Reduction and Speciation of Monoglycerides to produce high quality biodiesel

Srikanth Rapaka

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Faculty of Engineering

University of Ottawa

Abstract

Biodiesel is rapidly growing as a fuel of interest due to the various advantages it has over conventional diesel fuel. While the pros – non-toxic, biodegradable, low green house gas emissions seem advantageous, the major issue that plagues the use of biodiesel is its cold weather operability. Biodiesel can present challenges in cold-weather operation, because certain of its constituent compounds can form precipitates in the fuel. These precipitates can cause undesired effects like plugging of fuel filters and deposits. This issue has been attributed to the presence of impurities (mostly saturated monoglycerides, di-glycerides, soap etc) in biodiesel and has been discussed in the literature. There is a move by users and standards associations to implement more stringent norms and quality control to avoid problems in the widespread use of biodiesel. This study involves ways to reduce MG's in biodiesel by mitigating to a greater extent the possibility of side reactions (formation of soap). The effect of selective transesterification of oil as a function of alcohol, temperature and catalyst concentration was also studied. Although saturated MG's with high melting points are a greater source of deposits, it can be hypothesized that the polymorphic nature of unsaturated Monoglycerides could also be contributing to cold flow issues. It is hence vital to make sure the biodiesel is free from all forms of monoglycerides. It was also seen that there is very little specificity of selection of fatty acid types in the transesterification reaction and that the amount and type of MGs present in the biodiesel is reflected by the relative amount of fatty acids types present in the oil. In biodiesel derived from Canola oil, a preponderance of monoolein was found for all runs. The initial runs carried out as a two stage process using the membrane followed by batch reactor gave very low MG concentrations, well below ASTM standards.

Résumé

Le biodiesel se développe rapidement comme un carburant renouvelable en raison des divers avantages qu'il a au-dessus du carburant diesel conventionnel. Les avantages de ce carburant renouvelable- non-toxique, réduction d'émissions de particules et de gaz d'effet de serre, semblent avantageux, ses performances réduites par temps froid limitent son utilisation. Le biodiesel peut présenter des défis d'opération par temps-froid, parce qu'un certain nombre de ses composés constitutifs peuvent former des précipités dans le carburant. Ces précipités peuvent causer des effets peu désirés comme le colmatage de filtres à essence. Cette issue a été attribuée à la présence des impuretés (la plupart du temps monoglycérides saturés, diglycérides et savons) présentes dans le biodiesel. Il y a un mouvement par des utilisateurs et des associations de normes pour mettre en application des normes et un contrôle de qualité plus rigoureux pour éviter ces problèmes d'utilisation par temps froid. Cette étude traite de façons d'éliminer ces impuretés dans le biodiesel en atténuant dans une large mesure la possibilité des réactions secondaires (formation de savon). L'effet de la transestérification sélective d'huile en fonction de la concentration d'alcool, la température et de la concentration en catalyseur a été également étudié. Bien que les monoglycérides saturés avec les points de fusion élevés soient une plus grande source des dépôts, on peut présumer que la nature polymorphique des certains monoglycérides insaturés pourrait également contribuer aux propriétés réduites par temps froid. Il est par conséquent essentiel de s'assurer que le biodiesel est exempt de toutes les formes de monoglycérides. On a également observé très peu de spécificité evers les acides gras des glycérides dans la réaction de transestérification et que la quantité et le type de monoglycérides dans le biodiesel est reflétée par la quantité relative de types d'acides gras présents dans l'huile. Dans le biodiesel dérivé de l'huile de Canola, une prépondérance de monooléine a été trouvée pour toutes les essais. Les essais initiaux

effectués en deux stages utilisant un réacteur à membrane continu suivi d’un réacteur discontinu ont donné des concentrations très basses en monglycérides, bien inférieures aux normes d'ASTM.

Statement of Contributions of Collaborators

I hereby declare that I am the sole author of this thesis. I performed all the experiments and the data analysis. I have written all the chapters contained in this thesis.

Dr. Andre Y. Tremblay supervised this thesis project and provided continual guidance and support. He also made editorial comments and corrections to the written work presented. His day-to-day supervisions, discussions and never ending support have resulted in tremendous improvements of the thesis.

