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Biodiesel Production from Canola Oil Using a Membrane Reactor

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BIODIESEL PRODUCTION FROM CANOLA OIL USING A MEMBRANE REACTOR

by

Jie Liu

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ABSTRACT

Biodiesel, a transesterified product of vegetable oil and animal fats, is considered as the most promising diesel fuel substitute because of its similar properties to petroleum-based diesel fuel.

In this thesis, the miscibility of canola oil and fatty acid methyl esters (FAME or biodiesel) in methanol was determined. Results showed that FAME is miscible in pure methanol under a broad range of conditions. On the other hand, canola oil is not miscible in methanol under normal conditions. These findings led to the development of a two-phase membrane reactor to produce FAME from canola oil and methanol. The transesterification of canola oil was performed via both acid- or base-catalysis. The novel reactor enabled the separation of a FAME and methanol solution from canola oil/methanol/FAME mixtures. The two-phase membrane reactor was particularly useful in removing unreacted canola oil from the FAME product yielding high purity biodiesel.

A kinetic study of the acid- and base-catalyzed transesterification of canola oil to FAME was carried out to investigate reaction rates under different temperatures and catalyst concentrations in the two-phase membrane reactor. Results showed that increases in temperature, acid concentration and feedstock (methanol/oil) flowrate significantly increased the conversion of oil to biodiesel. However, the base-catalyzed reaction resulted in the production of soaps and slight damage to the carbon membrane used in the reactor. The kinetics of the reaction were more sensitive to temperature at high acid concentration.

Résumé

Le biodiesel, produit par la transestérification d'huiles végétales et de graisses animales, est considéré comme étant le substitut de combustion le plus prometteur grâce à ses propriétés semblables au diesel à base pétrolière.

Au cours de cette thèse, la miscibilité de l'huile de canola ainsi que des esters méthyliques d'acides gras dans le méthanol a été déterminée. Ces esters sont communément appelés biodiesel ou FAME (de l'anglais, fatty acid methyl esters). D'une part, les résultats ont démontré que le FAME est miscible dans le méthanol pur dans diverses conditions. D'autre part, l'huile de canola n'est pas miscible dans le méthanol dans les conditions normales. Ces découvertes ont mené à la conception d'un réacteur à membrane biphasée afin de produire le FAME à partir de l'huile et du méthanol. La transestérification de l'huile de canola a été effectuée par la catalyse acide et basique. Le nouveau réacteur a permis la séparation d'une solution de FAME et de méthanol à partir des mélanges d'huile, de méthanol et de FAME. Le réacteur à membrane biphasée a été particulièrement utile pour enlever l'huile de canola non réagi du produit de FAME, occasionnant ainsi un biodiesel de haute pureté.

L'étude de la cinétique de la transestérification de l'huile de canola en FAME (ou biodiesel), catalysée par un acide et une base, a été effectuée afin d'examiner les vitesses de réaction à différentes températures et aux différentes concentrations de catalyseur dans le réacteur. Les résultats ont démontré qu'une hausse de la température, de la concentration d'acide ou du débit de matière de départ (méthanol/huile) résulte en une augmentation significative du taux de conversion d'huile en biodiesel. Par contre, la réaction catalysée par une base entraîne la production de savons ainsi que de légers dommages à la membrane de carbone utilisée dans le réacteur. La cinétique de la réaction s'est avérée plus sensible à la température aux concentrations d'acide élevées.

Statement of Contributions of Collaborators

I hereby declare that I am the sole author of this written thesis. The experiments, data analysis and the associated reaction kinetics were all performed by myself.

My supervisors, Professors André Y. Tremblay and Marc A. Dubé provided editorial comments to my written work and devoted supervision throughout my Master of Applied Science research.

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Abbreviations and Nomenclature

a, b	calibration parameters
DG	diglyceride
FAME	fatty acid methyl ester
FFA	free fatty acid
GL	glycerol
H_{FAME}	height of FAME phase in vial (mm)
H_{oil}	height of oil phase in vial (mm)
H_{Total}	total height of mixture in vial (mm)
HPLC	high performance liquid chromatography
MG	monoglyceride
M	numbers of mass (g)
PM	particulate matter
PTFE	polytetrafluoroethylene
t	reaction time (h)
T	reaction temperature (°C)
TG	triglyceride
THF	tetrahydrofuran
X	fractional mass conversion

CHAPTER 1

INTRODUCTION

1.1 Biodiesel

Biodiesel is defined as a substitute for, or an additive to diesel fuel and is derived from vegetable oils and animal fats. Chemically, it is a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. Biodiesel has attracted considerable attention during the past decade as a renewable, biodegradable, and non-toxic friendly fuel.

In 1853, scientists E. Duffy and J. Patrick first conducted transesterification of vegetable oil. In 1893, at Augsburg, Germany, Rudolf Diesel invented the first compression (diesel) engine; the engine was able to operate using vegetable oil. In the mid 1970s, fuel shortages spurred interest in diversifying our fuel resources and, thus, interest in developing biodiesel as an alternative to petroleum diesel.

Biodiesel can be made from various vegetable oils, tallow, and waste cooking oil. Attractive advantages of biodiesel fuel include:

i) it is plant-, not petroleum-, derived and as such its combustion produces less greenhouse gases;
ii) it is biodegradable;
iii) it can be domestically produced, offering the possibility of reducing petroleum imports
iv) relative to conventional diesel fuel, its combustion products have reduced levels of particulates, carbon monoxide, and, under some conditions, nitrogen oxides.

It was found that biodiesel could afford substantial reduction in SO_X emissions and considerable reductions in CO, hydrocarbons, soot, and particulate matter (PM). Yamane *et al.* 2001 reported that a biodiesel fuel with good ignitability, such as one with a high methyl oleate content, gives lower levels of NO, hydrocarbons, HCHO, CH_3CHO, and HCOOH, and also that soot formation is suppressed, since biodiesel is an oxygenated fuel having an oxygen mass fraction of 10%. In addition, Sheehan *et al.* (1998) carried out life cycle analyses and found that the benefit of using biodiesel is proportional to the level of blending with petroleum diesel. The overall life cycle emissions of CO_2 from 100% biodiesel fuel are 78.45% lower than those of petroleum diesel, and a blend with 20% biodiesel fuel reduces net CO_2 emissions by 15.66%. Substituting 100% biodiesel for petroleum diesel in buses reduces the life cycle consumption of petroleum by 95%, while a 20% blend of biodiesel fuel causes the life cycle consumption of petroleum to drop 19%.

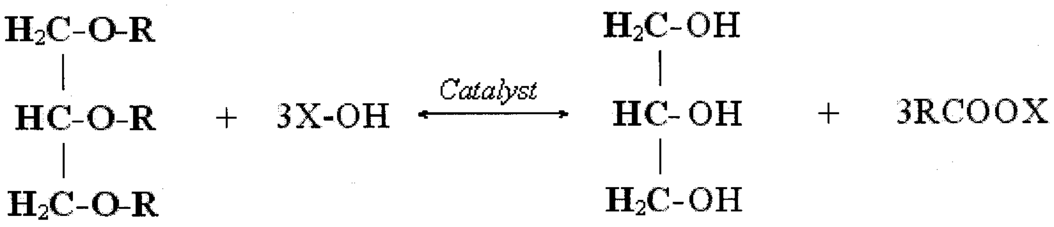
Although biodiesel presents many advantages, the applications of biodiesel are still facing some problems. High cost is one clear problem due to the high cost of virgin vegetable oil, the main feedstock used in the process. Currently, the sale price of biodiesel is about 0.37-0.63 US$/L, compared with 0.26-0.40 US$/L for petroleum diesel (Coltrain, 2002). Recent work by Zhang *et al.* 2003 indicates that the use of waste frying oil can reduce the cost of biodiesel. Also, the cost of biodiesel could be reduced by the use of animal fats (Nye *et al.*, 1983).

For many reasons, ranging from agricultural policy to environmental concerns, biodiesel production has been greatly developed during these last ten years. In recent years, biodiesel has been commercially available in public transportation in Japan, North America and Europe (Watanabe *et al.*, 2001). Biodiesel production and commercial use in the European Union (EU) has expanded due to the union's Common Agricultural Policy that enables farmers to receive a premium for growing industrial oilseeds on set-aside land (US Department of Agriculture, 1995). Also, Germany, Denmark, Sweden, Italy, Austria, France and the Czech Republic exempted the excise taxes for biodiesel (Körbitz, 1995). The EU plans to develop a 5% market share for biofuels by the year 2005 (Connemann and Fischer, 1998).

Recently, a continuous plant in Bakersfield, CA, U.S.A. was constructed to generate 2.5 million US gallons of biodiesel per year with claims that the plant could eventually be expanded to produce 35 million gallons per year, which would be more than twice the U.S. production of biodiesel fuel in 2002. The Canadian federal government has already set up a goal to increase the production of biodiesel to 500 million litres to reach its Kyoto target for reducing greenhouse gas emissions (Thompson, 2002).

1.2 Transesterification

Fatty acid alkyl esters or biodiesel, are products of transesterification (also called alcoholysis) of vegetable oils and fats with an alcohol in the presence of a suitable catalyst. In addition, the process yields glycerol. The reaction scheme is shown in Figure 1. 1.



$$\begin{array}{c} H_2C\text{-}O\text{-}R \\ | \\ HC\text{-}O\text{-}R \\ | \\ H_2C\text{-}O\text{-}R \end{array} + 3X\text{-}OH \xleftrightarrow{\textit{Catalyst}} \begin{array}{c} H_2C\text{-}OH \\ | \\ HC\text{-}OH \\ | \\ H_2C\text{-}OH \end{array} + 3RCOOX$$

Figure 1.1: Stoichiometric reaction for conversion of triglyceride to fatty acid alkyl esters

This conversion comprises three consecutive reversible reactions with diglyceride (DG) and monoglyceride (MG) as intermediate products. After the reaction, the glycerol is separated by settling or centrifugation and is purified for use in its traditional application. In addition, the co-product glycerol can be used in recently developed applications for animal feed, as carbon feedstock in fermentations, and as polymers, surfactants, intermediates and lubricants (Claude, 1999).

The transesterification reaction can be catalyzed by both homogeneous and heterogeneous catalysts. The most commonly used alkali catalysts are sodium hydroxide, sodium methoxide and potassium hydroxide. Sulphuric acid, hydrochloric acid and sulfonic acid are usually preferred as acid catalysts. Finally, the heterogeneous catalysts include enzymes, titanium-silicates, anion exchange resins and guanadines heterogenized on organic polymers.

The basic catalysts are the most common, since the process is faster and the reaction conditions are moderated (Reid, 1911; Freedman *et al.*, 1984). However, their utilization in vegetable oil transesterification produces soaps by neutralizing the free fatty acid in the oil and thus causes triglyceride saponification. Both soap formations are undesirable side-reactions, because they partially consume the catalyst, decrease the biodiesel yield and complicate the separation and purification steps.

1.3 Membrane Reactors

According to the IUPAC definition, a membrane reactor is a device that combines a membrane-based separation process with chemical reactions in one unit. Publications discussing the membrane reactor concept first appeared in the late 1960's. Most of the real progress in this area, however, has happened in the last twenty years. The interest in membrane-type reactors is continually increasing due to the broad range of possible applications, but attention has been mainly focused on their application to catalytic reactions where the continuous selective removal of one or more products in equilibrium limited reactions allows the increase of the yield beyond the corresponding equilibrium value. Membrane reactors can contain the catalyst in the walls of the membrane, or the catalyst may be packed into the inside of the membrane reactor.

In this thesis, this concept was applied to enhance the yield and selectivity in transesterification of triglycerides (canola oil) to fatty acid methyl esters (FAME or biodiesel) by dosing alcohols and catalyst along the membrane reactor.

1.4 Objectives

The first objective of this thesis was to find a new means of separating FAME produced from the acid-catalyzed transesterification from canola oil by using a membrane-based reactor. The feasibility of such a reactor was first tested by measuring the miscibility of canola oil in methanol and FAME in methanol. The second objective of the thesis was to demonstrate the use of the membrane reactor and to report on the reliability of the data.

1.5 Thesis Structure

The thesis consists of five chapters. The second chapter presents a literature review of biodiesel research and membrane reactors. This is followed by two articles to be submitted for publication (Chapters 3 and 4). Chapter 3 discusses the miscibility of canola oil in methanol and FAME, respectively, and demonstrates the viability of a membrane reactor for transesterification of canola oil to biodiesel. Chapter 4 contains the results of several experiments at varying catalyst concentrations and reaction temperatures using the membrane reactor. Finally, Chapter 5 contains a general discussion, conclusions and recommendations for future work. References and appendices (as appropriate) for each chapter are provided throughout the thesis.

