrafiltration; and the 100 nm, 250 nm and 800 nm as microfiltration.

Table 3.1: Specifications of the ceramic membranes

Parameter	**Value**
Design	Single tube per housing, single channel per tube
Material	Titanium dioxide and aluminium oxide
Mean pore size	1, 3, 5, 30, 100, 250 and 800 nm
Outside tube diameter	10 mm
Inside tube diameter	7 mm
Length	500 mm
Membrane area	0.011 m^2

The water content analysis was performed using a Karl Fischer TitroLine KF trace analyzer (Schott Instruments, Mainz, Germany). The solvents used were hydranal-coulomat oil (Sigma-Aldrich, Oakville, ON, Canada) and hydranal-coulomat CG (Sigma-Aldrich, Oakville, ON, Canada).

The gas chromatography (GC) instrument used for analysis was a Varian CP-3800 GC. The chemicals used were *n*-heptane anhydrous 99%, N-methyl-N-

trimethylsilyl-trifluoroacetamide (MSTFA), 1,2,3-tricaproylglycerol (tricaprin) and 1,2,4-butanetriol (Sigma-Aldrich, Oakville, ON, Canada).

3.2 Methods

3.2.1 Feedstock Preparation

The waste vegetable oil was filtered to remove any solid food particles. Filtration was performed using a micro-filter cartridge with a pore size of 25 μm. The FFA content was determined by titration using sodium hydroxide and phenolphthalein indicator. It was found that the waste vegetable oil contained 4.8% FFA. Oleic acid was added to this oil to vary the FFA content depending on the desired levels, according to the experimental design.

3.2.2 Batch Reactor

Batch experiments were performed to determine the methanol:oil molar ratio to be used. The reactions were performed in a one litre Mettler Toledo LabMax™ reactor. The stainless steel reaction vessel was equipped with an anchor-shaped stirring blade and three feed ports. The reactants (i.e., vegetable oil, oleic acid, catalyst and methanol) were charged into the reactor and heated. The temperature and stirring speed were automatically controlled at 65°C and 200 rpm, respectively. The reaction time was 60 min. Experiments were performed at a methanol to oil molar ratio of 6:1 and 20:1 and a FFA content of 4.8 mass% and 10 mass%. At the end of each experiment, the products

were neutralized using hydrochloric acid, to quench the reaction. The experiments were carried out in random order to minimize systematic errors.

3.2.3 Membrane Reactor

A lab-scale membrane reactor was designed and built. An important design consideration was the operational safety; therefore, the reactor was designed to fit inside a walk in fume hood. The safety precautions are presented in Appendix A.

Figure 3.1 shows a schematic diagram of the membrane reactor used in this project. The methanol and oil were fed into the reactor using gear pumps (Micropump, Aurora, ON, Canada). A seal-less centrifugal canned motor pump (Cole-Parmer, Montreal, QC, Canada) was used to circulate the mixture around the loop. The reaction temperature was controlled using a temperature-controlled, heated circulating bath (Cole-Parmer Polystat, Montreal, QC, Canada). The reaction temperature was measured using a temperature probe placed in the loop, as shown in Figure 3.1.

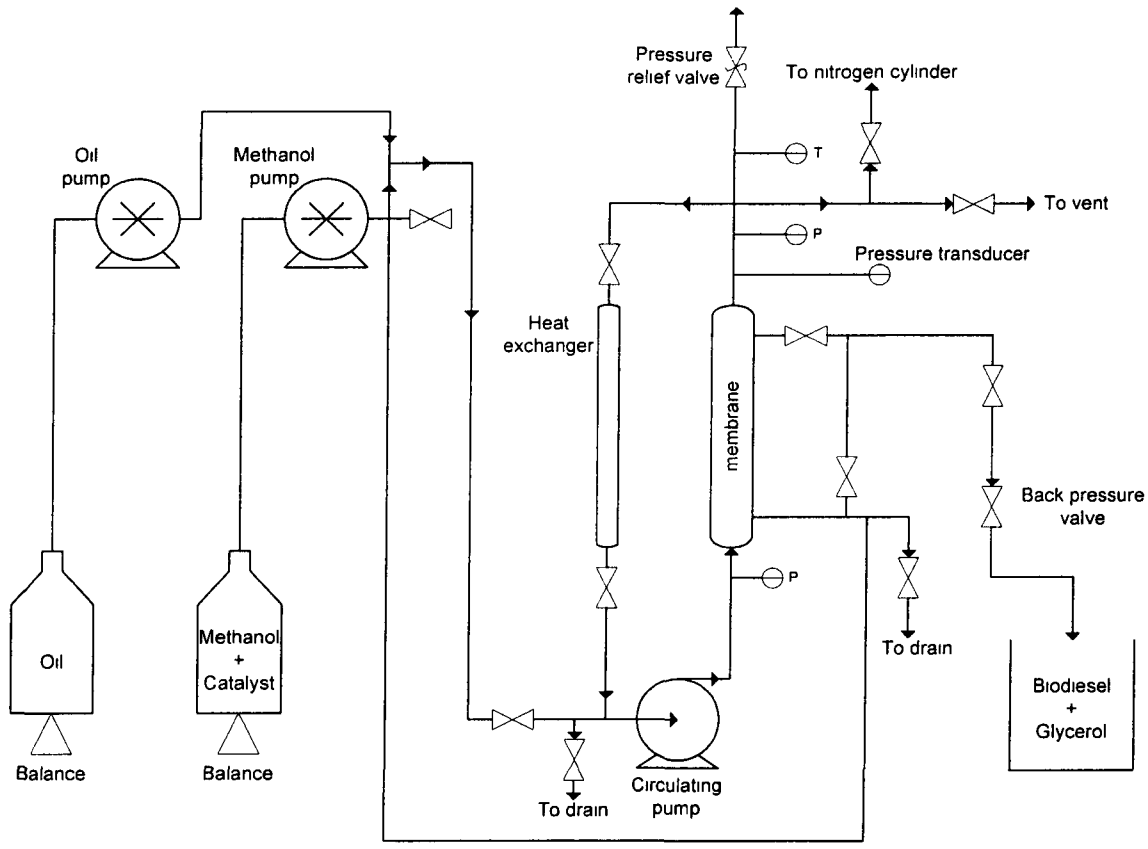

Figure 3.1: Schematic diagram of the continuous membrane reactor

The experimental conditions are presented in Table 3.2. The volume of the reactor was 460 mL. Using the feed pump, the methanol/catalyst solution was fed into the reactor until the reactor was full. The drain valve was opened and a predetermined amount of waste vegetable oil was fed into the reactor using the oil feed pump (the purpose of opening the drain valve was to allow the excess methanol/catalyst solution to exit the reactor). The circulating pump and heat exchanger were then turned on. When the desired temperature of 65°C was reached, the oil and methanol pumps were switched on

to start the continuous feeding. The trans-membrane pressure was set to 15 psi (103.4 kPa). Regulating the pressure was essential in order to prevent cavitation and to avoid boiling at the heat exchanger surface (the temperature of the shell side was 70°C). The flow rates of the methanol and oil feed pumps were set to 2.18 g/min and 2.51 g/min, respectively. The residence time was 84 min. The methanol:oil molar ratio was 20:1. The catalyst (sodium methoxide) concentration was 1 mass% above neutralization.

Table 3.2: Experimental conditions

Parameter	Value
temperature	65°C
residence time	84 min
flux	30 L/(m^2h)
catalyst concentration	1 mass%
oil to methanol molar ratio	20:1

At the end of each experiment, the pumps and heat exchanger were turned off. The system was then drained and the retentate collected. After that, the membrane was back-flushed using 500 mL of methanol. The permeate was poured into a separatory funnel and left to phase separate overnight. It consisted of FAME, glycerol, methanol and catalyst. The permeate and retentate were then neutralized using hydrochloric acid to quench the reaction. The FAME-rich phase of the permeate was evaporated using a rotary vacuum evaporator at 90°C and 0.9 bar (90 kPa) vacuum, for 40 min to ensure that

neither methanol nor water was present. The sample was then centrifuged at 1500 rpm for 45 min, using a Hermle Z400K centrifuge (Hermle Labortechnik, Wehingen, Germany). The FAME was then water washed 4 times with distilled water, at room temperature, using a biodiesel to water volume ratio of 2:1. The experiments were carried out in random order to minimize systematic errors.

3.2.4 Characterization Methods

Several characterization techniques were utilized, including Karl Fischer titration, gas chromatography and acid-base titration. Karl Fischer coulometric titration was used to quantify the water content; gas chromatography was used to determine the free and total glycerol content in the product; and acid-base titration was used to measure the soap content.

Karl Fischer titration was used to quantitatively measure the water content in the FAME, glycerol and retentate by way of the EN 12937 method. To prepare the instrument for titration, the solvent in the titration vessel was observed. If it was a single-phase light orange solution, then the titration was carried out. However, if it was a two-phase dark solution, then the solvents were refilled before proceeding to the titration. The vessel was emptied and then refilled with hydranal-coulomat oil and hydranal-coulomat CG.

The titration proceeded by conditioning the system. Using a syringe, approximately 1 mL of the sample was injected into the vessel. Then the 'fill' button was pressed and the mass of the sample was entered into the system. The mass of each sample

was measured by weighing the syringe before and after injecting the sample. After a couple of minutes the water content appeared on the display screen.

Gas chromatography (GC) was used to determine the free and total glycerol content of the FAME phase by way of the ASTM D6584 method. A Varian CP-3800 GC was utilized, equipped with 1079 programmable temperature vaporizing (PTV) injector, CP-8410 auto injector sampler, and flame ionization detector (FID) using helium as the carrier gas. The column was made of fused silica, wall coated open tubular (WCOT), 15 m long with an inner diameter of 0.32 mm and an outer diameter of 0.45 mm. The VF-5ht stationary phase was used.

Calibration curves were generated from four standards and two internal standards. The standards were monoolein, diolein, triolein (for MG, DG, TG, respectively) and glycerol. The internal standards were 1,2,3-tricaproylglycerol (tricaprin) and 1,2,4-butanetriol.

The silylating agent, N-methyl-N-trimethylsilyl-trifluoroacetamide (MSTFA), was used. The GC analysis sample was prepared by weighing 100 mg of the biodiesel sample and placing it in a clean vial. Then 0.100 mL of tricaprin, 0.100 mL of 1,2,4-butanetriol and 0.100 mL of MSTFA were added to the vial. The vial was shaken by hand then the mixture was left to stand at room temperature for 10 min. After that, 8 mL of *n*-heptane were added to the vial and mixed well. The mixture was then injected into the GC for analysis. The detailed operating guide is presented in Appendix B.