To my parents

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Table of Contents

List of Tables

List of Figures

Nomenclature

This nomenclature lists some of the most frequently used abbreviations in this thesis. It is not meant to be exhaustive. Other abbreviations used in tables and figures are explained in the text as they appear.

List of abbreviations

ASTM – American Society for Testing and Materials

CP – Cloud Point

CFPP – Cold filter plugging point

PP – Pour Point

DG – Diglyceride

EN – European standard

FAAE – Fatty acid alkyl ester

FAME – Fatty acid methyl ester

FFA – Free fatty acid

FID – Flame ionization detector

GC – Gas chromatography

kD – kilo Dalton

KF – Karl Fisher

MG – Monoglyceride

MSTFA – N-methyl-N-(trimethylsilyl) trifluoroacetamide

ppm – Parts per million

TG – Triglyceride

TMP – Transmembrane Pressure

Chapter 1

Introduction

Chapter 1

1.1 Introduction

The world energy demand is steadily increasing with each passing year. The majority of this increase is met by conventional sources which include crude oil, coal, and natural gas. This dependence on non-renewable sources is even more obvious when considering the energy used for transportation where 94% of the demand is supplied by crude oil. (IEA, 2010)

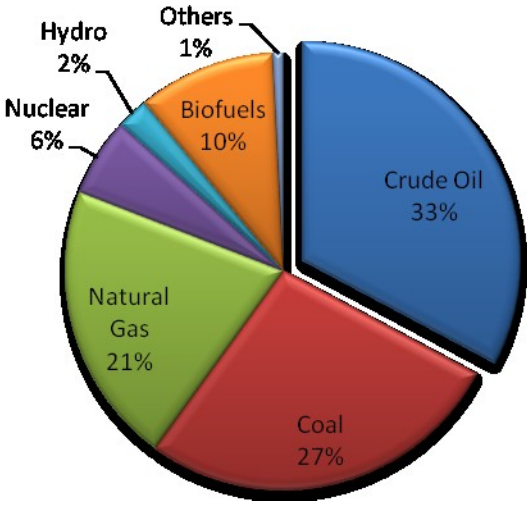


Figure 1.1 Work energy demand by fuel (IEA, 2010 b)

Carbon dioxide is known to be one of the main contributors to global warming. Currently, the transportation sector accounts for about 25% of global CO_2 emissions and roughly 50% of global oil consumption (IEA, 2010). Climate change, a repercussion of global warming, and along with the dwindling petroleum reserves has raised global concerns regarding energy sustainability and security. To combat this issue, the scientific and the industrial world are shifting to using more renewable and less toxic fuels. As a result, biofuels, which are receiving more interest for use as transportation fuels.

Biodiesel is a renewable and biodegradable fuel used in diesel engines produced from vegetable oils and animal fats via alcohol transesterification using, for example, methanol or ethanol. It is comprised of fatty acid alkyl esters (FAAE). The similarities biodiesel shares with diesel fuel make it an interesting replacement to conventional fuel sources (Demirbas, 2003; Jehad 2010).

However, the main drawback of biodiesel is its cold weather operability. The presence of saturated monoglycerides is widely reported as the reason for high cloud point of fatty acid esters and it is widely accepted as a global issue plaguing the biodiesel industry. Monoglycerides are impurities present in biodiesel that result from incomplete reaction. They cannot be easily washed as they are amphiphilic in nature. There has been not much work reported on reducing the monoglycerides concentrations below 0.1 wt%. Reaction kinetics still remains a topic of low understanding. Therefore, work on the reduction and speciation of monoglycerides to a great extent would invite great deal of interest as it would improve the cold flow properties of biodiesel.

1.2 Objective

In this thesis project, the main objective was to develop a membrane process, where components of fatty acid methyl esters are separated based on the reactivity. This would provide a continuous process to improve the operability of biodiesel by removing saturated monoglycerides during the reaction. It was postulated that saturated fatty acids chains are relatively slow in reacting in comparison with unsaturated fatty acid chains. The idea was to perform continuous elusion reaction studies, to see if speciation of saturated monoglycerides was occurring as a function of time. Therefore, the specific objectives of the project where,

(a) To select feedstocks low in saturated fatty acids and investigate the effect of continuous elusion reactions in a membrane reactor.