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CHAPTER 2

LITERATURE REVIEW

2.1 Transesterification

Transesterification is the chemical process of converting one ester into another such as the alkyl monoesters that compose biodiesel. This process occurs by reacting a triglyceride (vegetable oil) with alcohol in the presence of a catalyst to produce a methyl ester. Methanol, ethanol and butanol are the recommended alcohols (Freedman *et al.,* 1984). Methanol and ethanol are utilized most frequently. Ethanol is a preferred alcohol in the transesterification process compared to methanol because it is derived from agricultural products and is renewable and biologically less objectionable in the environment, however methanol is used because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). The transesterification process has been widely used to reduce the viscosity of triglycerides, thereby enhancing the physical properties of renewable fuels to improve engine performance.

Three basic catalysts are used to catalyze the transesterification to produce methyl esters from oils and tallow. The most commonly used alkali catalysts are sodium hydroxide, sodium methoxide and potassium hydroxide, which give high levels of conversion of triglycerides to their corresponding methyl esters in short reaction times. Sulphuric acid, hydrochloric acid and sulfonic acid are usually preferred as acid catalysts. Finally, the heterogeneous catalysts include enzymes, titanium-silicates, anion exchange resins and guanadines heterogenized on organic polymers.

The use of an enzyme-catalyzed process was discussed by Nelson *et al.* (1996). Results showed that product separation and waste disposal problems could be simplified using an enzyme-catalyzed system. Most enzymatic-catalyzed transesterifications use immobilized lipase as the catalyst in order to be able to reuse the lipase (Fukuda *et al.*, 2001; Hsu *et al.*, 2001). Around 95% conversion was achieved at relatively low temperatures from the lipase-catalyzed transesterification of waste edible oil to biodiesel after 50 h (Watanabe *et al.* 2001). Since the alkali-catalyzed transesterification process is much faster than that catalyzed by the acid catalyst and enzyme (Freedman, 1984), it is most commonly applied both at the laboratory and industrial scales.

Many investigations of the alkali-catalyzed process have been performed. Freedman *et al.* (1984) studied the effect of temperature, the molar ratio of the alcohol to oil, and the type of catalyst. It was found that 98% conversion was observed in one hour at a 6:1 molar ratio of methanol to soybean oil, 65°C and 1 wt.% sodium hydroxide. They also found that greater than 90% oil was converted to methyl esters after 60 hours at a 30:1 molar ratio of methanol to soybean oil, 65°C and 1 wt.% sulphuric acid. They investigated the effect of temperature on reaction rate and found that it had a significant effect on the reaction rate early in the reaction. They suggested that the vegetable oil and alcohol must be anhydrous and low in free fatty acids.

Boocock *et al.* (1998) showed that using tetrahydrofuran (THF) as a co-solvent could accelerate the miscibility of vegetable oil in methanol and speed up the alkali-catalyzed reaction. They found that 95% conversion of oil to methyl esters was observed in 20 minutes at a 6:1 molar ratio of methanol to soybean oil, 23°C, 1.3 wt.% sodium hydroxide and a 5:4 volume ratio of THF to methanol. It was pointed out that THF was involved in the reaction process, thus making it more difficult to separate the reaction mixture.

Separation of FAME product from the reaction mixture poses some important challenges to the production of biodiesel. Karaosmanoglu *et al.* (1996) studied three different separation methods and found that hot water washing at 50°C was the best way to separate and purify the biodiesel product. Bam *et al.* (1995) also investigated the washing method to purify the methyl esters. They suggested that glycerine could be added as a solvent to wash impurities. Hayafuji *et al.* (1999) studied the use of a solid absorbent to purify the resulting esters, such as activated clay, activated carbon, activated carbon fiber, etc.

Freedman *et al.* (1985) studied the kinetics of soybean oil transesterification with butanol in the presence of sodium butoxide. In that study, reaction rate constants were determined and the effect of type of alcohol, molar ratio of alcohol to soybean oil, type and amount of catalyst, and reaction temperatures on rate constants and kinetic order were examined. They found that forward reactions appeared to be first-order or second-order depending upon the conditions used while the reverse reactions appeared to be second order. They also observed a shunt reaction at a molar ratio of methanol to soybean oil of 6:1.

Noureddini and Zhu (1997) studied the kinetics of alkali-catalyzed transesterification of soybean oil with methanol. They found that a 90% conversion of oil was observed at a 6:1 molar ratio of methanol to oil, 60°C and 0.2 wt.% sodium hydroxide within 90 minutes. They proposed a reaction mechanism consisting of an initial mass transfer-controlled region followed by a kinetically controlled region. The data showed that the later region appeared to be represented by a second-order kinetic mechanism.

Most of the biodiesel that is currently made uses high quality vegetable oil. Fatty acid methyl esters (FAME) from vegetable oils have shown promise as biodiesel. At issue is the high cost of virgin oil feedstock. Due to their significantly lower cost, waste oils and fats are now being used. However, there are large amounts of oils (restaurant waste, frying oils, trap grease, etc) that contain significant amounts of free fatty acids (FFA) that make the transesterification process using an alkaline catalyst difficult. These FFA react with the alkaline catalyst to produce soaps that inhibit the separation of the ester, glycerol, and wash water. An alternative method is to use acid catalyst.

Nye *et al.* (1983) have shown the transesterification of used frying oil with various alcohols using an acid catalyst. They found that 80% conversion of oil to methyl esters was obtained at a 3.6:1 molar ratio of methanol to oil, 65°C and 0.1 wt.% sulphuric acid after 40 hours. Freedman *et al.* (1984) investigated the acid-catalyzed transesterification of soybean oil with various alcohols. They found that the reaction temperature was a significant factor in conversions.

Ripmeester (1998) and McBride (1999) studied the transesterification of waste cooking oil with methanol using sulfuric acid catalyst. They found that around 100% conversion of oil to FAME was observed at 245:1 molar ratio of methanol to oil, 70°C and 1.5 mol% sulfuric acid catalyst. They proposed a first-order kinetics model and calculated the reaction rate constant. Their work indicated a strong dependence of the conversion on the molar ratio of methanol to oil.

Canakci and Van Gerpen (1999) studied the transesterification of soybean oil with various alcohols using sulfuric acid. They investigated the effect of the molar ratio of alcohol to oil, the reaction temperature, catalyst amount, reaction time, water and free fatty acids level on conversion. They found that the ester conversion efficiency was strongly affected by the molar ratio of alcohol to oil especially for the acid-catalyzed reaction. The completeness of ester formation increases with increasing acid catalyst amount.

Freedman *et al.* (1985) investigated the kinetics of acid-catalyzed transesterification with butanol. They found that the forward reactions followed pseudo-first order kinetics and reverse reactions followed pseudo-second order kinetics.

2.2 Membrane Reactors

Membrane technology has occupied an important position in various chemical processes. Publications discussing the membrane reactor concept first started appearing in the late 1960's. Most of the real progress in this area has happened in the last twenty years (Hsieh, 1996). A membrane reactor is usually defined as a single apparatus that combines a reactor and a membrane separator. The membrane reactor has many advantages over the conventional chemical reactor because of its simultaneous function of chemical reaction and separation (Llias *et al.*, 1989; Hsieh, 1989; Harold *et al.*, 1989). A membrane reactor in which simultaneous reaction and product separation occurs could out-perform a conventional reactor because continuous and selective separation of product leads an equilibrium-limited reaction to be released from its limitation (Michaels, 1968).

Most investigations on membrane reactors have been concentrated on inorganic membrane reactors due to their excellent thermal stability at high reaction temperatures (Kameyama *et al.* 1981; Stoukides *et al.* 1984; Michael *et al.* 1984; Shinji *et al.* 1982). Two generic types of membrane reactors exist, product separation or selective reactant addition. The first type of membrane reactor, which is called a permselective membrane reactor, uses the membrane to remove one product from the reaction zone, which allows the reaction to proceed farther to the right. The second type of membrane reactor uses the membrane to control how the reactants contact each other. Either a permseletive or non-permselective membrane, which has a high trans-membrane pressure drop, is used to distribute the feed.

A membrane reactor does have tremendous potential for several reaction types, but transesterification reactions have not been investigated until now. Current batch methods of producing biodiesel are slow, labour intensive, and not well adapted to automation (Peterson *et al.*, 2002). A continuous flow esterification process for producing biodiesel from rapeseed oil and ethanol was investigated by Peterson *et al.* (2002). It was found that the continuous flow reactor successfully produced ester from canola oil at a rate three times that for the existing batch system.

Carbon membranes are of particular interest as they can be stable at high temperatures and resist chemical attack. In this work, a carbon membrane reactor was used to develop a continuous acid-catalyzed process to produce biodiesel from canola oil. Major process equipments including membrane reactor, utilities and the required heater were considered. Acid and base-catalyzed transesterifications were carried out in a carbon membrane reactor.

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CHAPTER 3

BIODIESEL PRODUCTION FROM CANOLA OIL USING A MEMBRANE REACTOR:

Miscibility Analysis and Membrane Separation Assessment (Paper 1)

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Abstract

The miscibility of canola oil in methanol and fatty acid methyl esters (FAME or biodiesel) in methanol was determined. Results showed that FAME is miscible in pure methanol under a broad range of conditions. On the other hand, canola oil is not miscible in methanol under normal conditions. These findings led to the development of a two-phase membrane reactor to produce FAME from canola oil and methanol. The transesterification of canola oil was performed via both acid- or base-catalysis. The novel reactor enabled the separation of FAME from canola oil/methanol/FAME mixtures. The two-phase membrane reactor was particularly useful in removing unreacted canola oil from the FAME product yielding high purity biodiesel.

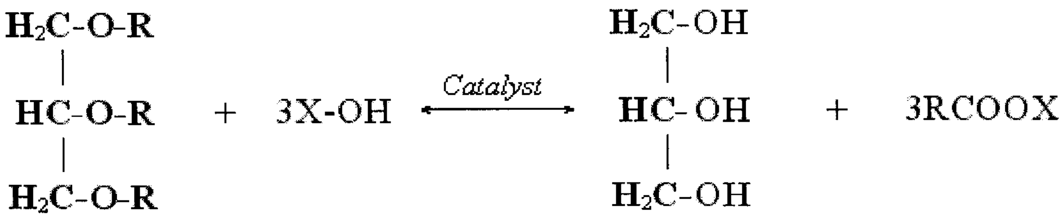
Keywords: biodiesel, methanol, transesterification, two-phase membrane reactor.

3.1 Introduction

Biodiesel is a renewable energy fuel produced from animal fats and vegetable oils by the transesterification of triglyceride (TG). Chemically, it is a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats.

In recent years, because of increases in crude oil prices, limited fossil oil resources and environmental concerns, significant attention has been paid to the use of alternative fuels such as vegetable oils and animal fats to make biodiesel fuels. While the impact of such fuels as replacements to petroleum diesel is small, their use as lubricity enhancers is highly promising. Environmental regulations have targeted the reduction of sulfur and aromatics in diesel fuel in order to obtain cleaner air. Unfortunately, the process used to remove sulfur and aromatics from petroleum diesel also removes components that help provide the fuel with its lubricating properties (i.e. lubricity). Biodiesel has been shown to compensate for the lower levels of lubricity of low-sulfur petroleum diesel fuels when blended at even relatively low percentages (Dmytryshyn *et al.*, 2004). Biodiesel can completely offset the lack of lubricity in these low-sulfur fuels.

Currently, there are about 28 countries producing biodiesel with Germany and France being the largest producers in the world. Recently, a continuous plant in Bakersfield, CA, U.S.A. was constructed to generate 0.66 million litres of biodiesel per year with claims that the plant could eventually be expanded to produce 9.25 million litres per year, which would be more than twice the U.S. production of biodiesel fuel in 2002. In the biodiesel industry, several methods exist for the production of FAME. Current commercial practice involves the use of alkali-catalyzed transesterification. A representation of the transesterification reaction is shown in Figure 3.1. ***R***s represent fatty hydrocarbon chains (14-20 carbon atoms, 0-2 double bonds), and ***X*** represents alkyl groups on the alcohol.



$$\begin{array}{c} H_2C\text{-}O\text{-}R \\ | \\ HC\text{-}O\text{-}R \\ | \\ H_2C\text{-}O\text{-}R \end{array} + 3X\text{-}OH \xleftrightarrow{\mathit{Catalyst}} \begin{array}{c} H_2C\text{-}OH \\ | \\ HC\text{-}OH \\ | \\ H_2C\text{-}OH \end{array} + 3RCOOX$$

Figure 3.1: Stoichiometric reaction for conversion of triglyceride to FAME

Recent work by Zhang *et al.* (2003) indicates the promise of producing FAME by an acid-catalyzed reaction. At issue is the high cost of virgin oil feedstock. However, due to their significantly lower cost, waste oils and fats are now being used. These are high in FFA and necessitate corrective action such as the use of a pre-esterification reactor using an acid-catalyst (Kinast, 2003). In alkali-catalyzed transesterification, the alcohol and triglycerides must be anhydrous and devoid of free fatty acids (FFA), otherwise significant saponification will take place (Wright *et al.*, 1944). Alkali-catalyzed transesterification is much faster than that using an acid catalyst (Freedman *et. al.*, 1984; Schwab *et al.*, 1987; Liu, 1994). Freedman *et al.* (1984) and Liu (1994) noted that the acid catalyst would be much more effective than the alkaline catalyst in the presence of greater than 1% FFA in the feedstock. Thus, despite the lower reaction rate, the use of a lower cost feedstock coupled with a one-step acid-catalyzed transesterification is economically advantageous compared to the base-catalyzed process when using waste oil as the feedstock (Zhang *et al.*, 2003).