Acid-base titration was used to analyze the soap content in the FAME, glycerol and retentate. The modified version of AOCS method Cc 17-95 was used (Van Gerpen *et*

al., 2004). The procedure consisted of 2 main stages. Firstly, the sample was titrated with a 0.1 N solution of hydrocholoric acid until the phenolphthalein indicator changed colour from pink to colourless. In this step, the acid neutalized the base catalst in the sample. Secondly, a few drops of bromophenol blue indicator were added and then the titration continued until the bromophenol blue indicator changed colour from blue to yellow. The volume of acid required for this colour change indicated the amount of soap in the sample.

3.3 References

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CHAPTER 4
Results and Discussion

4.1 Batch Reactor Experiments

Batch experiments were performed to determine the methanol:oil molar ratio to be used. Figure 4.1 shows the FAME and glycerol phases that resulted from batch transesterification reactions carried out at a methanol:oil molar ratio of 6:1. Similarly, Figure 4.2 shows the FAME and glycerol phases that resulted from batch transesterification reactions carried out at a methanol:oil molar ratio of 20:1. The quality of the experiments performed at 6:1 was significantly lower than 20:1. Therefore, the methanol:oil molar ratio used in this project was 20:1.

Figure 4.1: Batch transesterification using 6:1 methanol:oil molar ratio. Feedstock contained 4.8 mass% FFA (left) and 10 mass% FFA (right)

Figure 4.2: Batch transesterification using 20:1 methanol:oil molar ratio. Feedstock contained 4.8 mass% FFA (left) and 10 mass% FFA (right)

4.2 Membrane Reactor Experiments

The experiments were carried out at 65°C to increase the rate of reaction and shorten the total reaction time. The catalyst used was sodium methoxide because sodium-based catalysts typically result in relatively lower soap formation (this is critical since high FFA feedstock was used). The methoxide was used as opposed to the corresponding hydroxide because it results in a relatively higher yield.

In the experiments with a membrane pore size of 1 nm and a molecular weight cut-off of 750 Daltons, no permeate was observed. This implied that the size of the molecules retained in the reactor did not correspond to the molecular weight cut-off of the membrane. This indicates that membrane pore sizes greater than 1 nm should be used.

Another finding was that the locations of the FAME-rich phase and methanol/glycerol-rich phase in the permeate were switched. Typically, the top layer of the permeate is FAME-rich and the bottom layer is methanol/glycerol-rich. However, it was found that the top layer was the methanol/glycerol-rich phase and the bottom layer was the FAME-rich phase. This shows that the amount of FAME in the FAME-rich phase was such that the density of this phase was greater than that of the methanol/glycerol-rich phase. Therefore, care should be taken when separating the permeate to ensure that the correct phase is analyzed.

4.3 Free and Total Glycerol Content in FAME

4.3.1 Free and Total Glycerol after Water Washing

The quality parameters of most interest to biodiesel producers are the levels of free and total glycerol. According to the EN standard, the maximum allowed level of MG in biodiesel is 0.8 mass%. Figure 4.3 presents the mass% of MG in the FAME produced using the membrane reactor, for the different membrane pore sizes and FFA levels. It can be seen that the MG content in the FAME was significantly below 0.8 mass%. Furthermore, there was no trend associating changes in membrane pore size with MG concentration.

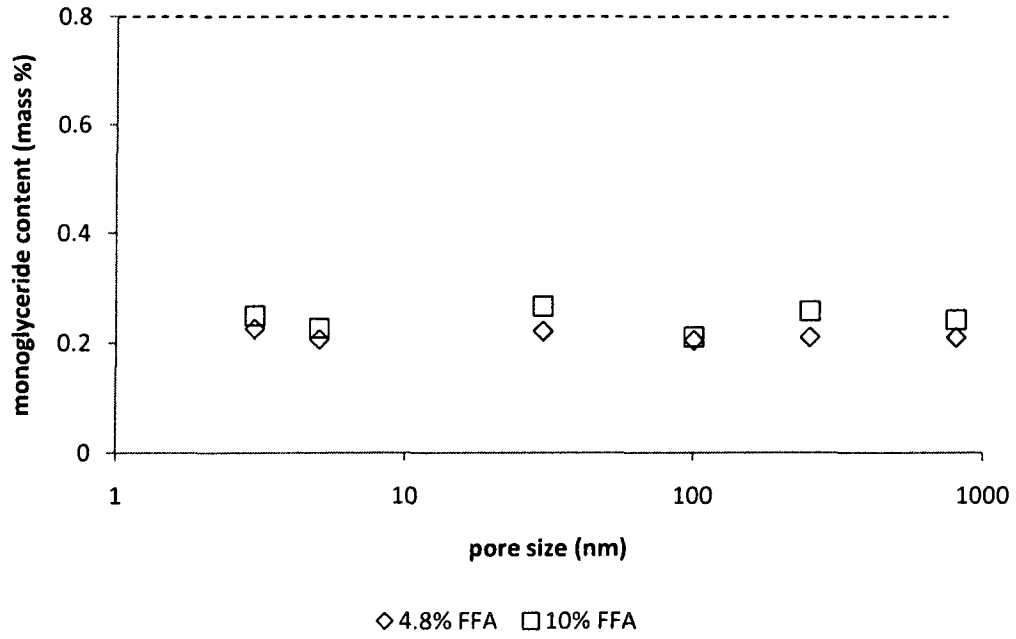

Figure 4.3: MG content in water washed FAME vs. membrane pore size *(note: EN limit = 0.8 mass%)*

The above result can be explained by the octanol-water partition coefficient, K_{OW}, of MG and methanol. K_{OW} is defined as the ratio of the concentration of a chemical in octanol to its concentration in water at equilibrium, at a specified temperature (Lyman *et al.*, 1982). Values of K_{OW} represent the tendency of a chemical to partition itself between an organic and an aqueous phase. Hence, chemicals with close K_{OW} values will be miscible and vice-versa. The K_{OW} values of all the reaction components are presented in Table 4.1 (the reader should note the log scale). MG has a log K_{OW} of 6.04 and is miscible in methanol. Therefore, MG is present in the polar methanol phase in the reactor and passes through the membrane. However, MG is unstable and it is readily transesterified to FAME (Komers *et al.*, 2001). This means that MG could permeate through the membrane but will likely react readily. Consequently, the permeate contained only minute amounts of MG.

Table 4.1: Octanol-water partition coefficients (K_{OW}) values

Component	**Log K_{OW}**
Glycerol	− 1.8
Water	− 1.5
Methanol	− 0.74
MG	6.04
FFA	7.64
FAME	8.02
DG	14.64
TG	23.29

Figure 4.4 presents the percent by mass of DG in the FAME, for the different membrane pore sizes and FFA levels. According to the EN standard, the maximum allowed level of DG in biodiesel is 0.2 mass%. Figure 4.4 shows that the DG content in the FAME was significantly below 0.2 mass%. Furthermore, there was no trend associating changes in membrane pore size with DG concentration. DG is an intermediate product of the transesterification reaction. The DG molecules are surface active i.e., having the properties of a surfactant or soap. They are either solubilized in the continuous FAME-rich methanol phase, enclosed within the hydrophobic oil droplet, or form a micelle. The log K_{OW} values of DG and methanol are 14.64 and -0.74, respectively. This difference in K_{OW} values indicates that DG is poorly soluble in methanol. On the other hand, the log K_{OW} values of DG and FAME are comparatively close. Thus, the FAME-rich methanol phase can dissolve and solubilize the DGs and in so doing, allowed them to pass through the membrane.

According to the EN standard, the maximum allowable level of TG in biodiesel is 0.2 mass%. In all the runs (with different membrane pore sizes and different FFA levels) no TG was detected in the FAME phase, as demonstrated in Figure 4.5. This implies that the smallest oil droplet diameter was greater than 800 nm and consequently could not pass through the membrane pores, as illustrated in Figure 4.6. This is in agreement with previous results using virgin oils; according to Cao (2008) the droplet size lies between the lower limit of 12 μm and the upper limit of 400 μm, with an average size of 44 μm.

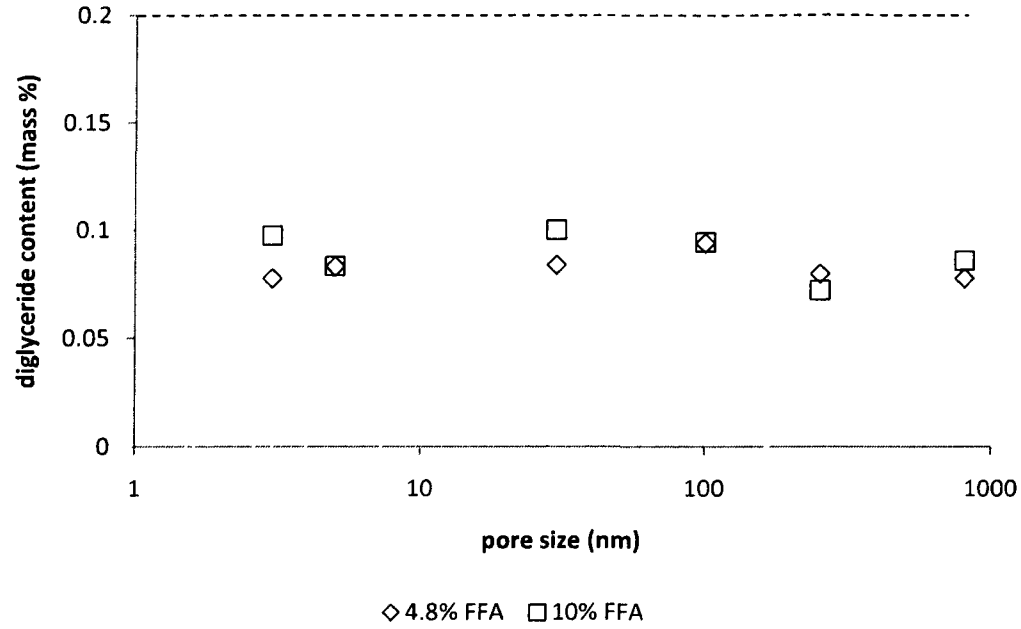

Figure 4.4: DG content in water washed FAME vs. membrane pore size (*note: EN limit = 0.2 mass%)*