(b) To investigate the effect of temperature on speciation.

(c) To investigate the effect of methanol to oil ratio on speciation.

(d) To investigate the effect of catalyst concentration on speciation.

A secondary objective was to study ways to greatly reduce the monoglyceride concentration in the biodiesel thus improving the cold flow characteristics. With this objective in mind, and based on the results from the above mentioned approach, the following steps were performed.

(a) A multi stage transesterification process was developed with membrane reactor in the first stage followed by batch reactor in the second.

(b) The effect of initial catalyst concentration in the membrane reactor was analysed over two different configurations.

(c) The effect of temperature, catalyst concentration and methanol to oil ratio on the biodiesel yield and purity in the second reactor were analysed.

(d) The system was studied to achieve highest purity and lowest yield loss at the lowest catalyst concentration, methanol to oil ratio and temperature.

1.3 Thesis Structure

This thesis is divided into of six chapters.

In chapter 2, an overview of biodiesel history, chemistry, production and purification are given. A comparative study on the properties of diesel and biodiesel is also presented.

Chapter 3 covers the problem definition related to the reaction of specific fatty acid chains is presented. A review on available transesterification techniques and mechanisms and a background on the work carried out is presented.

Chapter 4 is a manuscript of experimental work carried out. This chapter also discusses the materials and analytical techniques used for speciation studies. The effects of variables such as alcohol ratio, catalyst concentration and temperature were also studied. An explanation to the results of the elution studies is presented.

Chapter 5 covers the second stage of work carried as part of my thesis. The performance of multi-stage membrane and batch reactors are discussed in detail. Most papers in the literature are concerned with single stage processes. These are of limited value industrially as few if any industrial processes are run in a single stage. The results of this work will provide new information previously unavailable in the literature pertaining to two stage reactions.

The conclusions and recommendations and scope for future work are covered in chapter 6.

Chapter 2

Overview of Biodiesel History

Chapter 2

Overview of Biodiesel History

2.1 Introduction

Definition

Biodiesel is a clean burning, non-toxic, biodegradable renewable fuel that is usually produced from vegetable oils and animal fat by a process of transesterification. It comprises of fatty acid alkyl esters, resulting from the reaction of a triglyceride molecule with an alcohol. The nomenclature is based upon the type of alcohol used, for e.g. if methanol is used, biodiesel is called Fatty Acid Methyl Ester and so on. Biodiesel can be used in its natural form (B100) or can be blended in different proportions with conventional diesel fuel. The similarities biodiesel shares with conventional diesel fuel have drawn interest worldwide as a promising alternative to the dwindling fossil based fuels (Demirbas, 2003). Going forward, we shall briefly look into the history of biofuels, understand how the diesel engine works and the similarities between conventional diesel fuel and the diesel fuel derived from vegetable oils and animal fat.

2.2 History of Biofuels

The advent of use of biofuels as a source of alternate fuel is not contemporary in its nature. Over a century ago, Rudolf Diesel tested vegetable oil as a fuel for his internal combustion engine. In the engineering society meeting of St.Louis in 1912, he quotes:

“The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in course of time as important as petroleum products of the present time”

The diesel fuel produced from vegetable oils during the war eclipsed times of mid 1930's and early 1940's was mostly used in emergency situations. Research on vegetable oils was not developed extensively because of the high prices of vegetable oils and the low and stable prices of crude oil at that time. Recent instabilities and sharp increases in the oil prices and the speculations on depleting reserves coupled with serious environmental issues associated with global warming has forced researchers to shift focus on fuels derived from vegetable oils and animal fats as an alternative to conventional diesel fuel to run diesel engines. The use of fuel derived from vegetable oils and animal fats helps reduce the carbon-dioxide levels in the atmosphere as shown in figure 2.1. (Pryde, 1983; Shay et al. 1993; Ma et al. 1999; Fukuda et al. 2001; Myint 2007; Jehad et al 2010).