Miscibility is an important factor in biodiesel production. The conventional transesterification method results in a two-phase reaction which is, as a result, mass-transfer limited. More specifically, the vegetable oils and methanol are not miscible. Tetrahydrofuran (THF) was used to circumvent this problem for methanol/soybean oil mixtures and thus produce a single reaction phase and causing a dramatic increase in reaction rate compared to the conventional two-phase reaction (Boocock *et al.*, 1996). However, this immiscibility is of benefit for product separation and can be used to our advantage when membrane separation technologies are employed.

Membrane technology has occupied an important position in various chemical processes and membrane reactors have attracted considerable research interest over the past few years. Membrane reactors can be used to carry out reaction and separation in a single process. Separative membrane reactors can be used to selectively remove either products or byproducts from the reaction zone. This can overcome low conversions in equilibrium-limited reactions. Moreover, membrane-based separative reactors can also be used to selectively permeate reactant into the reaction zone in order to control excessive byproduct formation. All these characteristices of separative membrane reactors can be suitably applied to transesterification.

In this paper, we report on an investigation of the miscibility of canola oil and FAME, respectively, with methanol. The objective was to identify suitable experimental conditions for the production of biodiesel using a membrane reactor.

3.2 Materials and Methods

3.2.1 Materials

Methanol (95% Tech. Grade) was supplied by (Commercial Alcohols Inc., Brampton, ON) and the canola oil by (No Name®, Toronto, ON, and purchased at the local foodstore). Biodiesel was produced from the acid-catalyzed transesterification of waste oils from a previous study (Zheng, 2003). Sulfuric acid (95%-98%, Reagent Grade) and tetrahydrofuran (99.95%, Chromatography Grade) were supplied by (EMD Chemicals Inc., Gibbstown, New Jersey, U.S.A.).

3.2.2 Experimental Design

The aim of this work was to determine the relative miscibility of canola oil in methanol and that of FAME in methanol at several temperatures and compositions. Nine volume ratios of canola oil to methanol and FAME to methanol were investigated: 10, 20, 30, 40, 50, 60, 70, 80 and 90% at temperatures of 25, 30, 40, 50, 60 and 70°C. Mixtures were prepared in 30 mL glass vials, shaken and placed in a temperature-controlled water bath. The relative volume of each phase was calculated by measuring the height of the meniscus separating the two phases.

After the measurements for miscibility, a membrane reactor was constructed. A carbon membrane (Koch Membrane Systems, Inc., Wilmington, DE, U.S.A.) was used in the reactor. The pore size of the membrane was 0.05 μm. The inside and outside diameter of the membrane were 6 mm and 8 mm respectively. The length of the carbon membrane tube was 1200 mm, which yielded a total surface area 0.022 m^2. A schematic diagram of the membrane reactor system is showed in Figure 3.2. A controller volume pump (Milton Roy Company, Ivyland, PA, U.S.A.) was used to feed the methanol to the system while seal-less centrifugal canned motor pumps (Labcor Inc. Concord, ON) were used to circulate the mixture. A heat exchanger (Neslab Instruments, Inc., Portsmouth, NH, U.S.A.) was used to control the reaction temperature.

Experiments were carried out at 60, 65 and 70°C in a 300 mL membrane separative reactor for 6 h. 0.5, 2, 4 and 6 wt% concentrations of sulfuric acid catalyst were investigated. 100 g of canola oil were used in each run. Pressure was controlled at 138 kPa between the permeation side and reaction side of the membrane. A schematic of the separation of oil and FAME by a separative membrane is shown in Figure 3.3. All experiments and sample analyses were carried out in random order to minimize any potential experimental errors.

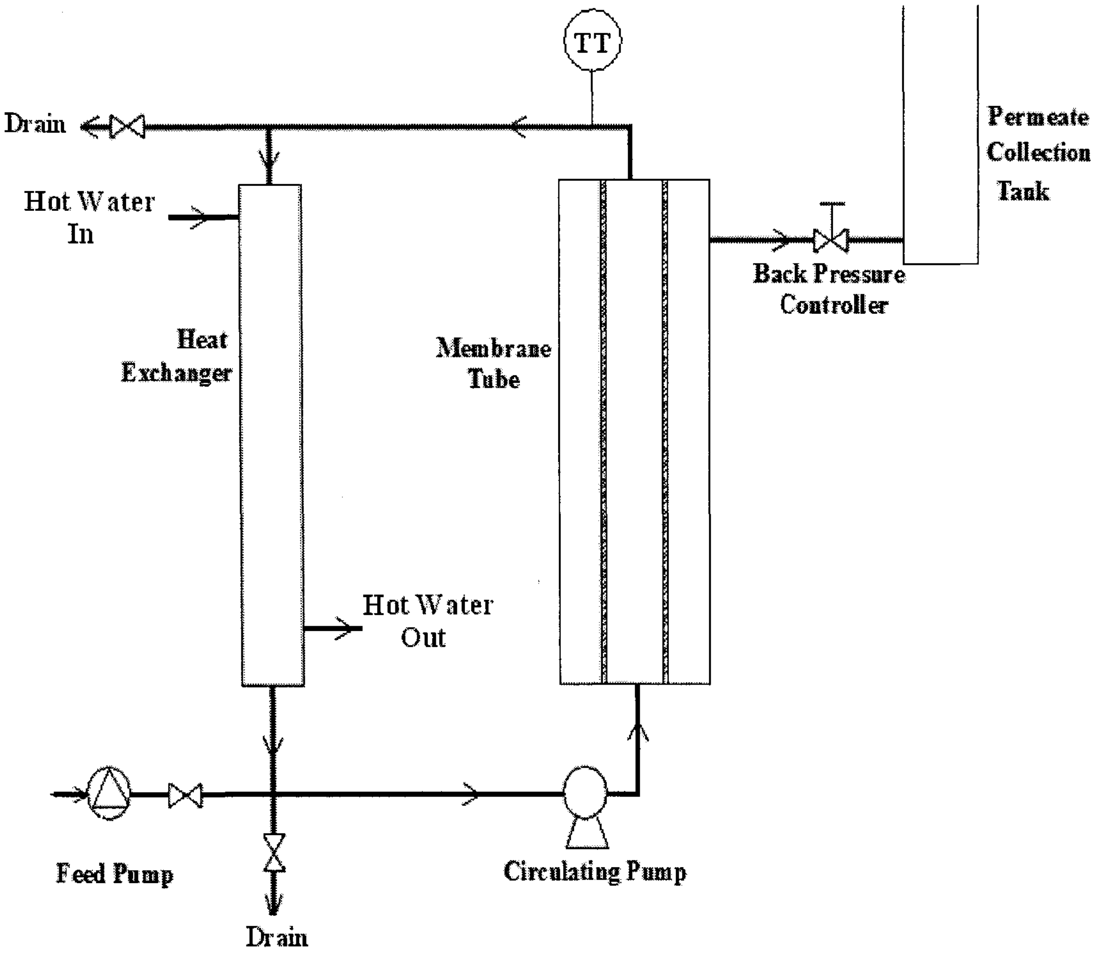


Figure 3.2: System diagram of separative membrane reactor

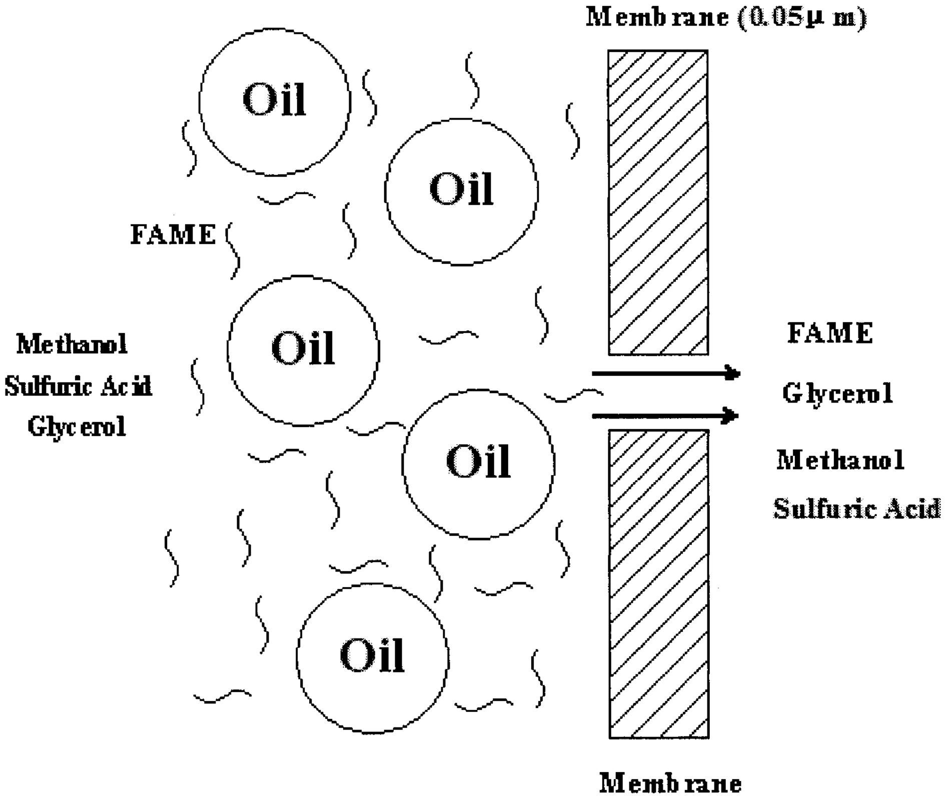


Figure 3.3: Separation of oil and FAME by a separative membrane

Methanol and acid catalyst were pre-mixed and charged into the reactor system prior to each reaction. Canola oil was charged into the membrane reactor, the membrane reactor was sealed, the circulation pump was started. The reaction temperature was monitored using a thermocouple placed in the circulation loop. After circulating the reactor contents for 10 minutes, methanol and acid catalyst were continuously charged into the membrane reactor during the transesterification and the heat exchanger was switched on. The permeate product was taken from each experiment. The permeate product was mixed with the same volume of water and the resulting mixture was allowed to settle for 24 h. The upper layer of the mixture was retained, then washed with 1 L reverse osmosis water. The mixture was again allowed to settle for 24 h, after which the sample was placed in a

30 mL vial until analysis. High performance liquid chromatography (HPLC) analysis showed the purificiation method to be effective and no residual acid was found in the sample. The oil left in the membrane reactor was then placed in a container and analyzed.

3.2.3 High Performance Liquid Chromatography

A Waters Corp. HPLC system consisting of an HPLC pump, a controller, a differential refractometer and autosampler was used to analyze the contents of the permeate and retentate streams. Waters Millennium 32^{TM} software (Waters) was utilized for analysis. The columns used were two 300×7.5 mm Phenogel columns of 3 μm particles and 100 Å pore size (Phenomenex, Torrance, CA, U.S.A.) connected in series. The mobile phase was tetrahydrofuran (THF) at a flow rate of 0.5 mL/min at 23°C.

THF was used to make a 20 mg/g solution of the sample. Two grams of the solution were prepared. Prior to analysis, the solutions were filtered through a 0.5 μm polytetrafluoroethylene (PTFE) syringe filter.

For HPLC analysis, a calibration curve was generated from 5 standards: triolein (TG), diolein (DG), monoolein (MG), methyl oleate (FAME), glycerol. The injection masses were plotted against the peak area (see Appendix A-3). Each standard was injected 3 times at 5 different concentrations. The calibration curves of the standard solutions showed good linearity. The retention times of the standards are shown in Table 3.1. Although the retention time of a standard sometimes varied from injection to injection, the relative retention times remained constant (Table 3.1). Figure 3.4 shows a typical chromatogram of a mixture of standards (note: sample concentrations were 0.548 mg/mL TG, 0.654 mg/mL DG, 0.602 mg/mL MG, 0.642 mg/mL FAME and 0.584 mg/mL glycerol. Injection volume was 2 μL).