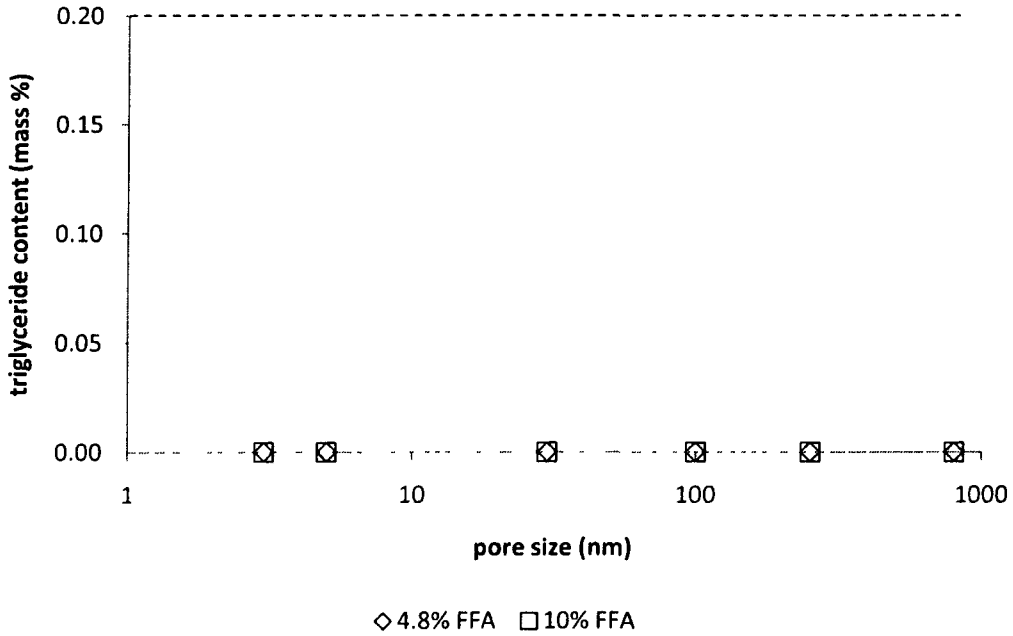

Figure 4.5: TG content in water washed FAME vs. membrane pore size *(note: EN limit = 0.2 mass%)*

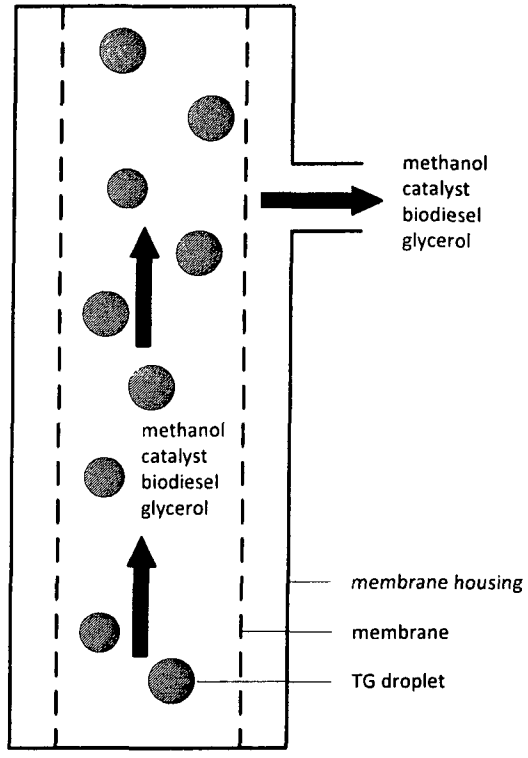

Figure 4.6: Schematic diagram of membrane cross section. Diagram not to scale.

Figure 4.7 presents the percent by mass of free glycerol in the FAME for the different membrane pore sizes and FFA levels. According to the ASTM standard, the maximum allowable level of free glycerol in FAME is 0.02 mass%. Figure 4.7 shows that the free glycerol content in the FAME was well below 0.02 mass%. Furthermore, there was no trend associating changes in membrane pore size with free glycerol concentration. All the glycerol was distributed in the methanol/glycerol-rich phase because methanol and glycerol have similar polarities. The log K_{OW} values of methanol and glycerol are -

0.74 and -1.8, respectively (see Table 4.1); thus glycerol and methanol are miscible. Therefore, it is reasonable to expect that glycerol would be present in the methanol phase and permeate through the membrane.

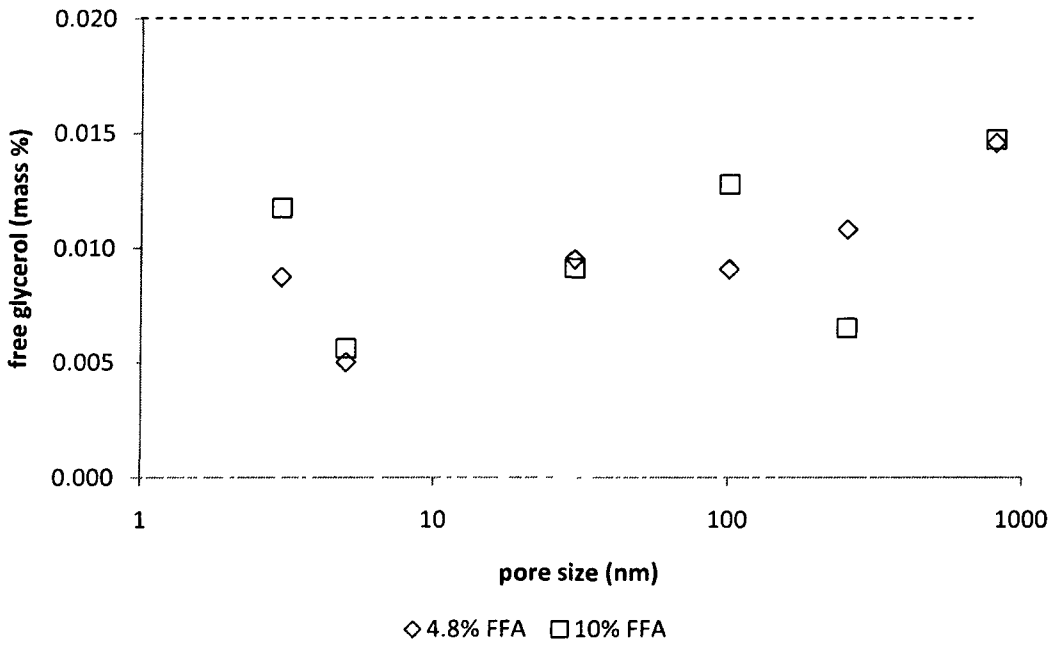

Figure 4.7: Free glycerol content in water washed FAME vs. membrane pore size *(note: ASTM limit = 0.02 mass%)*

Figure 4.8 presents the percent by mass of total glycerol in the FAME, for the different membrane pore sizes and FFA levels. According to the ASTM standard, the maximum allowable level of total glycerol in biodiesel is 0.24 mass%. Figure 4.8 shows that the total glycerol content in the FAME was significantly below 0.24 mass%. Furthermore, there was no trend associating changes in membrane pore size with total glycerol concentration.

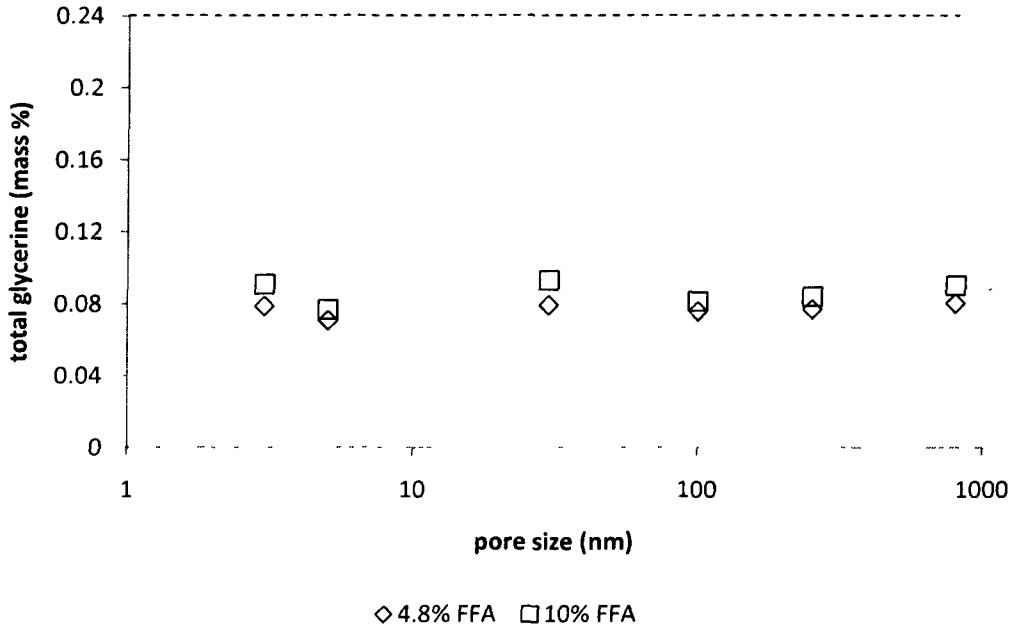

Figure 4.8: Total glycerol content in water washed FAME vs. membrane pore size *(note: ASTM limit = 0.24 mass%)*

4.3.2 Effect of Water Washing

After the FAME was evaporated using a rotary vacuum evaporator, it was water washed. Water and FAME are immiscible; therefore, distilled water was used to wash the FAME. The aim of water washing is to remove excess catalyst, glycerol, methanol and soap. The amounts of free and total glycerol before and after water washing were measured to determine the significance of the water washing step.

The amounts of MG in the FAME before and after the water wash are presented in Figures 4.9 and 4.10 for the 4.8% and 10% FFA feedstock, respectively. Similarly, the

amounts of DG in the FAME before and after the water wash are presented in Figures 4.11 and 4.12 for the 4.8% and 10% FFA feedstock, respectively. Clearly, water washing did not reduce the amount of MG and DG in the FAME because they are not soluble in water.