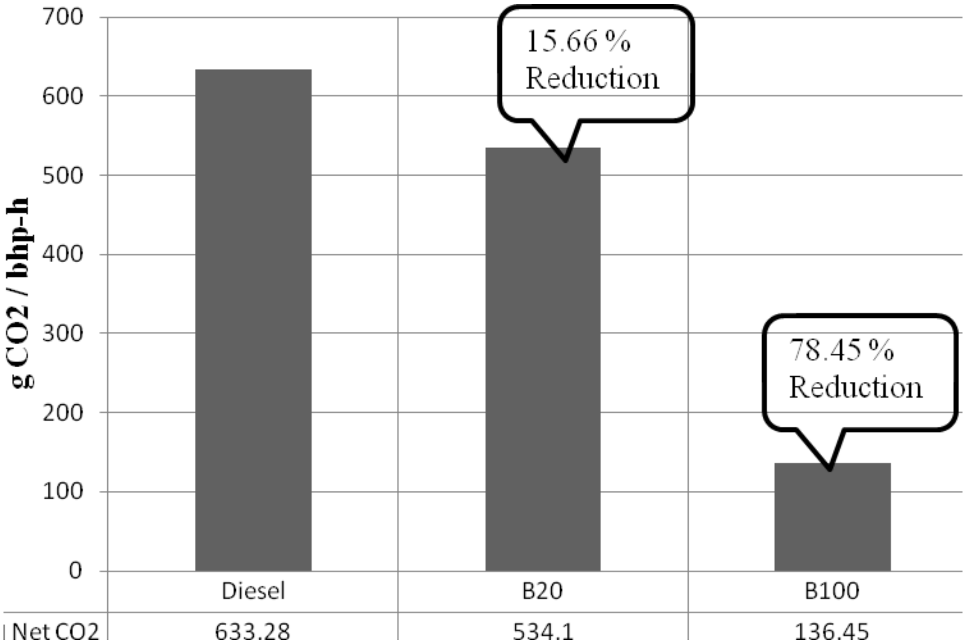


Figure 2.1 Life Cycle Emissions of Petro Diesel and Biodiesel (NR Raje, 2006)

2.3 Diesel Engine

Diesel engine has been the primary choice of engine for heavy duty applications ranging from the agricultural industry to highway transport. The diesel's durability, high torque capacity and fuel efficiency could be attributed to its wide spread acceptance and use in most demanding applications. Diesel engines in the United States consume more than 30 billion gallons of fuel every year and most of this fuel comes from conventional fossil based sources. However, with dwindling petroleum reserves and with newer oil wells hard to reach, biodiesel is fast growing as the fuel of replacement to fossil based diesel fuel. It is important to understand the operating principles of a diesel engine to best understand the fuel needs to consider biodiesel as a promising substitute. This chapter also looks at the advantages and disadvantages biodiesel provides over fossil fuels. (Broge, J.L et al. 2002; Van Gerpen et al. 2005)

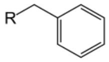
2.4 Diesel Combustion

A diesel engine works significantly different from other internal combustion engines as it does not require a spark plug for fuel ignition. The fuel is ignited by compression and that is the reason they are also known as compression – ignited engines. In spark-ignited engines, mostly used where the fuel is gasoline (petrol), fuel and air are compressed to stoichometric proportions and then ignited by a spark. But, in the case of diesel engines, the air is compressed to high temperature and pressure, and then fuel, finely atomised is sprayed in the combustion chamber at high velocity causing auto ignition. The power of the engine is basically controlled by varying the amount of fuel injected into the cylinder, thus ruling out the necessity of a throttle (Van Gerpen et al. 2005).

2.5 Diesel Fuel

ATSDR (1995) reports that diesel fuel derived from petroleum is mainly composed of 64 % aliphatic hydrocarbons, 35% aromatic hydrocarbons and approximately 1-2% olefinic hydrocarbons. However, the composition is variable resulting from different refining and blending processes. The hydrocarbons contained in crude oil can be divided into 5 groups, of which 3 groups are predominant and 2 are minor. Table 2.1 shows the list of groups and their properties (OTM, 1999; Myint. 2007)

Table 2.1 List of hydrocarbons in crude oil (ATSDR, 1995; OTM, 1999; Myint 2007)