Table 3.1: Retention time of standards

Standard	Retention time (min)	Relative retention time
Triolein (TG)	24.57	1
Diolein (DG)	25.45	1.04
Monoolein (MG)	27.12	1.10
Methyl oleate (FAME)	28.68	1.17
Glycerol	30.95	1.26

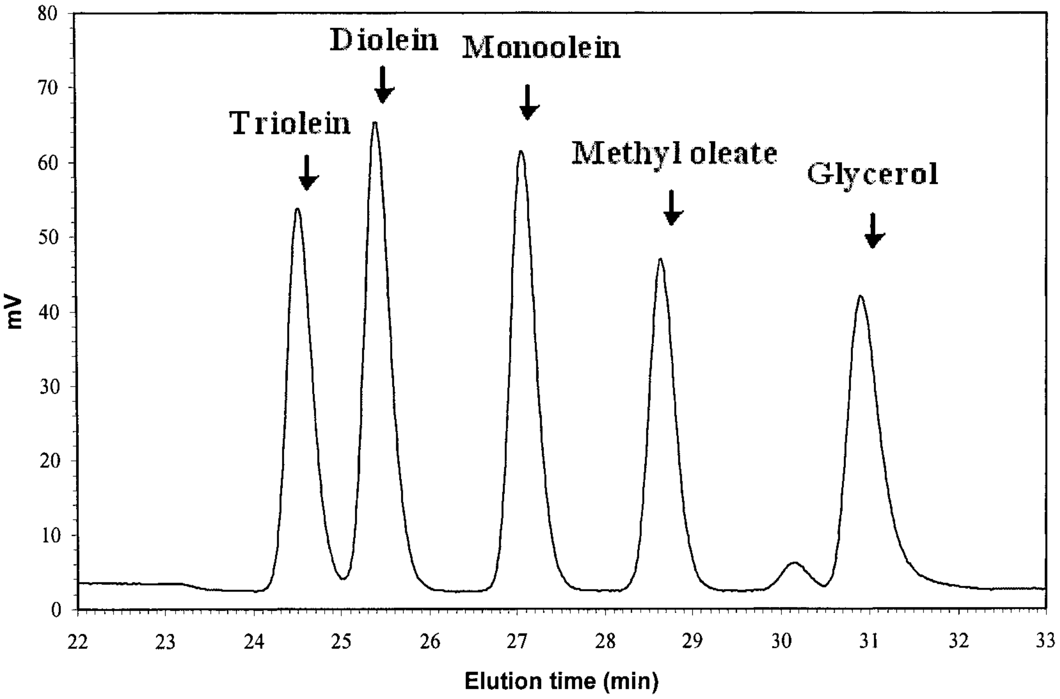


Figure 3.4: HPLC chromatogram of mixture of standards

3.3 Results and Discussion

3.3.1 Miscibility of Oil/Methanol Mixtures

The volumetric ratio of canola oil to methanol was calculated according to:

$$\text{Volumetric ratio of canola to mixture} = \frac{\text{Height of oil phase in vial}}{\text{Total height of mixture in vial}} \tag{3.1}$$

The volume ratio of the lower phase (i.e. the canola oil phase) was plotted against the actual content of canola oil in Figure 3.5 (see Appendix A-1). It is clear from the figure, that temperature had only a slight effect on the miscibility of the canola oil and methanol. From all indications, it appears that methanol is slightly miscible in canola oil. For all practical purposes, however, one could say that the two phases are immiscible.

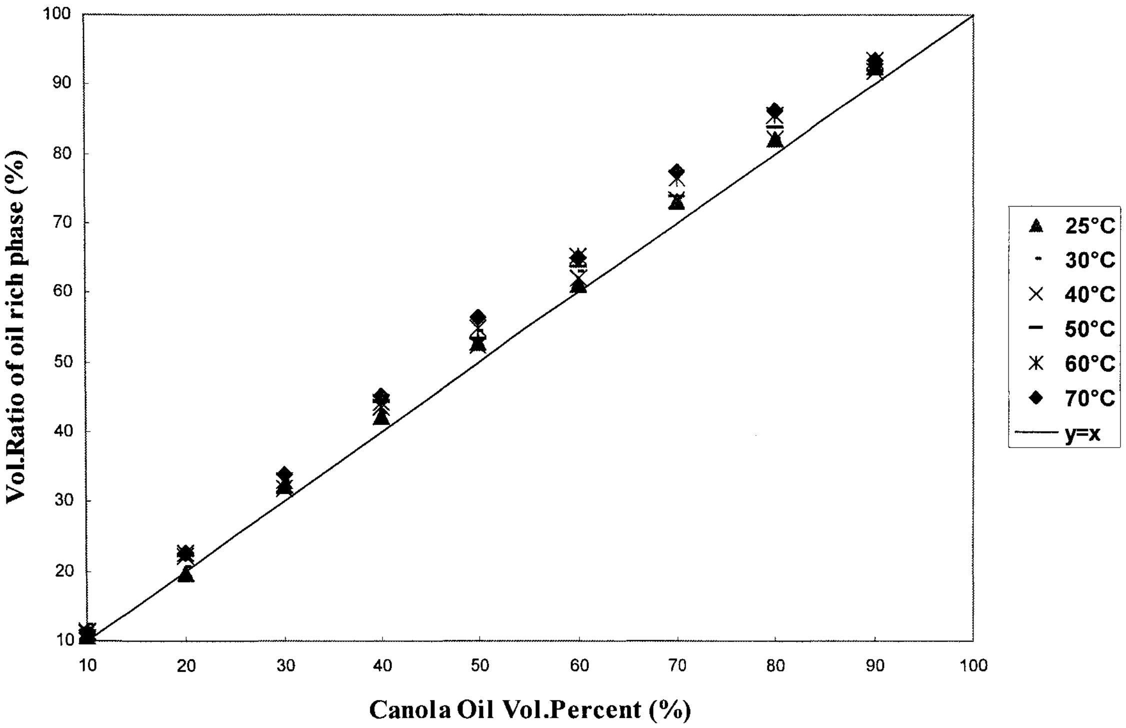


Figure 3.5: Volume ratio of lower phase (canola oil) to entire mixture vs. volume percent canola oil in mixture

3.3.2 Miscibility of FAME/Methanol Mixtures

The temperatures were plotted against the actual content of FAME in Figure 3.6 (see Appendix A-2, A-3). In this case, temperature had a significant effect on the miscibility of FAME and methanol. It appears that FAME is conditionally miscible in methanol. We observed that FAME and methanol were immiscible between 20% and 70% over a broad range of temperatures. In practice, transesterification reactions are carried out above 60°C. Both FAME and methanol are miscible at this temperature. The microporous membrane used in the reactor can separate the oil droplets from the methanol solution containing FAME, glycerol and the catalyst. As reactants are removed from the reactor, the equilibrium of the reaction will lie towards the production of FAME and glycerol giving higher conversions.

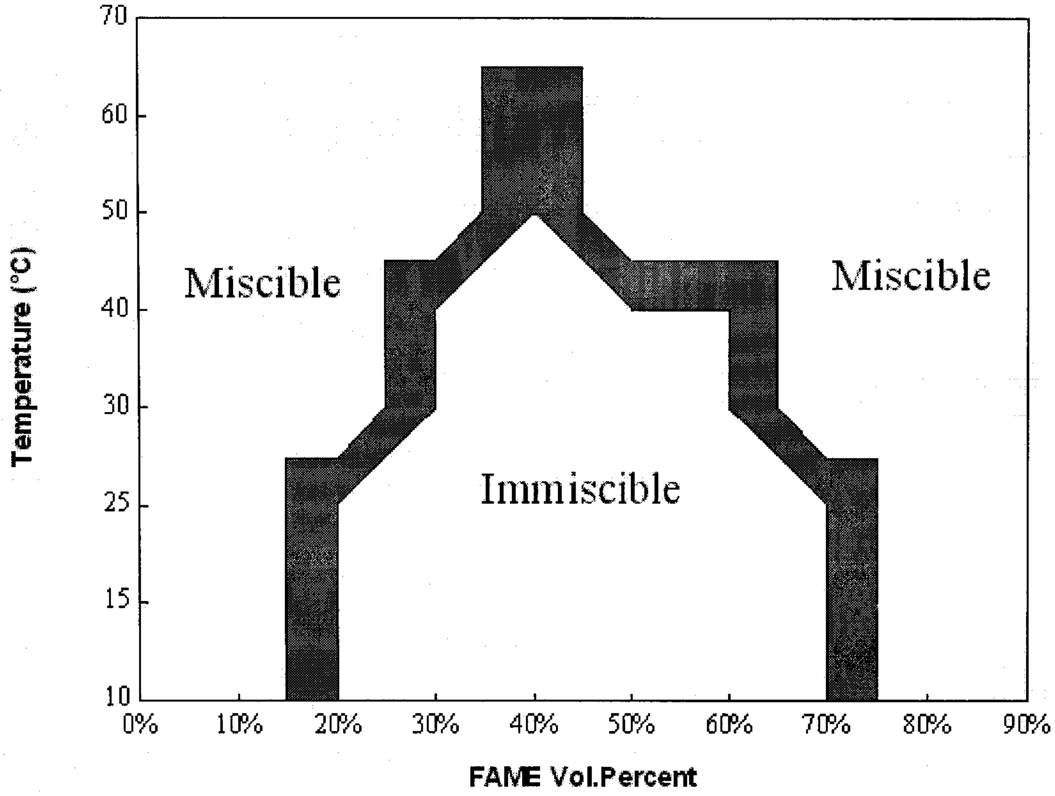


Figure 3.6: Temperatures vs. volume percent FAME in mixture

3.3.3 Principle of Reactor Operation

Transesterification occurs at the surface of canola oil droplets suspended in methanol. After the reaction, the FAME will form a layer near the canola oil droplet surface (see Figure 3.3). As shown in Figure 3.6, the canola oil and methanol are immiscible at the reaction temperature. On the other hand, at the reaction temperatures, one should expect that the FAME would be soluble in the methanol (see Figure 3.3). The concentration of FAME in the methanol can be controlled by the addition of methanol to the reactor.

The main reaction for producing FAME is shown in Figure 3.1. The reaction is reversible, although the equilibrium, under current operating conditions, favours the production of FAME and glycerol. In order to increase the production of FAME, FAME or glycerol should be removed during the reaction in order to shift the equilibrium to the product side.

A microporous carbon membrane reactor can selectively permeate FAME, methanol and glycerol during the transesterification from the reaction zone. The molecule of canola oil is trapped in droplets forming an emulsion. The droplets cannot pass through the pores of the membrane because they are larger than the pore size of the carbon membrane. Results showed that during the reaction, canola oil did not appear in the permeate side. HPLC was used for the determination of compounds in both the permeate and retentate. A typical HPLC chromatogram of the retentate is shown in Figure 3.7. It is observed from the figure that the retentate is composed almost completely of TG (i.e., canola oil). The conversion of TG to FAME was directly calculated by:

$$X = \frac{M_{oil(t=0)} - M_{oil(t=t)}}{M_{oil(t=0)}} \tag{3.3}$$

where X is the fractional mass conversion, $M_{oil(t=0)}$ is the initial mass of oil (or TG equivalents) in the reactor. $M_{oil(t=t)}$ is the mass of TG left in the reactor after 6 h of reaction. A conversion of 99% was obtained after 6 h of operation.

Figure 3.8 shows a typical chromatogram of the permeate. It is observed that very high purity FAME was produced by our method.

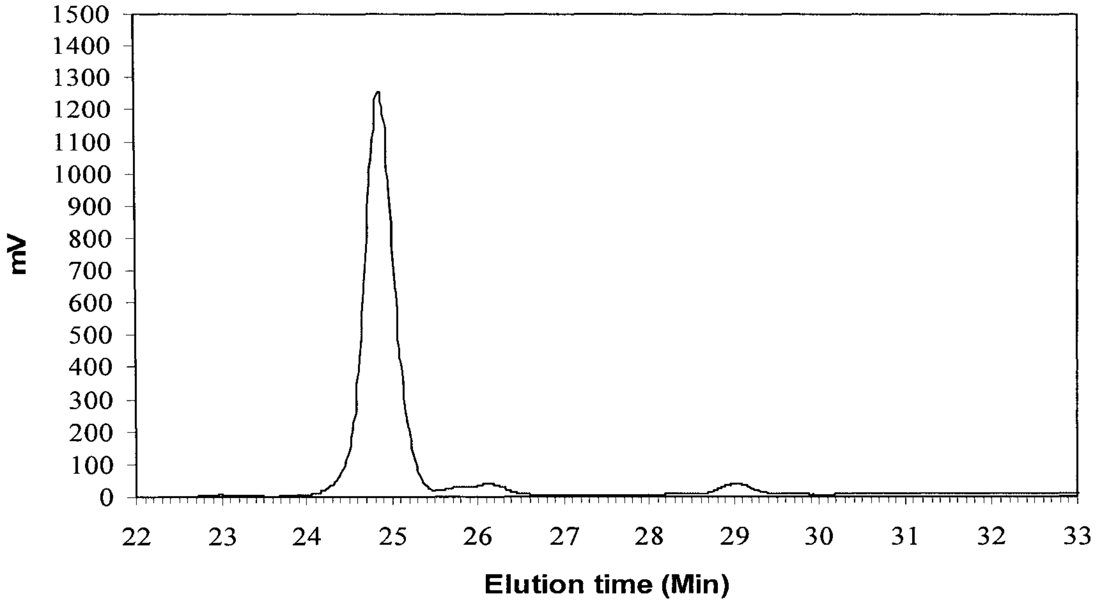


Figure 3.7: HPLC chromatogram of the phase-separated oil phase of the emulsion in the reactor after 6 h of operation (reaction at 65°C, 2 wt.% acid catalyst)