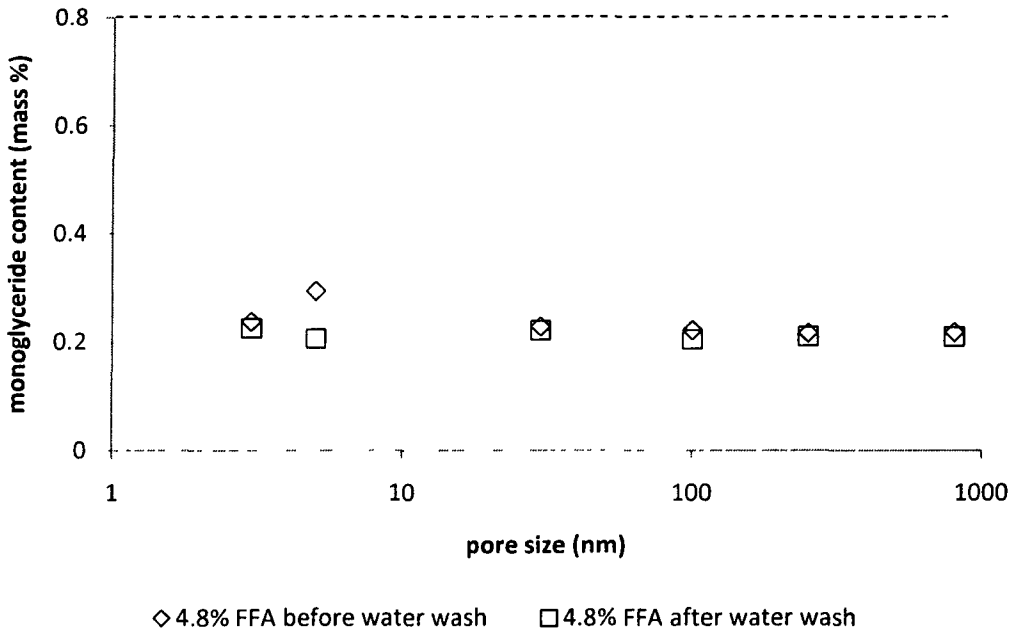

Figure 4.9: MG content in the FAME before and after water washing, versus membrane pore size, for the 4.8% FFA feedstock *(note: EN limit = 0.8 mass%)*

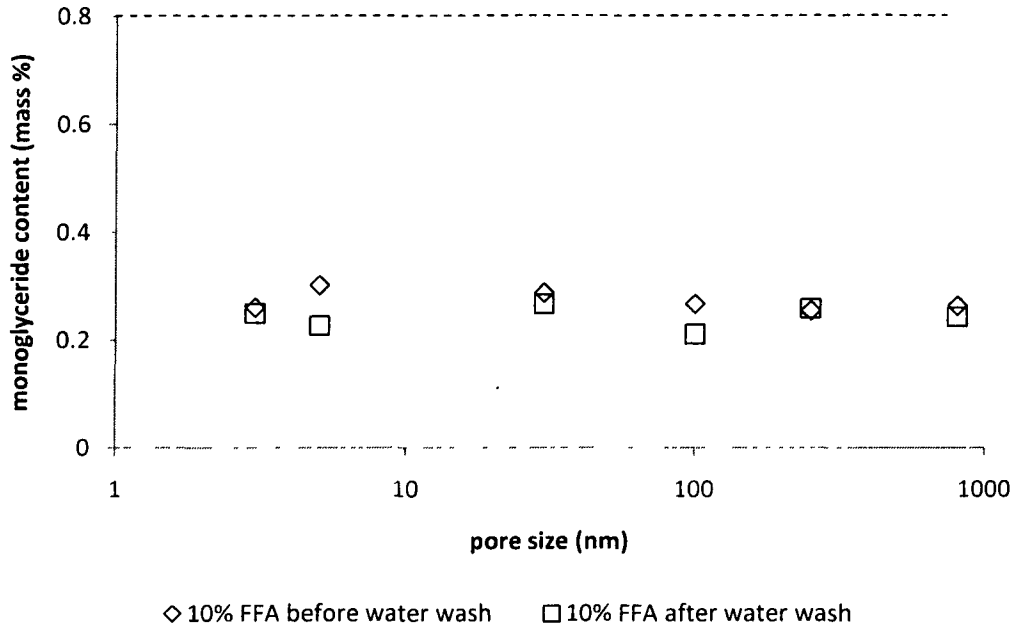

Figure 4.10: MG content in the FAME before and after water washing, versus membrane pore size, for the 10% FFA feedstock *(note: EN limit = 0.8 mass%)*

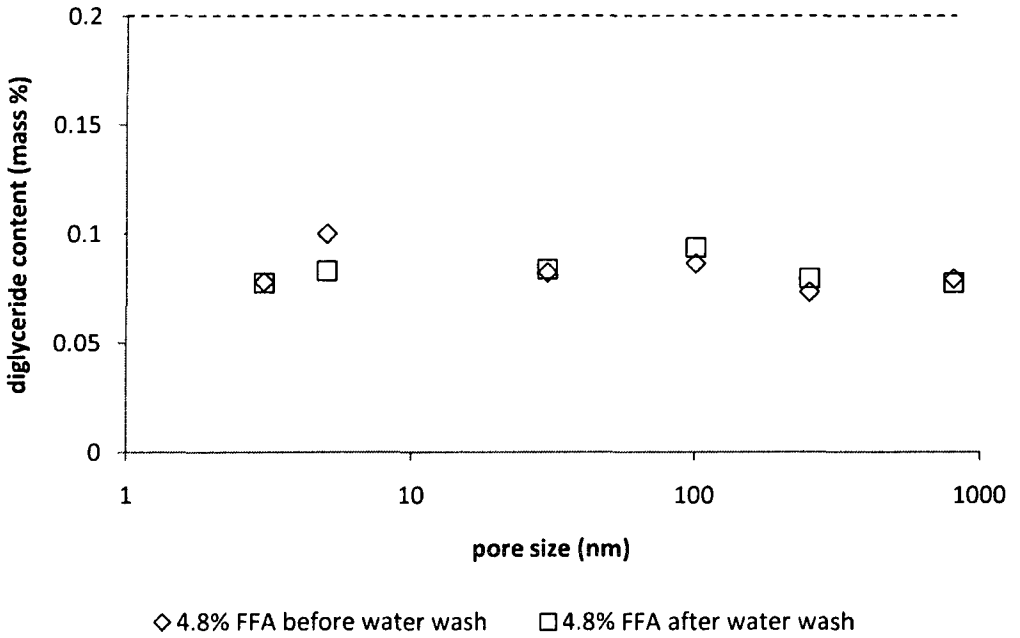

Figure 4.11: DG content in the FAME before and after water washing, versus membrane pore size, for the 4.8% FFA feedstock *(note: EN limit = 0.2 mass%)*

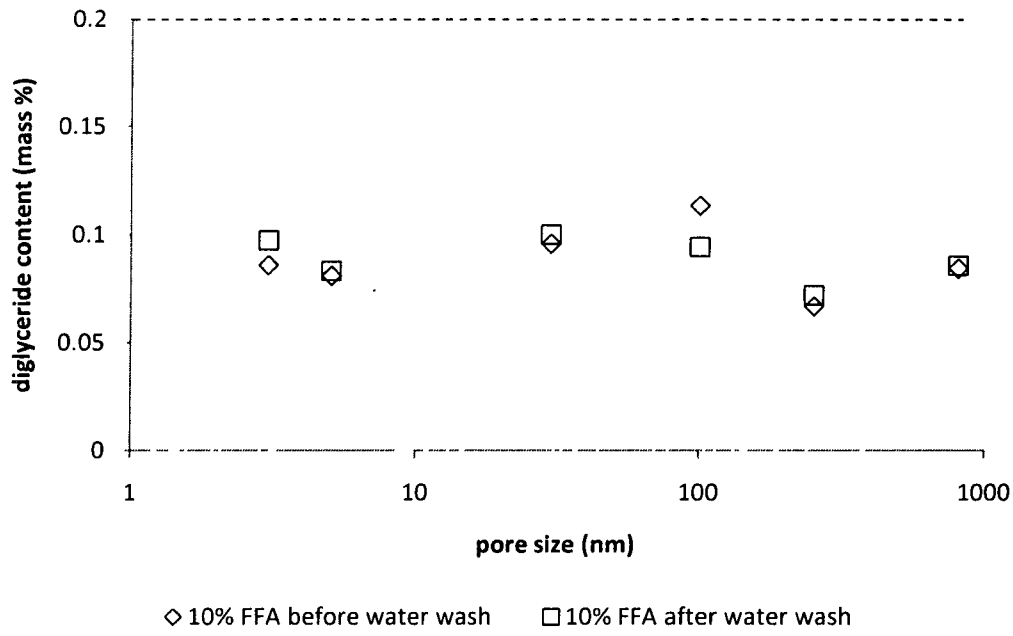

Figure 4.12: DG content in the FAME before and after water washing, versus membrane pore size, for the 10% FFA feedstock (*note: EN limit = 0.2 mass%)*

The free glycerol contents in the FAME before and after water-washing are presented in Figures 4.13 and 4.14 for the 4.8% and 10% FFA feedstock, respectively. Glycerol is polar and readily soluble in water. As a result, water-washing reduced the amounts of free glycerol in the FAME. It can be seen from the figures that the free glycerol content was greater than 0.02 mass% before water-washing. Therefore, to meet the ASTM standard for free glycerol content, water-washing or some other form of glycerol removal is necessary. The total glycerol contents in the FAME before and after water-washing are presented in Figures 4.15 and 4.16 for the 4.8% and 10% FFA

feedstock, respectively. The total glycerol content decreased after water-washing, although it had already met the ASTM standard prior to water-washing.