Hydrocarbons	**General Formula**	**Chain Type**	**Physical State**	**Examples**
Paraffins	C_nH_{2n+2}	Linear or Branched	Gas or Liquid	Methane, Propane, Hexane
Aromatic		One or more benzene rings with long chain hydrocarbons	Liquid	Naphthalene
Naphtenes	C_nH_{2n-2}	Polycyclic aromatic hydrocarbon	Liquid	Cyclo hexane
Alkenes	C_nH_{2n}	Unsaturated hydrocarbon	Gas or Liquid	Butene Ethene
Dienes and Alkynes	C_nH_n	Triple Bonds	Gas or Liquid	Acetylene

2.6 Fuel Characteristics

2.6.1 Soot Formation

In order to obtain optimum fuel efficiency and low emissions, it is necessary to control the timing of the combustion process. The heterogeneous mixture of fuel and air in the cylinder during combustion is the main contributing factor to soot particle formation. They are formed in the high temperature regions of the combustion chamber and the poly cyclic aromatic hydrocarbons in soot are known to be human carcinogens. Biodiesel on the other hand, produces less soot as opposed to fossil based fuels and this can be associated to the bound oxygen in the fuel. (Van Gerpen et al. 2005; IARC Summary and evaluation, 1985; McCormick et al. 1987)

2.6.2 Cetane Number

The most important characteristic of a fuel, to be used in a diesel engine, is its ability to auto-ignite readily with short delays. In other words, the fuel should have a high cetane number. Fuels with high cetane numbers have shorter ignition delays and vice versa. Most biodiesel fuels have a higher Cetane number than conventional diesel fuel. Biodiesel derived from vegetable oils and animal fat high on saturated content have a higher cetane number than the ones derived from oils rich in unsaturated content. For e.g. Soy bean oil, high on unsaturated content has a cetane number of 48-52, whereas biodiesel from yellow grease has a cetane number between 60 and 65. (Knothe et al. 1997; Van Gerpan et al. 1996)

2.6.3 Emissions

All carbon rich fuels burn to carbon-dioxide under ideal circumstances. However, if sulphur is present, they can oxidise to form sulphur dioxide or sulphur trioxide which on interaction with water vapour in the atmosphere will form sulphuric acid causing acid rain. According to the US Environmental protection agency, the sulphur limit in diesel fuel should not exceed 500 ppm. Biodiesel from soy bean oil, on the other hand, is very low in sulphur and contributes relatively less in sulphur dioxide emissions. Some feedstock's like some animal fat, high in sulphur content need to be pretreated to bring the levels down to Environmental protection agency norms. (Van Gerpan et al. 2005)

2.6.4 Viscosity

Viscosity is a measure of resistance to the flow of a liquid. Higher viscosity is not desired as it affects the atomisation of fuel upon injection in the combustion chamber. It is also an important factor which determines the logistics and also storage conditions of the fuel. Some of the most important issues related to high viscosity in an internal combustion engine can be summarised by the following points.

(a) Carbon deposition
(b) Coking and trumpet formation
(c) Oil rink slicking and
(d) Lubricating issues

Vegetable oils and animal fats are generally characterised by high viscosity. Biodiesel, transesterified oil, however has a lower viscosity than that of parent oil. The table below compares viscosities of different vegetable oils, diesel fuel and biodiesel (Tyson et al. 2006).

There has been a considerable work carried out in predicting the viscosity of the fatty materials and is reported by Van Gerpan et al. It is found that viscosity increases with increase in degree of saturation. It also shows a positive trend with increase in chain length. Factors like double bond configuration and type of alcohol used also impact viscosity. For e.g. Ethyl esters have higher viscosity than the methyl esters and similarly cis configuration gives a lower viscosity than the trans configuration. (De Filippis et al. 1995; Van Gerpan et al. 1999; Allen et al. 1999)

Table 2.2 Comparison of viscosities of petrodiesel, biodiesel and various feedstocks (Knothe et al. 1997)

Type	Heat of Combustion (MJ/Kg)	Kinematic Viscosity (mm^2/sec)	Flash Point (℃)	Iodine Value
Diesel	427	1-4	80	-
Biodiesel	372	4-6	100	<115
Palm Oil (Butter)	-	29.4	267	34-61
Palm Oil (Fat)	355	21.5	-	14-22
Soy bean oil	371	63.5	350	114-138
Nut oil	372	71	340	103
Coconut oil	353	21.7	-	-
Jatropha oil	396	757	340	13
Rapeseed Oil	376	74	317	94-110
Sunflower Oil	371	66	316	118-144
Olive Oil	378	83.8	-	76-90
Cottonseed Oil	368	89.40	320	90-117