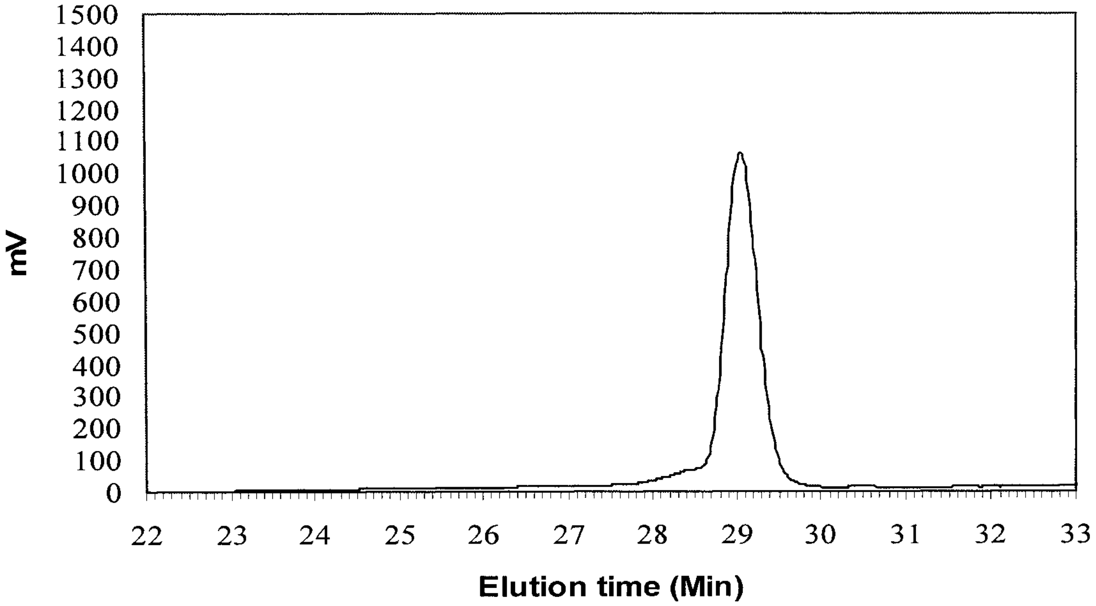


Figure 3.8: HPLC chromatogram of permeate after washing (reaction at 65°C, 2 wt.% acid catalyst)

3.4 Conclusions

It was shown that canola oil and methanol are only slightly miscible in the temperature range 25-70°C. The methanol was slightly dissolved in the canola oil from 1.1 vol.% to a maximum of 7.4 vol.% at 70°C. At low concentrations (<30 vol.%) FAME was almost completely miscible in methanol at 70°C. These miscibility characteristics indicate that the use of a two-phase membrane reactor for the production of biodiesel (FAME) from canola oil is feasible.

A separative membrane reactor was therefore constructed and an acid-catalyzed transesterification of virgin canola oil was performed at 65°C. All experiments consistently showed that no canola oil was found on the permeate side of the membrane yeilding a very high purity FAME. High conversions of up to 99% were achieved in the 6 h of reaction.

Acknowledgements

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CHAPTER 4

BIODIESEL PRODUCTION FROM CANOLA OIL USING A MEMBRANE REACTOR:

Membrane Reactor Set Up and Data Analysis (Paper 2)

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Abstract

A kinetic study of the acid- and base-catalyzed transesterification of canola oil to fatty acid methyl esters (FAME or biodiesel) was carried out to investigate reaction rates under different temperatures and catalyst concentrations. Runs were performed in a semi-batch two-phase membrane reactor at 60, 65 and 70°C. A carbon membrane was used in the membrane reactor. Temperatures, catalyst concentrations, and feed flowrates were chosen as independent factors in this study. Increases in temperature, acid concentration and feedstock (methanol/oil) flowrate significantly increased the conversion of oil to biodiesel. reaction is relatively insensitive to temperatures at the lowest acid catalyst concentration (i.e., 0.5 wt.%). The base-catalyzed reaction resulted in the production of soaps and slight damage to the carbon membrane.

Keywords: biodiesel, methanol, acid-catalyzed transesterification, base-catalyzed transesterification, two-phase membrane reactor, kinetics.

4.1 Introduction

Membrane technology has been widely used in various chemical processes. One important membrane technology is that of the membrane reactor. A membrane reactor is a system or device that combines membranes and chemical reactions (Michaels, 1968). The membrane reactor can significantly enhance the total reaction conversion for equilibrium-limited reversible reactions by removing reaction products continuously from the reactor through a membrane. The membrane reactor has many other advantages over the conventional chemical reactor because of its simultaneous function of chemical reaction and separation (Llias *et al.*, 1989; Hsieh, 1989; Harold *et al.*, 1989).

Membrane reactors can have some advantages over conventional packed-bed reactors (Armor, 1989):

a) An integration of reaction and separation into a single process, thus reducing separation costs and recycle requirements.

b) An enhancement of thermodynamically limited or product-inhibited reactions resulting in higher conversions per pass.

c) A controlled contact of incompatible reactants.

d) An elimination of undesired side reactions.

The membrane can be either organic in nature (i.e., polymeric) or inorganic, with much of the recent focus being on inorganic membranes due to their excellent thermal stability at high reaction temperatures (Kameyama *et al.*, 1981; Stoukides *et al.*, 1980; Michael *et al.*, 1980; Shinji *et al.*, 1982). There has been a flourishing review activity in the field of inorganic membrane reactors in recent years (e.g. Tsotsis *et al.*, 1993; Saracco *et al.*, 1994; Armor, 1995;). Carbon membranes are of particular interest as they can be stable at high temperatures and resist chemical attack.

Transesterification is the reaction of a fat or oil with an alcohol to form esters and a glycerol by-product. The use of vegetable oils to produce biodiesel is well documented (Canakci and Van Gerpen, 1999; Ma and Hanna, 1999). At issue is the high cost of virgin oil feedstock. However, due to their significantly lower cost, waste oils and fats are now being used. Recent work by Zhang *et al.* (2003) indicates the promise of a profitable production of FAME by an acid-catalyzed transesterification of waste oils. In alkali-catalyzed transesterification, the alcohol and triglycerides must be anhydrous and devoid of free fatty acids (FFA) lest significant saponification take place (Wright *et al.*, 1944). This would result in serious difficulties for downstream separation of the products from the reaction mixture. These, however, are high in FFA and necessitate corrective action, such as the use of a pre-esterification reactor using an acid-catalyst (Kinast, 2003). Alkali-catalyzed transesterification is much faster than that using an acid catalyst (Freedman *et. al.*, 1984; Schwab *et al.*, 1987; Liu, 1994). Freedman *et al.* (1984) and Liu (1994) noted that the acid catalyst would be much more effective than the alkaline catalyst in the presence of greater than 1% FFA in the feedstock. Thus, despite the lower reaction rate, the use of a lower cost feedstock coupled with a one-step acid-catalyzed transesterification is economically advantageous compared to the base-catalyzed process (Zhang *et al.*, 2003).

Some researchers have reported on the kinetics of transesterification of vegetable oils. Freedman *et al.* (1984) reported the effects of the type of alcohol, molar ratio, type and amount of catalyst (base vs. acid) and reaction temperature on rate constants and kinetic order. They reported that the acid catalysts would be more effective for oils that had a high concentration of FFA and that temperature showed a significant effect on the yield early in the reaction. Canakci and Van Gerpen (1999) studied the acid-catalyzed transesterification of soybean oil. In their study, alcohols with high boiling temperature increased ester conversion.

Membrane reactors can be used to carry out reaction and separation in a single process. Separative membrane reactors can be used to selectively remove either products or byproducts from the reaction zone. This can overcome low conversions in equilibrium-limited reactions. Moreover, membrane-based separative reactors can also be used to selectively permeate reactant into the reaction zone in order to control excessive byproduct formation. All these characteristices of separative membrane reactors can be suitably applied to transesterification. There are no investigations reporting the kinetics of the acid-catalyzed transesterification of vegetable oil in a membrane reactor. It is important to identify and quantify the effect of some important factors that affect the yield of biodiesel and set up a kinetic model of the transesterification to investigate the reaction mechanism in a membrane reactor. Therefore, in this study, an investigation of the effect of reaction temperature and acid concentrations was performed for the transesterification of canola oil to FAME using an acid catalyst.

4.2 Experimental Method

The aim of this work was to determine the effect of reaction temperature and catalyst concentration on the transesterification of canola oil in a membrane reactor. All experiments were carried out in a 300 mL membrane separative reactor for a period of 6 h each. The experimental conditions are shown in Table 4.1. Several replicate runs were conducted as indicated in the table. 100 g of canola oil were used in each experiment. Pressure was controlled at 138 kPa between the permeate side and reaction side of the membrane. All experiments and the sample analyses were carried out in random order to minimize any potential experimental errors. Additional experiments were conducted to verify the effect of methanol feed flowrate and the use of a base catalyst.

Table 4.1: Experimental conditions

Temperature (°C)	**Catalyst concentration (wt%)**	**# of replicates**
60	0.5	2
65	0.5	2
70	0.5	2
60	2	3
65	2	3
70	2	2
60	4	2
65	4	2
70	4	2
60	6	4
65	6	4
70	6	4

A carbon membrane (Koch Membrane Systems, Inc., Wilmington, DE, U.S.A.) was used in the membrane reactor. The pore size of the membrane was 0.05 μm. The inside and outside diameter of the membrane were 6 mm and 8 mm respectively. The length of the carbon membrane tube was 1200 mm, which yielded a total surface area 0.022 m^2. A schematic diagram of the membrane reactor system is shown in Figure 4.1. A controlled volume pump (Milton Roy Company, Ivyland, PA, U.S.A.) was used to feed the methanol and oil to the system while a seal-less centrifugal canned motor pump (LABCOR Inc. Concord, ON, Canada) was used to circulate the mixture. The pump speed was 15.2 mL/min. A heat exchanger (NESLAB Instruments, Inc., Portsmouth, NH, U.S.A.) coupled with LabView™ software was used to control the reaction temperature.

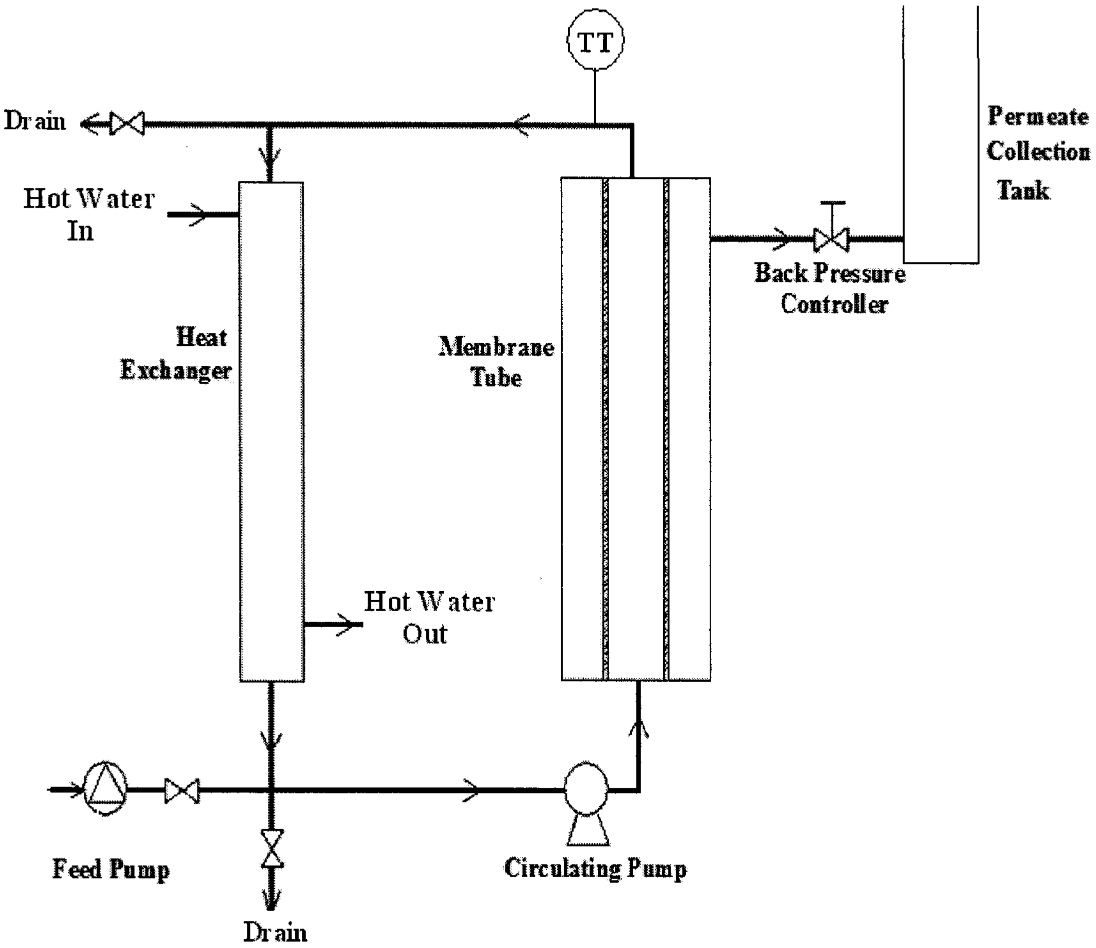

Figure 4.1: System Diagram of Separative Membrane Reactor

Methanol (95% tech. grade, Commercial Alcohols Inc., Brampton, ON, Canada) and sulfuric acid (95%-98%, reagent grade, EMD Chemicals Inc., Gibbstown, NJ, U.S.A.) were pre-mixed and charged into the membrane reaction system prior to each reaction. 100 g of canola oil (No Name® brand, Toronto, ON, Canada, purchased at the local foodstore) was charged into the membrane reactor, and the circulation pump was started. After a 10 min circulation time, methanol and acid catalyst were continuously fed into the membrane reactor with the feed pump (2.5 mL/min, 3.2 mL/min and 6.1 mL/min). The heat exchanger was switched on to achieve the reaction temperature (60°C, 65°C and 70°C). A thermocouple was used to monitor the reaction temperature. A stable reaction temperature (+/- 0.1° C) was achieved within 30 minutes for 60°C, 40 minutes for 65° C and 45 minutes for 70° C of starting the heat exchanger. Pressure was controlled at 138 kPa. The permeate product was collected in a 2000 mL flask. All experiments were conducted for 6 h.