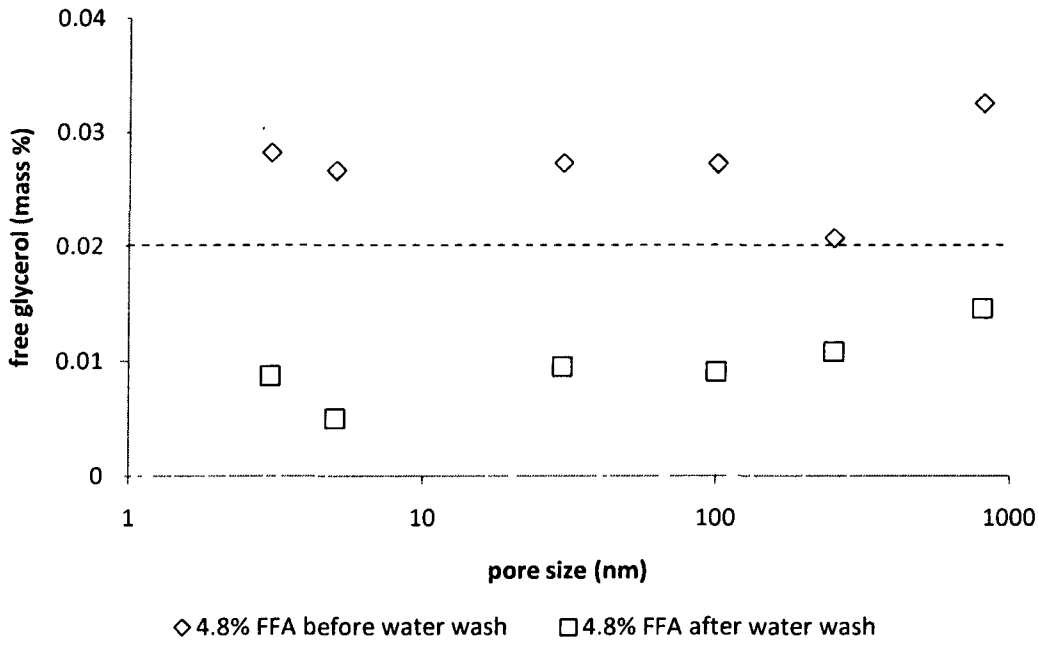

Figure 4.13: Free glycerol content in the FAME before and after water washing, versus membrane pore size, for the 4.8% FFA feedstock *(note: ASTM limit = 0.02 mass%)*

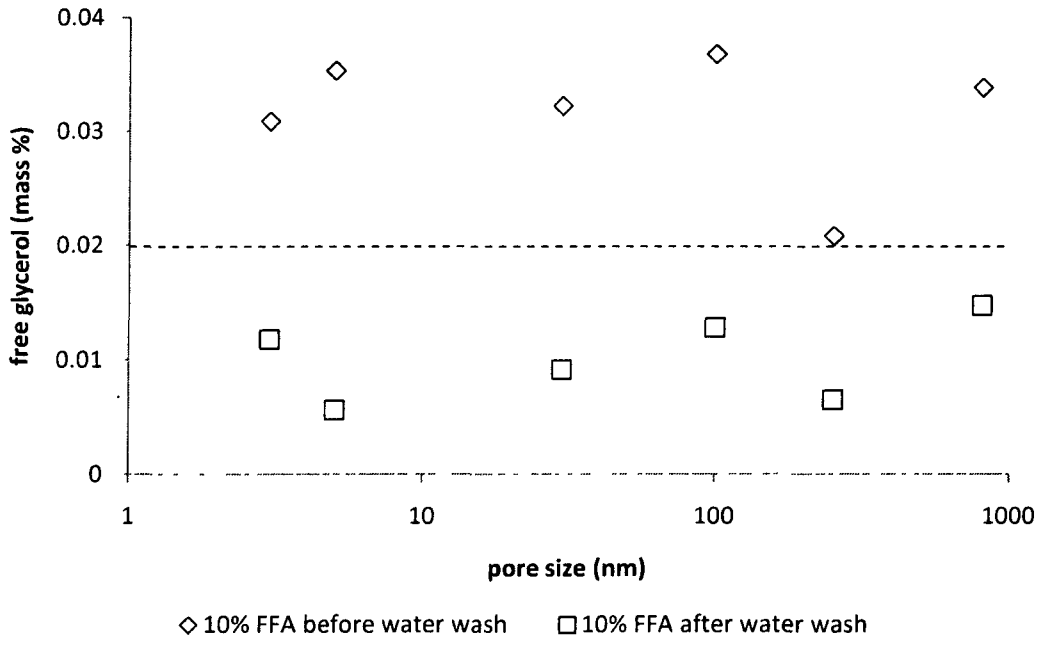

Figure 4.14: Free glycerol content in the FAME before and after water washing, versus membrane pore size, for the 10% FFA feedstock *(note: ASTM limit = 0.02 mass%*

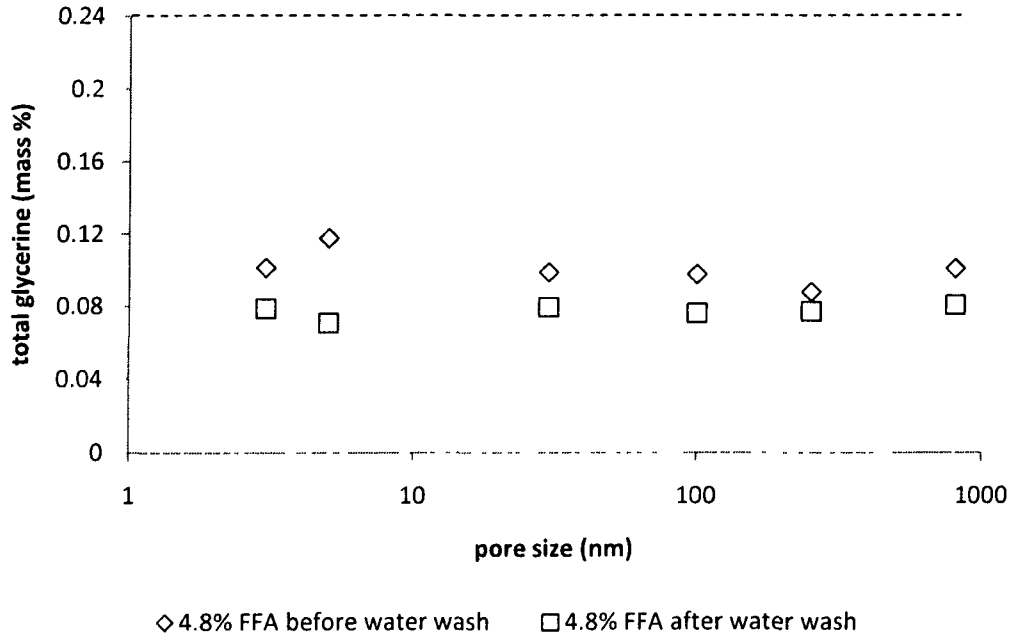

Figure 4.15: Total glycerol content in the FAME before and after water washing, versus membrane pore size, for the 4.8% FFA feedstock *(note: ASTM limit = 0.24 mass%)*

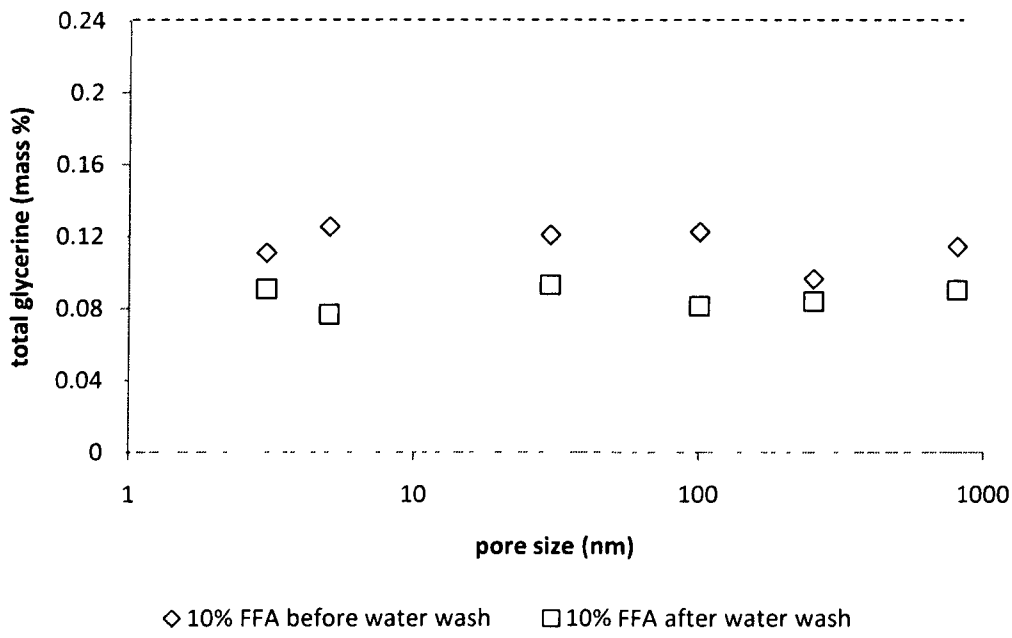

Figure 4.16: Total glycerol content in the FAME before and after water washing, versus membrane pore size, for the 10% FFA feedstock *(note: ASTM limit = 0.24 mass%)*

4.4 Evaporation

Before water-washing, the FAME was evaporated using a rotary vacuum evaporator. The evaporation of the methanol caused a fraction of the glycerol and soap in the FAME to congeal. The congealed substance was separated from the rest of the FAME by centrifugation. Table 4.2 shows the mass percentage of congealed material for the various membrane pore sizes and FFA. Table 4.3 shows the amount of free glycerol, MG, DG and TG in the congealed substance. This result is explained by the fact that methanol acted as a co-solvent and kept the free glycerol and soap in solution with the FAME. Consequently, when the methanol was removed, the soap congealed.

Table 4.2: Mass percentage of congealed substance after vacuum evaporation

		Congealed material (mass%)	
		FFA = 4.8 mass%	FFA = 10 mass%
Pore size (nm)	3	14.2	22.4
	250	18.1	28.9
	800	19.0	27.1

Table 4.3: Free glycerol, MG, DG and TG content in the congealed substance

Pore size (nm)	FFA (%)	Free glycerol (mass %)	MG (mass %)	DG (mass %)	TG (mass %)
3	4.8	0.222	0.059	0.010	n.d.
3	10	0.157	0.051	0.014	n.d.
800	4.8	0.171	0.146	0.009	n.d.
800	10	0.109	0.079	0.009	n.d.

Table 4.2 shows that the unwashed FAME produced from the 10% FFA feedstock resulted in a higher mass percentage of congealed material than for the 4.8% FFA runs. This was consistent with the fact that the 10% FFA feedstock resulted in

FAME with a higher soap level. This was because as the amount of FFA increased, the amount of base needed for neutralization increased and subsequently more soap was produced. No TG was detected, as shown in Table 4.3, and this once again implies that the smallest oil droplet diameter was greater than 800 nm and consequently could not pass through the membrane pores, as illustrated in Figure 4.6.