2.6.5 Low Temperature Operation

The presence of long chain hydrocarbons in large amount is undesirable as they begin to crystallise at low temperatures. If the temperatures go very low, these crystals start to agglomerate and plug the filters thus preventing engine operation. This phenomenon is predominantly found in biodiesel. The percent of saturated content in the feedstock has a great impact on the low temperature operatability. For e.g. palm oil, high on saturated content, starts to crystallise as high as 13-15℃, whereas soy bean oil, low on saturated content begins to crystallise relatively at a much higher temperature. The most common way to measure this phenomenon is to determine the cloud point and can be defined as the temperature at which the dissolved solids are no longer soluble and form a separate phase thus giving the fuel cloudy appearance. The more conventional way is to determine the pour point which can be defined as the lowest temperature at which the fuel loses its flow characteristics. ASTM D2500 and D97 are respectively used to determine the cloud and the pour point. Biodiesel is widely blended with conventional diesel fuel to address this issue. B5 is a widely used blend percent and has been reported to be working in cold climates without problems. (Van Gerpan et al. 2004)

2.7 Summary

The dwindling fossil fuel reserves and increase prices of crude oil coupled with the need for lower emissions has forced researchers to shift focus on vegetable oils as an alternative source of fuel. Although, the advantages are numerous in the areas of low emission, relatively low cost, low soot formation etc…, the disadvantages associated still hinder the wide spread use of biodiesel. Low temperature operability, high viscosity and purity have been two major issues that need to be address to facilitate wide spread use of fuels from vegetable oils and animal fat.

Chapter 3

Transesterification Mechanisms and Biodiesel Production

Chapter 3 - Transesterification Mechanisms and Biodiesel Production

3.1 Transesterification

In order to use vegetable oils and animal fat in diesel engines, without causing issues relating to oil ring sticking, coke deposition and lubrication it is necessary to reduce the viscosity. The four common methods to reduce the viscosity are:

(a) Blending with petroleum diesel
(b) Pyrolysis
(c) Micro emulsification and
(d) Transesterification

Transesterification is by far the most commonly used method and the only method that leads to the formation of products, we know as biodiesel (Van Gerpan et al. 2005). Transesterification is a process where a triglyceride molecule reacts with an alcohol in the presence of a catalyst to produce fatty acid alkyl esters and glycerol. The stoichometric reaction is shown below in figure 3.1

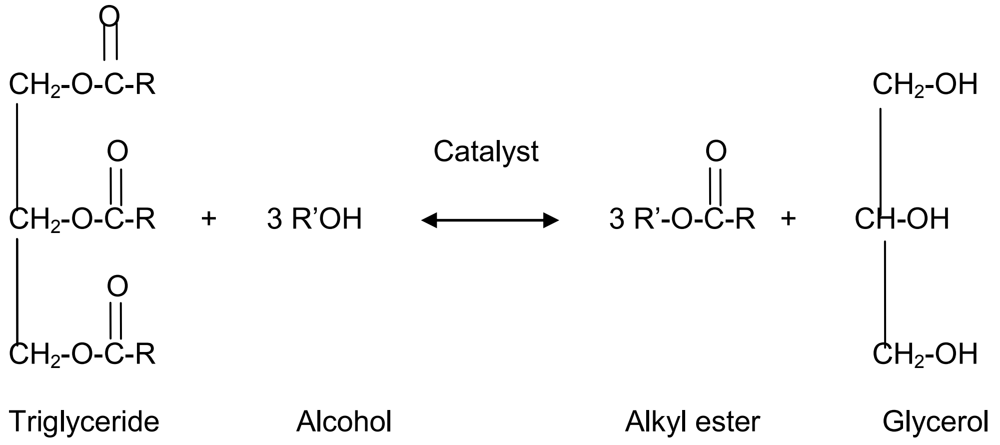


Figure 3.1 Transesterification reaction (Van Gerpen et al. 2005)

3.2 Feed Stocks

There are different types of vegetable oils and animals fats that can be used as feedstocks for biodiesel production. The property of the biodiesel is a function of the type of feedstock used. For example the biodiesel from soybean oil has a cloud point of 1 ℃, whereas biodiesel derived from palm oil has a cloud point of 13℃. The table 3.1 below gives a list of the types of fatty acids present in most of the vegetable oils and fats.