The final permeate product from the time the experiment was started was mixed with an equivalent volume of reverse osmosis water (produced from tap water) and briefly shaken by hand for about 5 minutes. The mixture was allowed to settle for 24 h and filtered using a 0.5 micrometer membrane filter (Nalge Company, New York, NY, U.S.A.). The upper layer of the resulting two-phase mixture was transferred to a separatory funnel and washed with 1 L of reverse osmosis water. The resulting mixture was allowed to settle for 24 h, after which the upper layer was analysed using high performance liquid chromatography (HPLC) according to the method used by Zheng *et al.* (2004). Any unreacted oil in the retentate stream was also analysed by HPLC. The retentate solution was neutralized by sodium hydroxide solution before analysis by HPLC.

A Waters Corp. HPLC system consisting of an HPLC pump, a controller, a differential refractometer and autosampler was used. Waters Millennium 32™ software (Waters) was utilized for analysis. The columns used were two 300×7.5 mm Phenogel columns of 3 μm and 100 Å pore size (Phenomenex, Torrance, CA, U.S.A.) connected in series. The mobile phase was tetrahydrofuran (THF) at a flow rate of 0.5 mL/min at 23°C.

THF was used to make a 20 mg/g solution of the sample. 2 g of the solution was injected into the autosampler vials. Prior to analysis, the solutions were filtered through a 0.5 μm polytetrafluoroethylene (PTFE) syringe filter.

For HPLC analysis, a calibration curve was generated from 5 standards: triolein (TG), diolein (DG), monoolein (MG), methyl oleate (FAME), and glycerol. The injection masses were plotted against the peak area (see Appendix A-4). Each standard was injected 3 times at 5 different concentrations. The calibration curves of the standard solutions showed good linearity. The retention time of the standards are shown in Appendix A-6: TG, 24.57 minutes; DG, 25.45 minutes; MG, 27.12 minutes; FAME, 28.68 minutes; glycerol, 30.95 minutes. Although the retention time of a standard sometimes varied from injection to injection, the relative retention times remained constant (Table 3.1). Figure 3.4 shows a typical chromatogram of a mixture of standards (note: sample concentration was 0.548 mg/mL TG, 0.654 mg/mL DG, 0.602 mg/mL MG, 0.642 mg/mL FAME and 0.584 mg/mL glycerol and injection volume was 2 μL).

The fractional conversion of oil to FAME based on the amount of oil remaining in the reactor was taken to represent the actual conversion . The oil to FAME conversion at time *t* was calculated from

$$X = \frac{M_{oil(t=0)} - M_{oil(t=t)}}{M_{oil(t=0)}} \tag{4.1}$$

where X is the fractional conversion, $M_{oil(t=0)}$ is the original of mass of oil (or TG equivalents) in the reactor. $M_{oil(t=t)}$ is the the mass of TG left in the reactor after the 6 hrs reaction time.

4.3 Results and Discussion

4.3.1 HPLC Analysis

Figure 4.2 shows a typical chromatogram of the oil remaining in the reactor after 6 h.

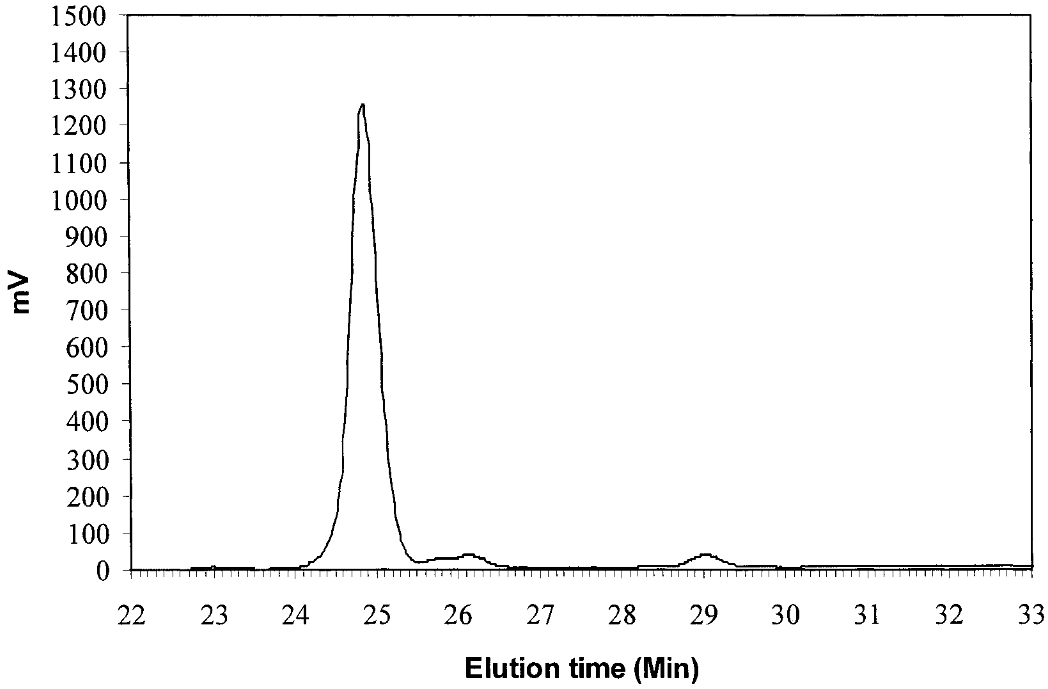

Figure 4.2: HPLC chromatogram of the phase-separated oil phase of the emulsion in the reactor after 6 h of operation (reaction at 65°C, 2 wt.% acid catalyst)

It is seen that the main component in the retentate is TG (retention time = 25 min) or canola oil. Trace amounts of DG (retention time = 26 min) and FAME (retention time = ~29 min) are also evident.

Figure 4.3 shows a typical chromatogram for the organic phase of the permeate. The complete absence of a peak at 25 min indicates that very high purity FAME was produced by the membrane reactor.

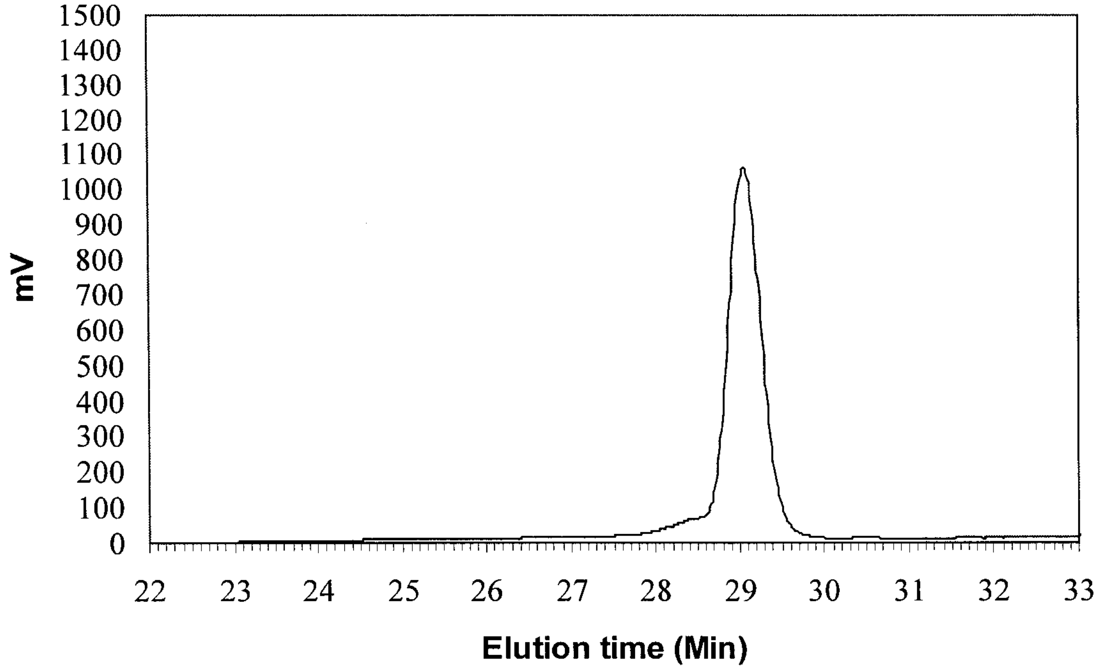

Figure 4.3: HPLC chromatogram of permeate after washing (reaction operated at 65°C, 2 wt% acid catalyst)

At the reaction conditions in this study, as mentioned previously, methanol is only slightly miscible in canola oil. At the same time, FAME and methanol are miscible. These physical characteristics are what permit the membrane reactor to separate the FAME from the oil.

4.3.2 Effect of Temperature

Liu (1994) noted that heating is required for faster reaction and the reaction time may vary from a few minutes to several hours for a temperature range of 60-90°C for acid–catalyzed transesterification.

From our experiments, three different reaction temperatures, 60°C, 65°C and 70°C, were selected. Figure 4.4 shows the conversion versus temperature data as a function of acid concentration. At each acid concentration, an increase in final conversion is evident as temperature is increased.

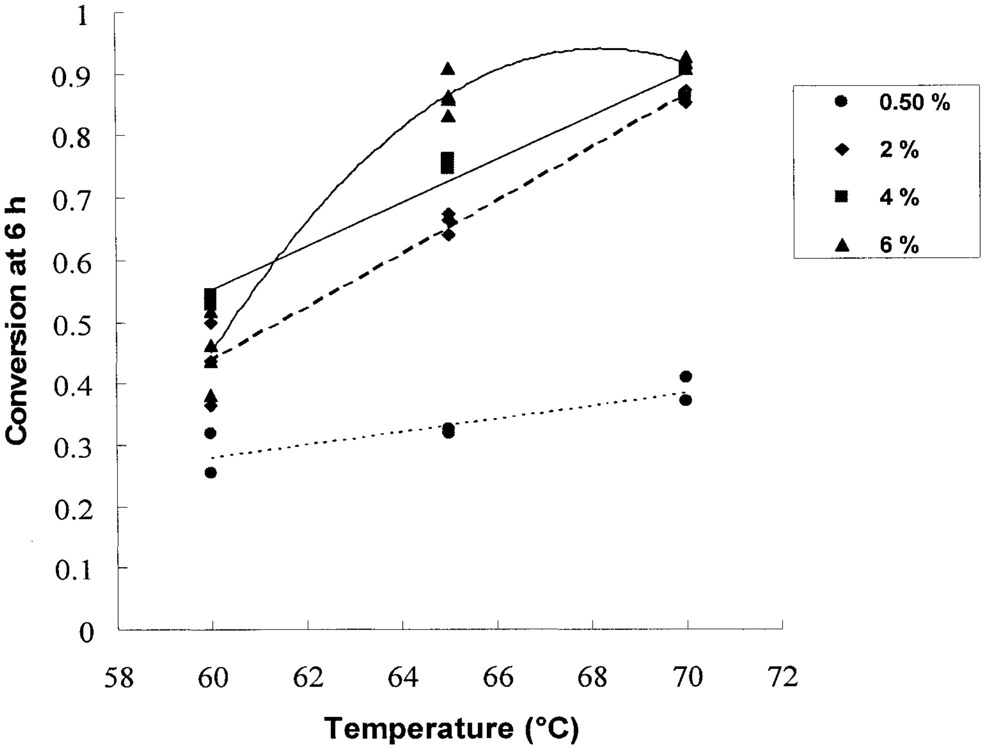

Figure 4.4: Effect of reaction temperature and acid-catalyst concentration (linear fit for 0.05, 2 and 4 wt%, data not plotted fit for 6 wt%)

4.3.3 Effect of Catalyst Concentration

The catalyst concentration was found to affect the conversion of canola oil to FAME. It is evident from Figure 4.4 that an increase in acid concentration served to increase the conversion of TG to FAME. Based on the Figure 4.4, one can see that between 0.5 and 2 wt.% acid concentration the conversion increases substantially at higher temperatures, but the conversions of 2, 4 and 6 wt.% are not very different. Thus, concentrations of acid beyond 2 wt.% are not necessary at 70°C. And the reaction was more sensitive to temperature at high acid concentration.