4.5 Soap Content before Water Washing

A complete soap analysis was performed by measuring the soap content in the FAME phase (before water washing), glycerol phase and retentate. Subsequently, the soap content in the permeate was calculated. It was found that the permeate and retentate contained roughly the same amount of soap. The results are shown in Table 4.4 and Figure 4.17. This implies that the soap dissolved in the methanol/glycerol-rich phase and was dispersed on a molecular basis (as opposed to micelles). The soap molecules passed through the membrane and were not completely retained in the reactor. Thus, the membrane pore size did not affect the passage of soap. Subsequently, the least expensive membranes (i.e., 100, 250 and 800 nm) could be used. The prices of the different membranes are shown in Appendix C.

Table 4.4: Soap content before water washing, at 4.8% FFA feedstock

Pore size (nm)	FAME soap content (ppm)	glycerol soap content (ppm)	permeate soap content (ppm)	retentate soap content (ppm)
1	–	–	–	–
3	8700	65250	36980	35360
5	7030	64160	35600	34380
30	7110	66440	36780	35530
100	8010	64960	36490	34800
250	8460	64830	36650	36160
800	8810	65250	37030	35820

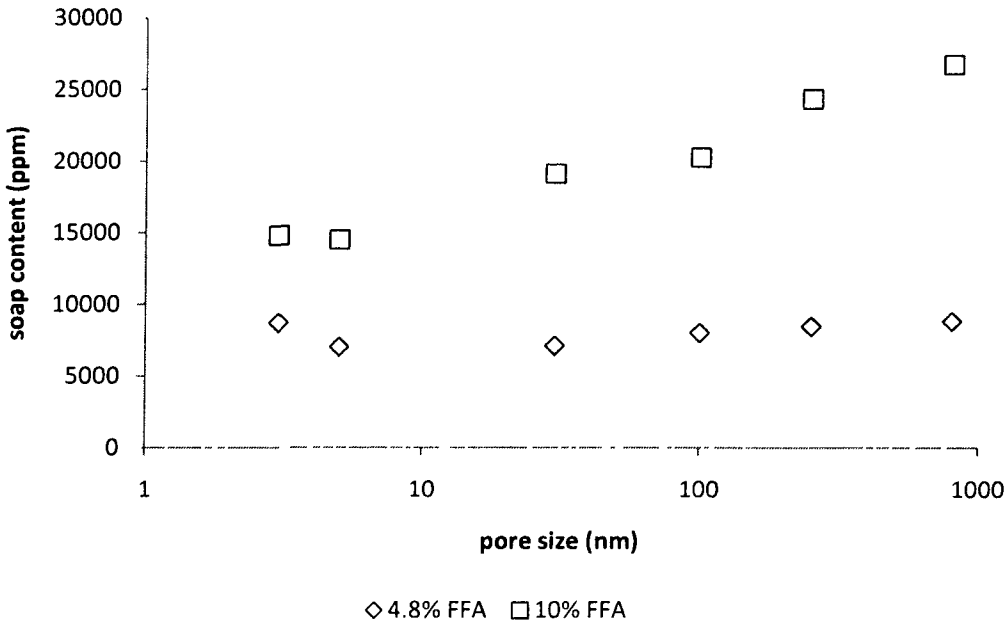

Figure 4.17: Soap content in the FAME, before water-washing

4.6 Soap and Sodium Content after Water Washing

The main concern in using waste vegetable oil as a feedstock is that the FFAs are likely to react with the base catalyst to form soap, as shown earlier in Figure 2.3. Although the ASTM standard for biodiesel does not include a direct test for soap content, measuring it was necessary in this project since high FFA feedstock was used. Table 4.5 presents the soap content in the FAME, after it was washed with distilled water 4 times. This level of water washing significantly reduced the soap content to around 11 times and 26 times in the 4.8 mass% and 10 mass% runs, respectively. Hence, the water-washing process did in fact reduce the large amount of soap produced as a result of using high

FFA feedstock. The soap produced from the high FFA feedstock did not hinder the production process, when a membrane reactor was utilized.

Table 4.5: Soap content in the water washed FAME

Pore size (nm)	Soap content (ppm)	
	FFA = 4.8 mass%	FFA = 10 mass%
1	-	-
3	817	701
5	624	867
30	785	773
100	806	766
250	800	782
800	691	812

Water-washing reduced the amount of soap present in the FAME because of the properties of the soap and water molecules. The sodium end of the soap molecule has an affinity for ionic substances with opposite ionic charge, i.e., it is hydrophilic. In contrast, the other end of the soap molecule is mostly hydrocarbon and has repulsion for ionic substances, i.e., it is hydrophobic. The overall soap molecule is described as amphiphilic. Water molecules are polar and accordingly attract the hydrophilic group of the soap

molecules – this is the basis for how the soap separates from the FAME. The hydrophilic ends of the soap molecules are attached to the water while the hydrophobic ends remain in the FAME. This association between the water and soap molecules tends to form structures called micelles. A micelle is a spherical agglomeration of soap molecules with the hydrophilic groups of the soap at the surface and the interior consisting of the hydrophobic tails of the soap. Therefore, during water washing, separation of soap from FAME takes place readily.

According to the EN standard, the maximum allowable level of alkali metals (sodium plus potassium) in biodiesel is 5.0 ppm. Using the molecular weight of sodium (23 g/mol) and sodium oleate (304.5 g/mol), the sodium content in the soap was calculated. The conversion factor to convert sodium oleate soap concentrations to sodium concentrations is 13.2 (White *et al.*, 2010). This conversion factor was used to find the sodium content of the soap results in Table 4.5. Table 4.6 presents the sodium content in the water washed FAME. It can be seen that the sodium content was greater than the maximum allowable level of 5.0 ppm. This implies that additional water washing of the FAME was required, in order to meet the sodium standard. Consequently, the cost increases and larger amounts of wastewater are produced. An alternative washing method is dry washing, which replaces water with magnesium silicate powder (Dugan, 2007).

Table 4.6: Sodium content in the water washed FAME

	Sodium content (ppm)	
Pore size (nm)	FFA = 4.8 mass%	FFA = 10 mass%
1	-	-
3	62	53
5	47	66
30	59	59
100	61	58
250	61	59
800	52	62

4.7 Water Content

Another important analysis, especially when using high FFA feedstock, is water content. The high FFA content in the feedstock reacts with the base catalyst to produce water, as shown earlier in Figure 2.3. The water content in the FAME phase, glycerol phase and retentate was measured before water washing and the results are shown in Tables 4.7, 4.8 and 4.9, respectively. According to the ASTM standard, the maximum allowed level of water in biodiesel is 500 ppm.

Table 4.7: Water content in the FAME

Pore size (nm)	Water content (ppm)	
	FFA = 4.8 mass%	FFA = 10 mass%
1	-	-
3	99	124
5	96	125
30	265	293
100	228	307
250	106	196
800	112	207

Table 4.8: Water content in the glycerol

Pore size (nm)	Water content (ppm)	
	FFA = 4.8 mass%	FFA = 10 mass%
1	-	-
3	415	583
5	509	526
30	660	403
100	466	454
250	403	518
800	605	596

Table 4.9: Water content in the retentate

Pore size (nm)	Water content (ppm)	
	FFA = 4.8 mass%	FFA = 10 mass%
1	-	-
3	506	658
5	343	431
30	348	305
100	366	393
250	369	403
800	343	573

Table 4.7 shows that the FAME produced from all runs (with different membrane pore sizes and different FFA levels) met the ASTM standard. When using the membrane reactor, the water content in the FAME was significantly below 500 ppm, before vacuum evaporation. Even when an FFA level as high as 10% was used, the water produced during neutralization did not compromise the quality of the FAME. For each membrane pore size, the water content was relatively higher in the FAME produced from the 10% FFA feedstock compared to the 4.8% FFA (see Table 4.7). This is because as the

amount of FFA increased, the amount of base needed for neutralization increased and subsequently more water was produced.

The water content in the glycerol phase was higher than that in the FAME phase (compare Table 4.8 to Table 4.7). This is because the solubility of water is higher in glycerol than in FAME. The hydroxyl (–OH) groups of the glycerol molecule allow hydrogen bonding with the water molecules. Thus, glycerol is completely miscible with water. The water content in the retentate is shown in Table 4.9. The water content in the waste vegetable oil was measured and found to be 510 ppm. This implies that water passed through the membrane.

4.8 References

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Lyman, W. J., Reehl, W. F., & Rosenblatt, D. H. (1982). *Handbook of Chemical Property Estimation Methods, Environmental Behavior of Organic Compounds.* New York: McGraw-Hill.

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CHAPTER 5
Conclusions and Recommendations

5.1 Conclusions

A major obstacle facing the successful commercialization of biodiesel is its high manufacturing cost. At the heart of this obstacle is the high cost of the feedstock and the technological difficulties in achieving high fuel quality in an economical way. Thus, an optimal solution is a feedstock that is cheaper yet does not compromise the quality of the biodiesel. Waste vegetable oils and animal fats are promising feedstock options that could lower the cost of biodiesel production. However, the high amounts of free fatty acids (FFAs) in the cheaper feedstock give rise to production challenges. Using a feedstock with a high percent of FFAs causes major problems such as soap formation, water formation and lower yield. This project investigated the possibility of using a membrane reactor for the production of biodiesel from waste vegetable oil feedstock with high FFA content. Furthermore, the effect of membrane pore size on the biodiesel quality and production process was studied. This was achieved through the construction and operation of a lab scale continuous membrane reactor.

Waste vegetable oil was successfully transesterified using methanol and sodium methoxide catalyst, in a continuous membrane reactor. In all cases, the FAME produced in the membrane reactor met the ASTM D6751 standard. Gas chromatography analysis, based on the ASTM D6584 standard, confirmed the production of high quality FAME from feedstocks with FFA levels up to 10 mass%. The monoglyceride, diglyceride, triglyceride and total glycerol content met the standards. All ceramic membranes tested, of different pore sizes, were able to retain the triglycerides in the reactor. This indicated that the oil droplets present in the reactor were larger than all the pore sizes. Additionally, it was found that the water content in the FAME produced met the ASTM D6751 standard. Furthermore, the results of the soap analysis indicated that the soap dissolved in the alcohol and passed through the membrane. Thus, soap was not completely retained in the reactor. Therefore, the soap produced as a result of using the high FFA feedstock in a base-catalyzed transesterification did not affect the quality of the FAME produced, when using a membrane reactor. However, further washing of the FAME was required in order to meet the EN 14214 level of alkali metals (sodium plus potassium).