Table 3.1 List of common fatty acids present in vegetable oils and animal fats

(Tyson et al. 2004)

Name	Component	Acid	Ester
Mystiric acid	C 14:0	$C_{14}H_{28}O_2$	$C_{15}H_{30}O_2$
Palmatic acid	C 16:0	$C_{16}H_{32}O_2$	$C_{17}H_{34}O_2$
Palmitoleic	C 16:1	$C_{16}H_{30}O_2$	$C_{17}H_{32}O_2$
Stearic acid	C 18:0	$C_{18}H_{36}O_2$	$C_{19}H_{38}O_2$
Oleic acid	C 18:1	$C_{18}H_{34}O_2$	$C_{19}H_{36}O_2$
Linoleic acid	C 18:2	$C_{18}H_{32}O_2$	$C_{19}H_{34}O_2$
Linolenic acid	C 18:3	$C_{14}H_{30}O_2$	$C_{19}H_{32}O_2$

In the component section of the table, the number preceding the colon represents the total number of carbons in the chain and the number succeeding the column represents the number of double bonds. The higher the unsaturation in a molecule, the lower the melting point, however they are also prone to oxidation. Table 3.2 below shows a list of vegetable oils and animal fats and their fatty acid compositions.

Table 3.2 Fatty acid profile of vegetable oils and animal fats (Knothe et al. 1997)

Oil or Fat	**Fatty Acid [C-O-O-R] Composition (Wt %)**							
	C14:0	C16:0	C18:0	C18:1	C18:2	C18:3	C20:1	C22:1
Canola		4-5	3.8-7	55-63	20-31	9-10	-	-
Coconut	13-18.5	7.5-10.5	1-3	5-8.2	1.0-2.6	-		
Corn	1-2	7-13	2.5-3	30.5-43	39-52	-		
Palm	0.6-2.4	32-46.3	4-6.3	37-53	6-12	-		
Soybean		2.3-11	2.4-6	22-30.8	49-53	2-10.5		
Lard	1-2	28-30	12-18	40-50	7-13	0-1		
Butter	7-10	24-26	10-13	28-31	1-2.5	0.2-0.5		
Sunflower		3.5-6.5	1.3-5.6	14-43	44-68.7			
Rapeseed	-	4.0	1.5	17.0	13.0	9.0	14.5	41.0

Currently over 95% of commercial biodiesel is produced from soybean, rapeseed, sunflower and palm oil (Balat, 2011). However, with high prices of virgin and refined oils, commercial production is not a profitable venture without government subsidies (Demirbas and Balat, 2006). This problem can be addressed by employing waste materials and non-edible triglycerides for biodiesel production. One way of making biodiesel production a profitable venture is by using waster frying oils from restaurants and households. Waste frying oil is relatively cheaper than the virgin and refined oils and is also a readily available source (Kulkarni and Dalai, 2006; Hastie, 2011). However, the major disadvantage of using frying oils is that they contain large amounts of free fatty acids that favour undesirable side reactions and form soap. Higher FFA also means the need to add higher amounts of catalyst owing to FFA neutralization costs. (Van Gerpan 2005; Encinar et al. 2005)

3.3 Alcohols and Catalysts

3.3.1 Alcohols

The most common alcohol used in transesterification process is methanol simply because it is the cheapest of all alcohols and does not complicate the phase separation dynamics. Also, higher alcohols form azeotropes with water. The presence of water in the reaction mixture reduces biodiesel yield by forming soap as a side reaction. It also boosts up catalyst consumption costs. However, ethyl esters are produced in countries where the price of ethanol is low (Van Gerpan, 2005). Table 3.3 below gives a list of alcohols and their properties.