An important consideration when dealing with acid catalyst concentration is the life of the carbon membrane used in the reactor. The carbon membrane was able to resist the high acid environment in our experiments. After ten months of operation and contact with methanol/acid solution, no tangible evidence of degradation of the membrane was observed.

4.3.4 Effect of Flow rate

The methanol/acid catalyst feed flowrate was set to 2.5, 3.2 and 6.1 mL/min for three separate experiments at 2 wt.% acid concentrations (see Table 4.2). A significant increase in conversion was observed as the flowrate was increased.

Table 4.2: Effect of flowrate on conversion

Expt.	Flowrate (mL/min)	Temperature (°C)	Conversion via acid-catalyst (%)	Conversion via base-catalyst (%)
1	2.5	65	35	95
2	3.2	65	48	96
3	6.1	65	64	96

4.3.5 Effect of Base Catalyst

The use of a 1 wt% NaOH catalyst concentration was tested at different flowrates (see Table 4.2). Comparison to the acid catalyzed case shows that the base catalyst provides a much higher conversion, than that of acid catalyst. Freedman *et al.* (1984) studied the effect of the type of catalyst on the reaction. It was found that 98% conversion was observed at 1 wt% sodium hydroxide. They also found that greater than 90% of the oil was converted to methyl esters at 1 wt% sulphuric acid. However, in the base-catalyzed experiments, suds, indicating the presence of soaps, were detected in the permeate stream after washing, these were not found in the acid-catalyzed runs. A possible reason would be that the canola oil might have contained significant amounts of free fatty acids that could not be converted to biodiesel using a base catalyst. This would have implications for the use of an acid catalyst, which, despite the slower reaction rate, may provide both a technological and economic advantage for the use of lower cost waste feedstock, which contain higher levels of free fatty acids (Zhang *et al.*, 2003). Furthermore, after several runs using a base catalyst, there was some evidence of slight damage to the carbon membrane.

4.4 Conclusions

The use of a membrane reactor for the transesterification of canola oil to biodiesel has been successfully demonstrated. The reaction setup allowed for the production of high purity FAME with no traces of canola oil in the permeate stream.

Increases in the reaction temperature resulted in higher conversions after a 6 h reaction time. An increase in acid catalyst concentration also resulted in an increase in conversion of TG to biodiesel. An increased flowrate of the methanol/oil feed resulted in significant increases in the reaction rate.

In comparison to a base-catalyzed reaction, the acid-catalyzed system gave a significantly lower conversion but resulted in no soap formation.

Acknowledgements

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Chapter 5

BIODIESEL PRODUCTION FROM CANOLA OIL USING A MEMBRANE REACTOR:

Discussion, Conclusions and Recommendations

5.1 Discussion

The purification of FAME from a canola oil/methanol/catalyst reaction mixture poses some important challenges in the production of biodiesel. Although many separation methods have been studied for separating and purifying the biodiesel product, they are often energy intensive and require the addition of extracting solvents to the process. Membrane reactors can be used to simultaneously carry out reactions and separations in a single process. Separative membrane reactors can be used to selectively remove either products or byproducts from the reaction zone. This can overcome low conversions in equilibrium-limited reactions. Moreover, membrane-based separative reactors can also be used to selectively permeate reactants into the reaction zone in order to control excessive byproduct formation. All these characteristics of separative membrane reactors can be suitably applied to transesterification.

A microporous carbon membrane reactor can selectively permeate FAME, methanol and glycerol during the transesterification from the reaction zone. The miscibility of canola oil in methanol and FAME (biodiesel) in methanol was discussed in Chapter 3. Results showed that temperature had a significant effect on the miscibility of FAME and methanol. It was found that FAME is conditionally miscible in methanol. On the other hand, it was also found that canola oil is not miscible in methanol. The operating principle of the membrane reactor is based on the miscibility of canola oil in methanol and of FAME in methanol. Transesterification is taught to occur at the surface of canola oil droplets suspended in methanol. The FAME will form a layer near the canola oil droplet surface after the transesterification reaction. Furthermore, since the canola oil and methanol are immiscible at the reaction temperature, the droplets of the canola oil cannot pass through the pores of the membrane because they are larger than the pore size of the carbon membrane. However, since the FAME (and glycerol) is soluble in the methanol, the microporous carbon membrane can permeate FAME, methanol and glycerol. The immense benefit of this is the production of high purity biodiesel; that is, biodiesel void of any unreacted canola oil. It was also observed via HPLC that the retentate is composed almost completely of TG. This implies that very little biodiesel is left in the reactor, attesting to the efficiency of such a process. Furthermore, the removal of biodiesel (and glycerol) promotes the formation of products (and glycerol byproduct) due to chemical equilibrium. This is one of the side benefits of membrane reactors that were mentioned earlier.

A kinetic study of the acid- and base-catalyzed transesterification of canola oil to FAME (biodiesel) was carried out to investigate reaction rates under different temperatures and catalyst concentrations in a two-phase membrane reactor (see Chapter 4). Temperature, catalyst concentration, and feed flowrate were chosen as independent factors in this study. As mentioned before, temperature had a significant effect on the reaction conversion. In our studies, final conversion was increased by increasing the reaction temperature. It was found that an increase in the conversion of TG to FAME was evident as the acid concentration was increased. The reaction was more sensitive to temperatures at high acid concentration. A significant increase in conversion was also observed as the flowrate of methanol/catalyst mixture was increased in both the acid-and base-catalyzed reactions. Not surprisingly, the base catalyst provided a much higher conversion. However, soaps were detected in the permeate stream after washing. The reason was that the canola oil might have contained significant amounts of free fatty acids that were converted to soaps rather than biodiesel by the base catalyst. Moreover, slight damage to the carbon membrane was observed after several base-catalyzed experiments.

5.2 Reactor Operation

A number of operating peculiarities were encountered when using the carbon membrane reactor for the production of biodiesel. As mentioned before, the reactor operating pressure was around 138 kPa for a total of 6 h reaction. One important issue concerns the control of the reactor pressure. During regular operation of the membrane reactor, it is necessary to release pressure from the system. It is important that this pressure relief be done slowly in order to avoid the transfer of oil through the membrane pores. A schematic of this problem is shown in Figure 5.1. A quick release of pressure can cause a high enough pressure driving force to push the oil into the permeate side of the membrane reactor. As a result, the purity of the biodiesel will not be maintained. A back pressure controller was used to control the pressure in the membrane reactor (see Figure 3.2). In order to prevent the oil from passing through the membrane, when venting the pressure, one should prevent any sudden pressure drops.

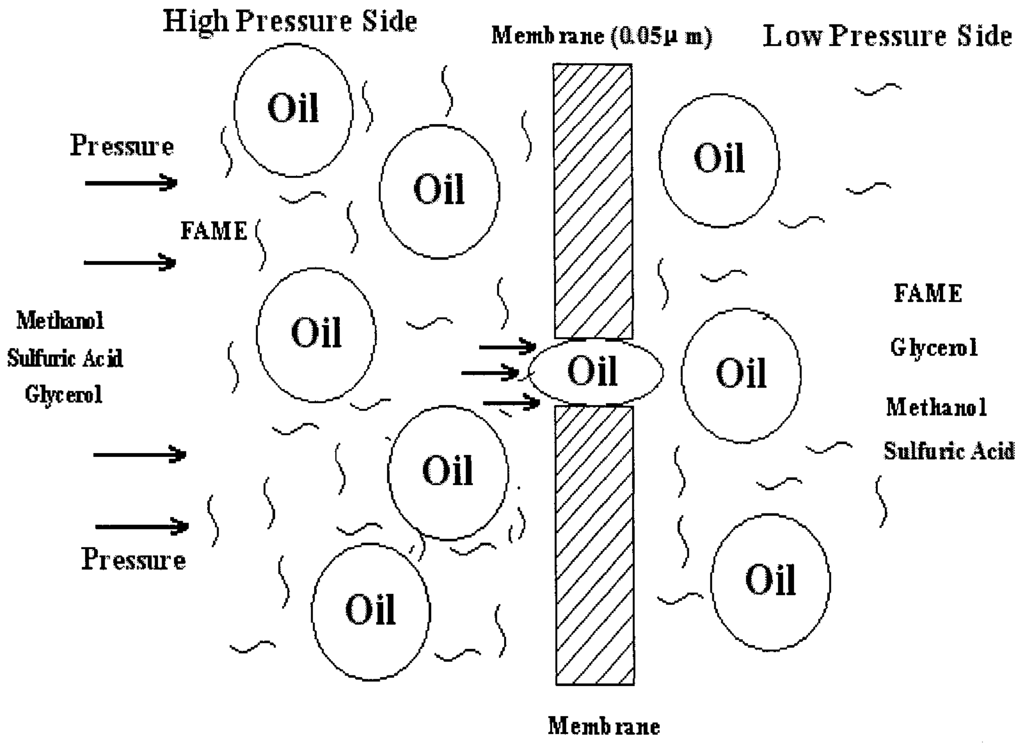

Figure 5.1: Membrane operation

Another experimental difficultly encountered in this process concerned the calculation of conversion of the triglyceride. Since the conversion was calculated by the amount of oil left in the reactor after 6 h, it was important to ensure that the reactor was entirely emptied of oil for this analysis. It was found that if the reactor was simply emptied by draining, there was still some oil left in the reactor. Therefore, a technique was developed to flush the oil out of the reactor. A schematic of the methanol flushing method is shown in Figure 5.2. In this scheme, methanol from the top 2 cm of a 2 liter Erlenmayer flask was drawn into the reactor loop at the suction side of the circulating pump. A stream drawn from the high pressure side of the loop was sent back to the Earlenmayer flask. The canola oil being denser than the methanol was traped in the Erlenmayer flask. The methanol was circulated for over 15 minutes. The procedure was repeated three times using pure methanol. This ensured the complete removal of the oil from the reactor.

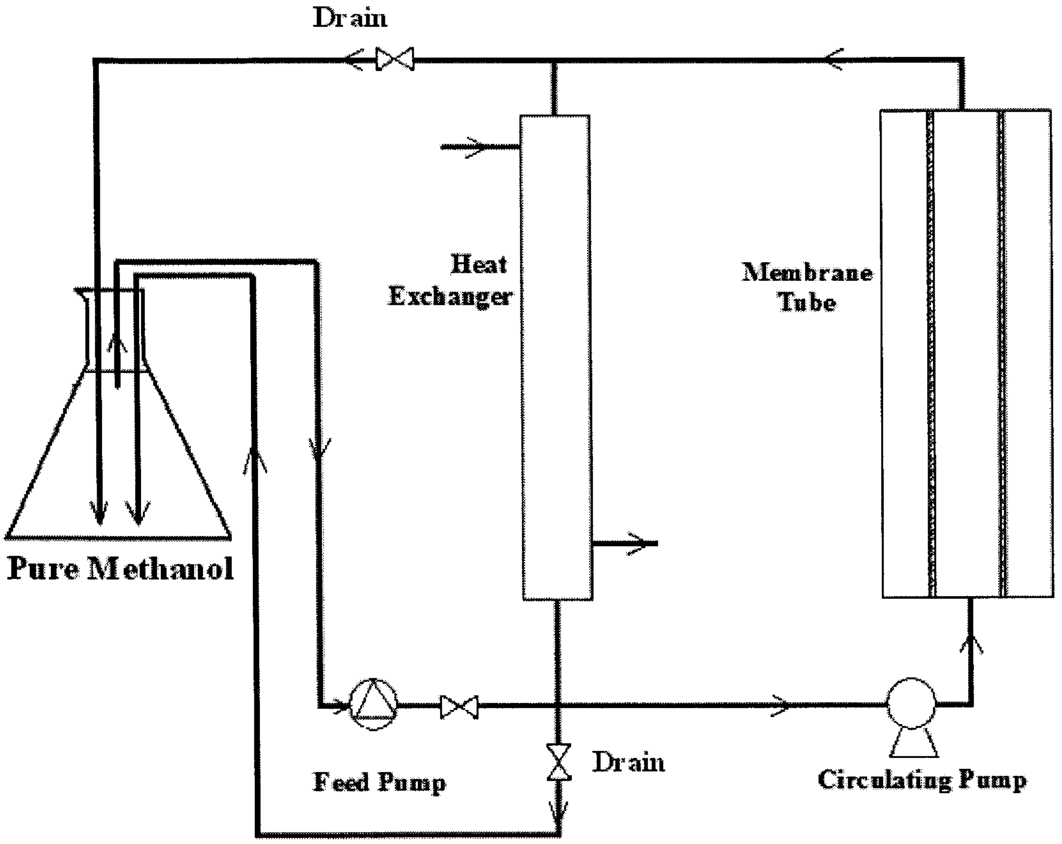

Figure 5.2: System diagram of the empty method of the membrane reactor

5.3 Conclusions

In this work, a study of the acid- and base-catalyzed transesterification of vegetable oil was carried out in a membrane reactor. The miscibilities of oil in methanol and FAME in methanol were investigated and the reaction kinetics were modeled.