A continuous membrane reactor can allow the direct use of waste vegetable oils, in a base-catalyzed transesterification reaction. Currently, the approach to using waste vegetable oil feedstock involves a pre-treatment step (acid-catalyzed esterification reaction). Therefore, the use of waste vegetable oil in a continuous membrane reactor, without pre-treatment, is a major advancement in the biodiesel industry.

5.2 Recommendations

The following recommendations are proposed and may be studied in future research projects to further enhance the biodiesel production process:

Further experiments can be carried out in order to optimize the experimental conditions. Different variables, such as temperature, pressure and catalyst concentration, can be optimized.

In this project, ceramic membranes were used because they can withstand the harsh environment of the base-catalyzed transesterification reaction. Other membrane materials can be tested, as long as they are able to withstand these extreme conditions and not affect the reaction. Perhaps a less expensive material can be used to achieve the same outcome. Additionally, the lifetime analysis of the membrane, including membrane fouling analysis, can be performed.

A comprehensive economic analysis comparing the biodiesel production in a membrane reactor to the two-step process is recommended. This will include energy costs, materials costs and all other costs associated with the production process.

APPENDIX A
Safety Precautions

The following safety precautions were observed:

- All appropriate safety equipment was worn. This included a lab coat, face mask, safety glasses and gloves.
- Before disposing of any wet gloves, they were placed in the fume hood to evaporate the methanol.
- The spill kit, spill pads and first aid kit were located.
- The fume hood sash was always lowered since methanol vapour is heavier than air.
- The MSDS sheets of all the chemicals used were thoroughly read to ensure safe handling of all materials.
- For complete safety, all solutions from the reactor were handled as one would handle methanol (which was the alcohol used in this project).

- The reactor temperature was monitored at all times.
- The reactor pressure was monitored at all times. If the pressure exceeded 80 psi, the pressure was released using the pressure relief valve.

Appendix B
Gas Chromatography Operating Guide

Sample Preparation

All steps should be done in the fume hood using the nitrogen glove bag. The following steps are used to prepare the GC sample:

1. Shake the sample
2. Place a clean vial on the balance and then zero the balance
3. Place a clean tip on the pipette
4. Add 0.100 g of the sample to the empty vial and record the mass
5. Zero the balance, place a clean tip on the pipette and add 100 μL of MSTFA to the vial on the balance
6. Zero the balance, place a clean tip on the pipette and add 100 μL of tricaprin to the vial on the balance

7. Zero the balance, place a clean tip on the pipette and add 100 μL of butanetriol to the vial on the balance
8. Shake the vial then let it stand at room temperature for 10 minutes
9. Using a syringe, add 8 mL of *n*-heptane to the vial and shake it for a few seconds
10. Using a syringe with a syringe filter, place a filter on it, then fill it with 2mL of the sample and place it in a GC auto-sampler vial

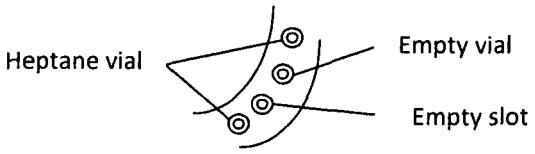
Preparing the GC Device

1. Check that gas filters are functional. All carrier and detector filters should be changed when indicator shows filter is spent. Oxygen contamination in carrier gas can produce excessive column bleed and hydrocarbons cause ghost peaks or increase detector noise.
2. Open the valves on the air, helium and hydrogen cylinders. Make sure they are set to the correct pressures:
    - air → 60psi
    - helium → 80psi
    - hydrogen → 40 psi
3. Leave at least 400 psi residual gas in a depleted cylinder. This is because as the cylinder pressure drops the concentration of the impurities (such as moisture and

hydrocarbons) increase and can lead to column damage. Furthermore, if the cylinder pressure drops below the supply pressure required by the GC, retention times and detector sensitivities can slowly change and affect the validity of the data.

Operating the GC Device

1. Fill the 2 small vials on the sides with *n*-heptane, as shown in the diagram below:



2. Switch on the GC.

3. As the GC begins its initializing step, go to the computer and open the program. It is the icon on top left corner on Varian workstation toolbar. This provides communication between the software and the GC device.

4. Click on File → activate method → CHG methods → Biodiesel ASTM6584 → Biodiesel6584 → open. The activated method name should then show in the system control window's toolbar.

5. Check the status of the column, injector and detector. When the GC is ready for sample injection, the 'Ready' light will light up in the system control window. Additionally, the lights for all the parameters will be green (as opposed to red, which is the case when the device is still not ready).

6. Type in the sample names and vial numbers by clicking on: File → new sample list then enter the name and vial number of each sample.

7. Click on 'Begin'

8. To shut down the system, switch off the GC and close the valves on the air, helium and hydrogen cylinders.

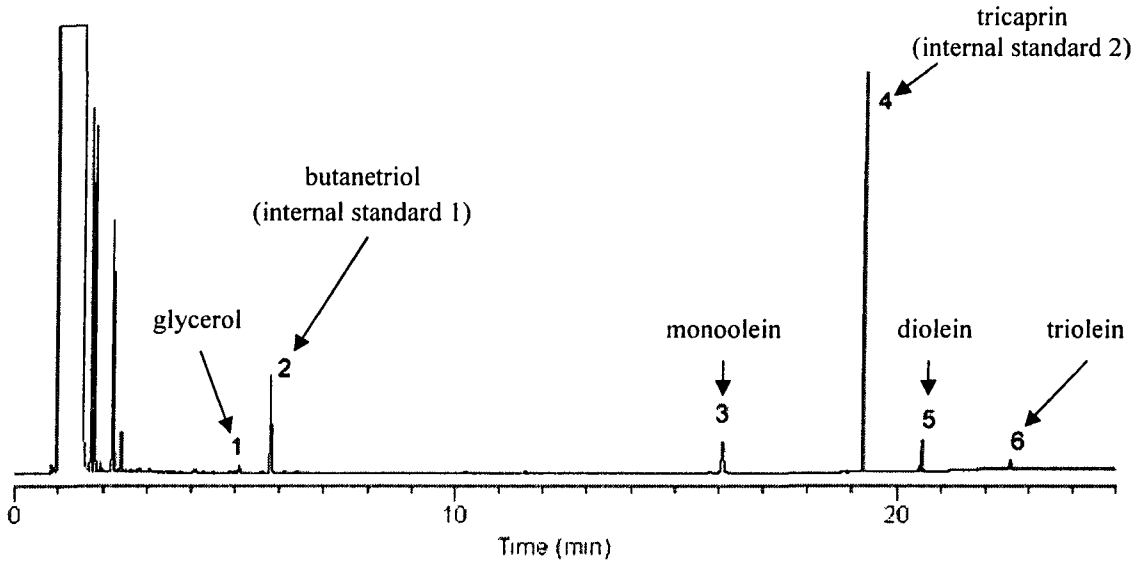
9. All the results are saved automatically on the computer, in the 'Data' folder.

Operating conditions (ASTM D6584 Standard, 2008)

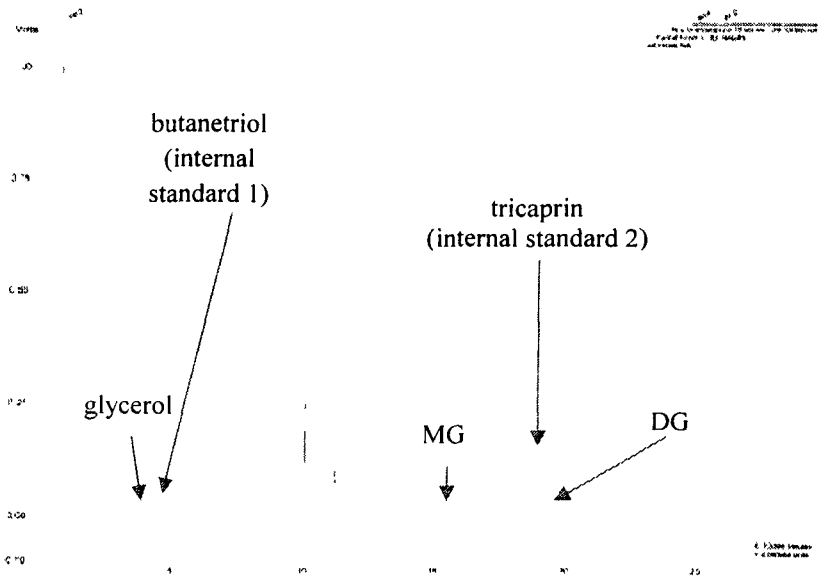
Injector		
Cool on column injector		
Sample size	1 µL	
Column Temperature Program		
Initial temperature	50°C	hold 1 min
Rate 1	15°C / min to 180°C	
Rate 2	7°C / min to 230°C	
Rate 3	30°C / min to 380°C	hold 10 min
Defector		
Type	Flame ionization	
Temperature	380°C	
Carrier gas		
Type	Hydrogen or helium	measured at 50°C
Flow rate	3 mL / min	

Approximate retention time of the standards

Standard	Retention time (min)
Glycerol	4.17
Internal standard 1	4.93
Monoolein (MG)	16.25
Internal standard 2	19.30
Diolein (DG)	20.79
Triolein (TG)	23.59



Reference chromatogram of standards (Sigma Aldrich, 2010)



GC chromatogram for water washed FAME producing using a 100 nm membrane pore size and 10 mass% FFA feedstock.

APPENDIX C
Raw Data and Sample Calculations

The continuous membrane reactor used in this project along with the computer used to monitor the experiments, are presented below:

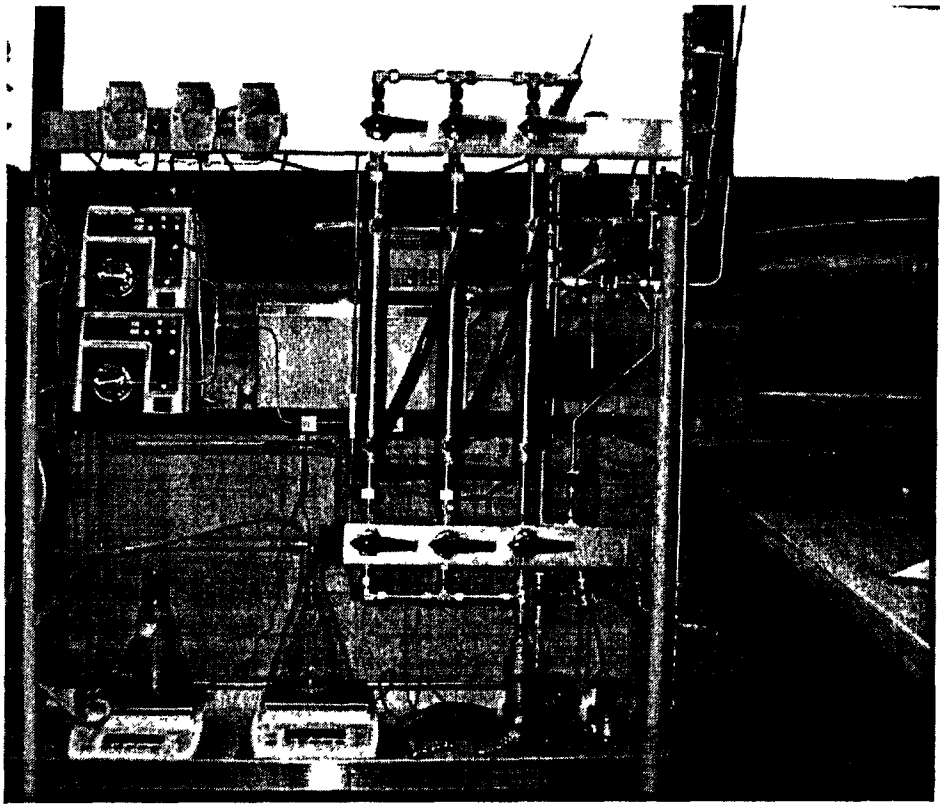


Photo of the continuous membrane reactor

The gas chromatography raw data collected during the FAME analyses, before and after water washing, are presented in the following tables.

Analytical results for the FAME, before water washing [1]

Reaction Conditions			Analytical Results						
Order of runs	FFA (%)	Pore size (nm)	MG (mass%)	DG (mass%)	TG (mass%)	Free glycerol (mass%)	Total glycerol (mass%)	Water content (ppm)	Soap content (ppm)
13	4.8	1	-	-	-	-	-	-	-
9	4.8	3	0.237	0.078	n.d.	0.028	0.114	99	8700
5	4.8	5	0.294	0.100	n.d.	0.027	0.132	96	7027
1	4.8	30	0.228	0.082	n.d.	0.027	0.111	265	7105
3	4.8	100	0.221	0.086	n.d.	0.027	0.110	228	8013
7	4.8	250	0.216	0.073	n.d.	0.021	0.098	106	8458
11	4.8	800	0.217	0.079	n.d.	0.033	0.114	112	8814
14	10	1	-	-	-	-	-	-	-
10	10	3	0.260	0.086	n.d.	0.031	0.124	124	14790
6	10	5	0.301	0.081	n.d.	0.035	0.139	125	14500
2	10	30	0.287	0.096	n.d.	0.032	0.136	293	19140
4	10	100	0.266	0.113	n.d.	0.037	0.140	307	20300
8	10	250	0.254	0.067	n.d.	0.021	0.107	196	24360
12	10	800	0.262	0.084	n.d.	0.034	0.128	207	26796

[1] n.d. = not detected

Analytical results for the water washed FAME [2]

Reaction Conditions			Analytical Results					
Order of runs	FFA (%)	Pore size (nm)	MG (mass%)	DG (mass%)	TG (mass%)	Free glycerol (mass%)	Total glycerol (mass%)	Soap content (ppm)
13	4.8	1	-	-	-	-	-	-
9	4.8	3	0.225	0.078	n.d.	0.009	0.079	817
5	4.8	5	0.206	0.083	n.d.	0.005	0.071	624
1	4.8	30	0.221	0.084	n.d.	0.010	0.079	785
3	4.8	100	0.204	0.094	n.d.	0.009	0.076	806
7	4.8	250	0.210	0.080	n.d.	0.011	0.077	800
11	4.8	800	0.209	0.078	n.d.	0.015	0.080	691
14	10	1	-	-	-	-	-	-
10	10	3	0.249	0.097	n.d.	0.012	0.091	701
6	10	5	0.227	0.083	n.d.	0.006	0.077	867
2	10	30	0.266	0.100	n.d.	0.009	0.093	773
4	10	100	0.210	0.094	n.d.	0.013	0.081	766
8	10	250	0.258	0.072	n.d.	0.007	0.084	782
12	10	800	0.242	0.086	n.d.	0.015	0.090	812

[2] n.d. = not detected

Sample calculation:

The following is a sample calculation of total glycerol, for the water washed FAME produced from 4.8% FFA feedstock, 3 nm membrane:

$$total\ glycerine = free\ glycerine + bound\ glycerine$$

where:

$$bound\ glycerine = \sum(Gl_M, Gl_D, Gl_T)$$

where:

$$Gl_M = 0.2591 \times monoglyceride\ mass\ \%$$

$$Gl_D = 0.1488 \times diglyceride\ mass\ \%$$

$$Gl_T = 0.1044 \times triglyceride\ mass\ \%$$

therefore:

$$total\ glycerine = 0.00874 + (0.2591 \times 0.22526) + (0.1488 \times 0.07754) + (0.1044 \times 0)$$

$$total\ glycerine = 0.079\ mass\ \%$$

The Karl Fischer raw data collected during analyses are presented in the following 3 tables.

Water content in FAME, produced from 4.8% FFA feedstock

Pore size (nm)	m_1 (g)	m_2 (g)	m_1-m_2 (g)	water content (ppm)
1	-	-	-	-
3	5.906	5.462	0.444	99.34
5	5.886	5.409	0.477	95.63
30	5.687	5.444	0.243	264.99
100	5.945	5.427	0.518	228.06
250	5.965	5.435	0.530	105.62
800	5.988	5.418	0.570	111.82

Water content in FAME, produced from 10% FFA feedstock

Pore size (nm)	m_1 (g)	m_2 (g)	m_1-m_2 (g)	water content (ppm)
1	-	-	-	-
3	5.962	5.447	0.515	123.89
5	5.977	5.482	0.495	124.60
30	5.912	5.424	0.488	293.33
100	5.918	5.452	0.466	306.68
250	5.917	5.444	0.473	196.47
800	5.792	5.455	0.337	207.41

Water content in glycerol phase, produced from 4.8% FFA feedstock

Pore size (nm)	m_1 (g)	m_2 (g)	m_1-m_2 (g)	water content (ppm)
1	-	-	-	-
3	6.018	5.447	0.571	415.37
5	5.925	5.453	0.472	509.32
30	5.897	5.447	0.450	660.23
100	5.855	5.442	0.413	465.79
250	5.830	5.435	0.395	403.17
800	5.802	5.405	0.397	605.45

Water content in glycerol phase, produced from 10% FFA feedstock

Pore size (nm)	m_1 (g)	m_2 (g)	m_1-m_2 (g)	water content (ppm)
1	-	-	-	-
3	6.020	5.489	0.531	582.88
5	6.060	5.455	0.605	525.58
30	5.829	5.460	0.369	402.92
100	5.798	5.435	0.363	453.82
250	5.924	5.488	0.436	518.09
800	6.001	5.498	0.503	596.49

Water content in retentate, produced from 4.8% FFA feedstock

Pore size (nm)	m_1 (g)	m_2 (g)	m_1-m_2 (g)	water content (ppm)
1	-	-	-	-
3	5.905	5.411	0.494	505.53
5	5.897	5.477	0.420	343.43
30	5.786	5.438	0.348	348.43
100	5.943	5.485	0.458	366.31
250	5.905	5.468	0.437	369.25
800	5.850	5.454	0.396	343.03

Water content in retentate, produced from 10% FFA feedstock

Pore size (nm)	m_1 (g)	m_2 (g)	m_1-m_2 (g)	water content (ppm)
1	-	-	-	-
3	5.942	5.426	0.516	658.45
5	5.994	5.448	0.546	431.41
30	5.807	5.455	0.352	304.68
100	5.877	5.426	0.451	392.50
250	5.985	5.498	0.487	403.10
800	5.777	5.409	0.368	572.81

The soap titrations raw data collected during analyses are presented in the following tables.

Soap content in unwashed FAME, produced from 4.8% FFA feedstock

Pore size (nm)	mass (g)	initial volume (mL)	final volume (mL)	soap (ppm)
1	-	-	-	-
3	4.2	43.0	44.2	8700
5	3.9	40.1	41.0	7027
30	3.0	39.4	40.1	7105
100	3.8	36.1	37.1	8013
250	3.6	46.8	47.8	8458
800	3.8	51.4	52.5	8814

Soap content in unwashed FAME, produced from 10% FFA feedstock

Pore size (nm)	mass (g)	initial volume (mL)	final volume (mL)	soap (ppm)
1	-	-	-	-
3	3.5	73.6	75.3	14790
5	4.2	41.0	43.0	14500
30	3.5	37.1	39.3	19140
100	3.0	76.8	78.8	20300
250	4.0	80.2	83.4	24360
800	5.0	67.6	72.0	26796

Soap content in water washed FAME, produced from 4.8% FFA feedstock

Pore size (nm)	mass (g)	initial volume (mL)	final volume (mL)	soap (ppm)
1	-	-	-	-
3	4.1	40.0	41.1	817
5	3.9	61.7	62.5	624
30	3.1	55.6	56.4	785
100	3.8	25.0	26.0	806
250	3.0	44.8	45.6	800
800	4.0	32.4	33.3	691

Soap content in water washed FAME, produced from 10% FFA feedstock

Pore size (nm)	mass (g)	initial volume (mL)	final volume (mL)	soap (ppm)
1	-	-	-	-
3	3.5	43.2	44.0	701
5	3.2	65.0	65.9	867
30	2.4	59.8	60.4	773
100	3.2	28.2	29.0	766
250	3.1	47.4	48.2	782
800	3.8	33.6	34.6	812

Sample calculation:

The following is a sample calculation of soap content, for the water washed FAME produced from 4.8% FFA feedstock, 3 nm membrane:

$$soap\ content = \left[\frac{volume\ of\ acid \times concentration\ of\ acid \times molecular\ weight\ of\ sodium\ oleate}{mass\ of\ FAME\ sample}\right] \times (1 \times 10^6)$$

$$soap\ content = \left[\frac{(1.1/1000) \times 0.01 \times 304.5}{4.098}\right] \times (1 \times 10^6)$$

$$\therefore soap\ content = 820\ ppm$$

The prices of the different membranes used in this project are presented in the following table:

Membrane pore size (nm)	Price ($)
1	148.68
3	117.64
5	117.64
30	117.64
100	79.52
250	79.52
800	79.52