In the miscibility study, it was found that canola oil could be considered as immiscible in methanol. On the other hand, FAME is miscible in pure methanol under a broad range of conditions. These findings led to the development of the membrane reactor to produce FAME from canola oil and methanol via both acid- or base-catalyzed transesterification. The membrane reactor enabled the separation of FAME from canola oil/methanol/FAME mixtures, yielding high purity biodiesel.

The effects of temperature, acid catalyst concentration, flowrates of feedstock and base-catalyst concentration were evaluated. Results showed that the conversion of canola oil increased significantly with increasing operating temperature and acid catalyst concentration. The effect of flowrate was investigated for both the acid-catalyzed and base-catalyzed reactions. Results showed that the conversion of canola increased with increasing flowrate. However, for the base-catalyzed reaction, the presences of saponified compounds were detected after the 6 hr reaction time. This was despite the use of virgin vegetable oil with a supposedly low free fatty acid content. The formation of soaps was not detected in the acid-catalyzed reaction. This would support the economic advantages of using acid-catalyzed transesterification rather than the base-catalyzed process.

5.4 Recommendations

Based on the results of this study, the following recommendations are proposed.

In order to increase the yield of biodiesel, further experimental conditions should be carried out in order to optimize reaction conditions and assess the limitations of this membrane reactor setup.

Attempts to assess the lifetime of the membrane should be undertaken. In addition, the testing of other membrane materials may be of use. In particular, membranes that are resistant to the base-catalyst would be of value.

Given the success of these preliminary findings, a continuous feed of the vegetable oil to the reactor and scale-up of the reactor should be investigated.

APPENDIX

A-1 The Volumetric Ratio of Canola Oil to Methanol

Experimental data and values of the volumetric ratio of canola oil to methanol at different experimental temperatures for studying the miscibility are shown below.

Table A.1: Experimental Data and the volumetric ratio of canola oil to methanol

V_R	25°C			30°C			40°C			50°C			60°C			70°C		
	H_{oil} (cm)	H_{Total} (cm)	Ratio %	H_{oil} (cm)	H_{Total} (cm)	Ratio %	H_{oil} (cm)	H_{Total} (cm)	Ratio %	H_{oil} (cm)	H_{Total} (cm)	Ratio %	H_{oil} (cm)	H_{Total} (cm)	Ratio %	H_{oil} (cm)	H_{Total} (cm)	Ratio %
10%	0.65	6.15	10.57	0.75	6.15	12.20	0.70	6.20	11.29	0.70	6.20	11.29	0.70	6.30	11.11	0.70	6.30	11.11
20%	1.20	6.10	19.67	1.25	6.10	20.49	1.35	6.10	22.13	1.35	6.10	22.13	1.40	6.20	22.58	1.40	6.20	22.58
30%	1.95	6.05	32.23	2.00	6.10	32.79	1.95	6.10	31.97	1.90	6.10	31.15	2.05	6.20	33.07	2.10	6.20	33.87
40%	2.55	6.05	42.15	2.65	6.20	42.74	2.70	6.20	43.55	2.70	6.10	44.26	2.75	6.20	44.36	2.80	6.20	45.16
50%	3.20	6.05	52.89	3.30	6.05	54.55	3.25	6.20	52.42	3.30	6.20	53.23	3.40	6.20	54.84	3.50	6.20	56.45
60%	3.80	6.20	61.29	3.90	6.20	62.90	3.85	6.20	62.10	3.95	6.20	63.71	4.05	6.20	65.32	4.10	6.30	65.08
70%	4.50	6.15	73.17	4.60	6.25	73.60	4.55	6.20	73.39	4.65	6.30	73.81	4.75	6.20	76.61	4.80	6.20	77.42
80%	5.05	6.15	82.11	5.10	6.20	82.26	5.10	6.20	82.26	5.20	6.20	83.87	5.30	6.20	85.48	5.35	6.20	86.29
90%	5.65	6.10	92.62	5.70	6.10	93.44	5.60	6.10	91.80	5.70	6.20	91.94	5.80	6.20	93.55	5.80	6.20	93.55

A-2 The Volumetric Ratio of FAME to Methanol

Experimental data and values of the volumetric ratio of FAME to methanol at different experimental temperatures for studying the miscibility are shown below.

Table A.2: Experimental Data and the volumetric ratio of FAME to methanol

	10°C			15°C			25°C			30°C		
V_R	H_{FAME} (cm)	H_{Total} (cm)	Ratio	H_{FAME} (cm)	H_{Total} (cm)	Ratio	H_{FAME} (cm)	H_{Total} (cm)	Ratio	H_{FAME} (cm)	H_{Total} (cm)	Ratio
10%	0	6	0	0	6	0	0	6.1	0	0	6.1	0
20%	0.25	6.1	4.10	0.25	6.1	4.10	0.2	6.2	3.23	0	6.2	0
30%	1.05	6.1	17.2	1	6.1	16.4	0.7	6.2	11.3	0.6	6.2	9.68
40%	2.3	6.1	37.7	2.25	6.1	36.9	2.1	6.2	33.9	2.3	6.2	37.1
50%	3.25	6.1	53.3	3.25	6.1	53.3	3.5	6.2	56.5	3.6	6.2	58.1
60%	4.4	6.1	72.1	4.4	6.15	71.6	5	6.2	80.7	5.1	6.2	82.3
70%	5.3	6.1	86.9	5.3	6.15	86.2	5.8	6.2	93.6	6.2	6.2	100
80%	6	6	100	6.05	6.05	100	6.1	6.1	100	6.1	6.1	100
90%	6.1	6.1	100	6.15	6.15	100	6.2	6.2	100	6.2	6.2	100

(Continued next page)

	40°C			50°C			60°C			70°C		
V_R	H_{FAME} (cm)	H_{Total} (cm)	Ratio	H_{FAME} (cm)	H_{Total} (cm)	Ratio	H_{FAME} (cm)	H_{Total} (cm)	Ratio	H_{FAME} (cm)	H_{Total} (cm)	Ratio
10%	0	6.15	0	0	6.2	0	0	6.2	0	0	6.3	0
20%	0	6.2	0	0	6.3	0	0	6.3	0	0	6.4	0
30%	0.7	6.2	11.3	0	6.3	0	0	6.3	0	0	6.3	0
40%	2.2	6.2	35.5	1.3	6.3	20.6	0.9	6.3	14.3	0	6.3	0
50%	3.5	6.2	56.5	6.3	6.3	100	6.3	6.3	100	6.3	6.3	100
60%	5	6.2	80.7	6.3	6.3	100	6.3	6.3	100	6.3	6.3	100
70%	6.2	6.2	100	6.3	6.3	100	6.3	6.3	100	6.3	6.3	100
80%	6.1	6.1	100	6.1	6.1	100	6.1	6.1	100	6.1	6.1	100
90%	6.2	6.2	100	6.25	6.25	100	6.25	6.25	100	6.25	6.25	100

A-3 The Miscibility Table of FAME and Methanol

Based on the Table A.2, a miscibility table of FAME and methanol is shown in the Table A.3. Here

1- Single phase
2- Two phases

Table A.3: Miscibility table of FAME and methanol

V_R T	0%	10%	20%	30%	40%	50%	60%	70%	80%	90%
10°C	1	1	2	2	2	2	2	2	1	1
15°C	1	1	2	2	2	2	2	2	1	1
25°C	1	1	2	2	2	2	2	2	1	1
30°C	1	1	1	2	2	2	2	1	1	1
40°C	1	1	1	2	2	2	2	1	1	1
50°C	1	1	1	1	2	1	1	1	1	1
60°C	1	1	1	1	2	1	1	1	1	1
70°C	1	1	1	1	1	1	1	1	1	1

A-4 HPLC Calibration

Five standards were calibrated; the calibration curves are shown in Fig A.1, and the calibration of injection masses are shown in Table A.4.

Table A.4: Calibrations of standard solutions, injection mass (mg)=$a\times$Peak Area +b

Component	a	b	R^2
Triolein	4.54×10^{-6}	0.00391	0.9926
Diolein	4.56×10^{-6}	0.0095	0.9964
Monoolein	4.62×10^{-6}	0.0099	0.9974
Methyl oleate	6.31×10^{-6}	0.0153	0.9983
Glycerol	5.57×10^{-6}	0.0367	0.9917

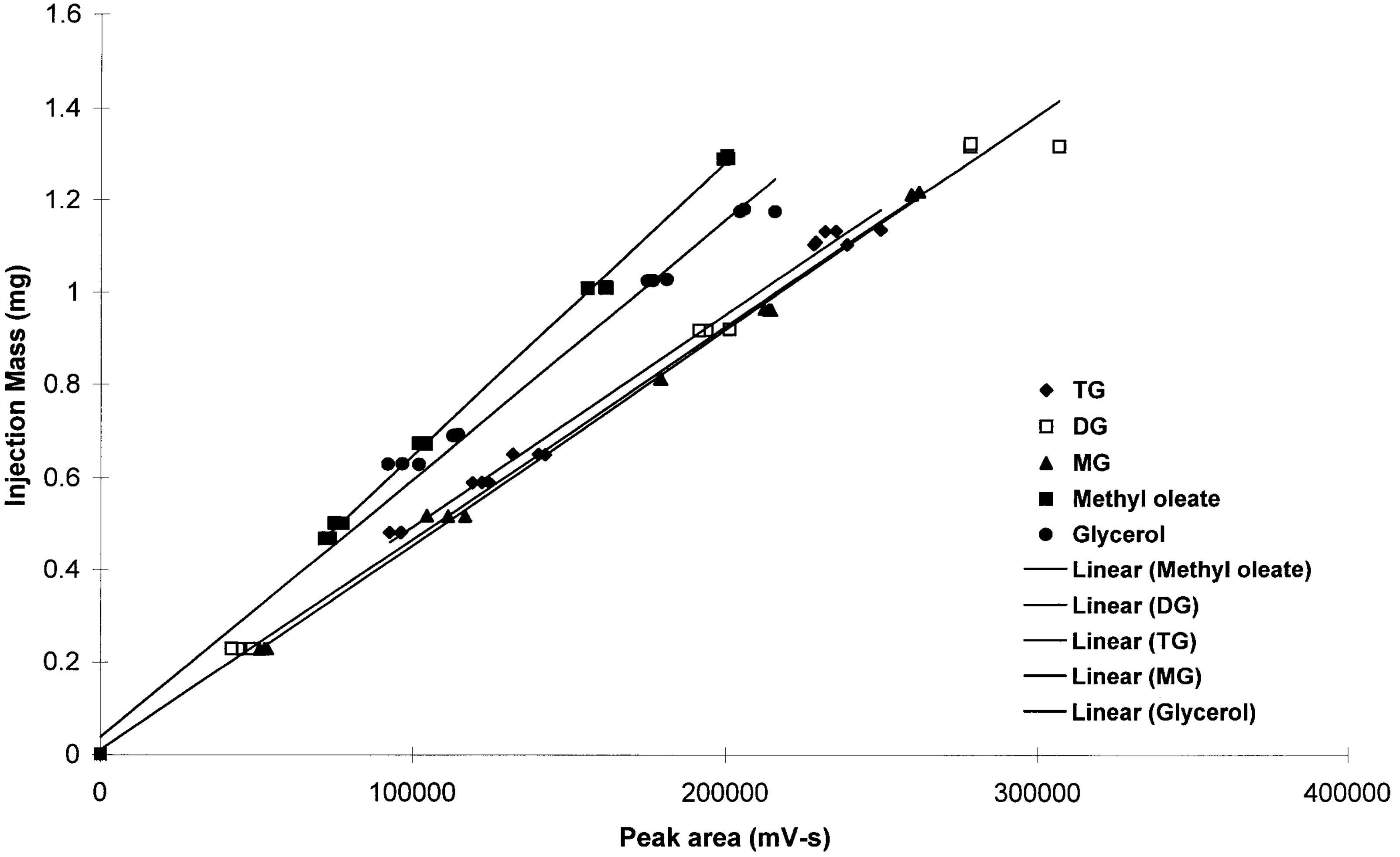

Figure A.1 Calibration curves of triolein, diolein, monoolein, methyl oleate (FAME) and glycerol