Table 3.3 Properties of C_1- C_4 alcohols

Alcohol	**Molecular Weight**	**Boiling point**	**Melting point**	**Density**
Methanol	32.04	65℃	-93.9	0.791
Ethanol	46.06	78.5℃	-117.3	0.783
1-Propanol	60.09	92.4℃	-126.5	0.803
2-Propanol	60.09	87.4℃	-89.5	0.7855
1-Butanol	74.12	117.2℃	-	0.809
2-Butanol	74.12	99.5℃	-	0.0808

3.3.2 Catalyst

A catalyst is a substance that increases the rate of a chemical reaction without undergoing a permanent chemical change. It reduces the activation energy necessary to initiate the reaction. (Vincente et al. 2004)

In general, catalysts can be classified as

(a) Homogenous Catalysts and,
(b) Heterogeneous Catalysts

Heterogeneous catalysts are still the least preferred option owing to their high costs and low yield of biodiesel. Homogenous catalysts are preferred for their ability to catalyze the reaction at relatively low temperatures and obtain high yield in a short time (Van Gerpan et al. 2004). Table 3.4 shows a list of homogenous and heterogeneous catalysts and their advantages and disadvantages.

The most commonly used alkali catalysts are –

(a) Sodium hydroxide (NaOH)
(b) Sodium Methoxide (CH_3ONa)
(c) Potassium Hydroxide (KOH)
(d) Potassium Methoxide (CH_3OK)

Jackson (2006) reported that methoxide ion has been the preferred catalyst for transesterification of triglycerides to produce biodiesel. The major advantage of using sodium methoxide is that it is virtually water free catalyst solution. Sodium hydroxide on the other hand, generates water when mixed with methanol, as shown in Figure 3.2 below, resulting in undesired reactions like formation of soap (Myint, 2007).

$$\underset{\text{Sodium Hydroxide}}{NaOH} + \underset{\text{Methanol}}{CH_3OH} \longleftrightarrow \underset{\text{Sodium Methoxide}}{CH_3ONa} + \underset{\text{Water}}{H_2O}$$

Figure 3.2 Reaction showing the interaction of sodium hydroxide and Methanol

Table 3.4 Comparative study of homogenous and heterogeneous catalysts (Hastie, 2011)

Catalyst	**Examples**	**Advantages**	**Disadvantages**
Heterogeneous alkali	Cao, Zeolites	Mild reaction conditions	Sensitive to FFA and water content, catalyst leaching, high alcohol and high temperature and pressure
Heterogeneous acid	Ion exchange resins and zirconium oxide	Insensitive to FFA, easy catalyst separation, reusable	Slow reaction rate, high alcohol requirement and high reaction temperature
Enzymes	Lipases	No by-product generation, mild reaction conditions, insensitive to FFA	High cost, slow reaction rates, low yield and enzyme deactivation
Homogenous alkali	NaOH, KOH, NaOCH3	Mild reaction conditions, high conversion and faster reaction rate	Sensitive to FFA and water content (soap formation), difficult catalyst separation
Homogenous acid	H_2SO_4, HCl	Insensitive to FFA	Slow reaction rate, high alcohol requirement and reaction temperature, sensitive to water content, difficult catalyst separation
Non- Catalytic	Super critical methanol	Fast reaction rate, no catalyst separation required	High temperature and pressure required

3.4 Reaction Mechanisms

The transesterification reaction involves a number of consecutive reversible reactions (Freedman et al. 1986; Schwab et al. 1987) as shown in the figure 3.3. A mole of ester is formed at each step in the three step process (Eckey, 1956).

3.4.1 Alkali catalysed Transesterification

Eckey (1956) reported that the alkali catalysed transesterification reaction as a three step mechanism, where in the first step; the anion of the alcohol attacks the triglyceride molecule to form a tetrahedral intermediate. This step is followed by the reaction of tetrahedral intermediate with alcohol to regenerate the anion. In the final step, the intermediate rearranges to form a mole of fatty acid ester and a di-glyceride. Figure 3.4 below shows the schematic representation of alkali transesterified mechanism.

3.4.2 Acid Catalysed Transesterification

The acid catalysed transesterification reaction mechanism was reported by Meher et al. (2006). The most common catalysts used are sulphuric or sulphuric acids. The reaction is a three step mechanism, where the first step involves protonation of carbonyl groups. This step is followed by nucleophilic attack of alcohol resulting in a tetrahedron intermediate. The intermediate rearranges to release an ester and proton catalyst. The reaction with acids is much slower than that of bases which explains why bases are preferred as industrial catalysts in transesterification.

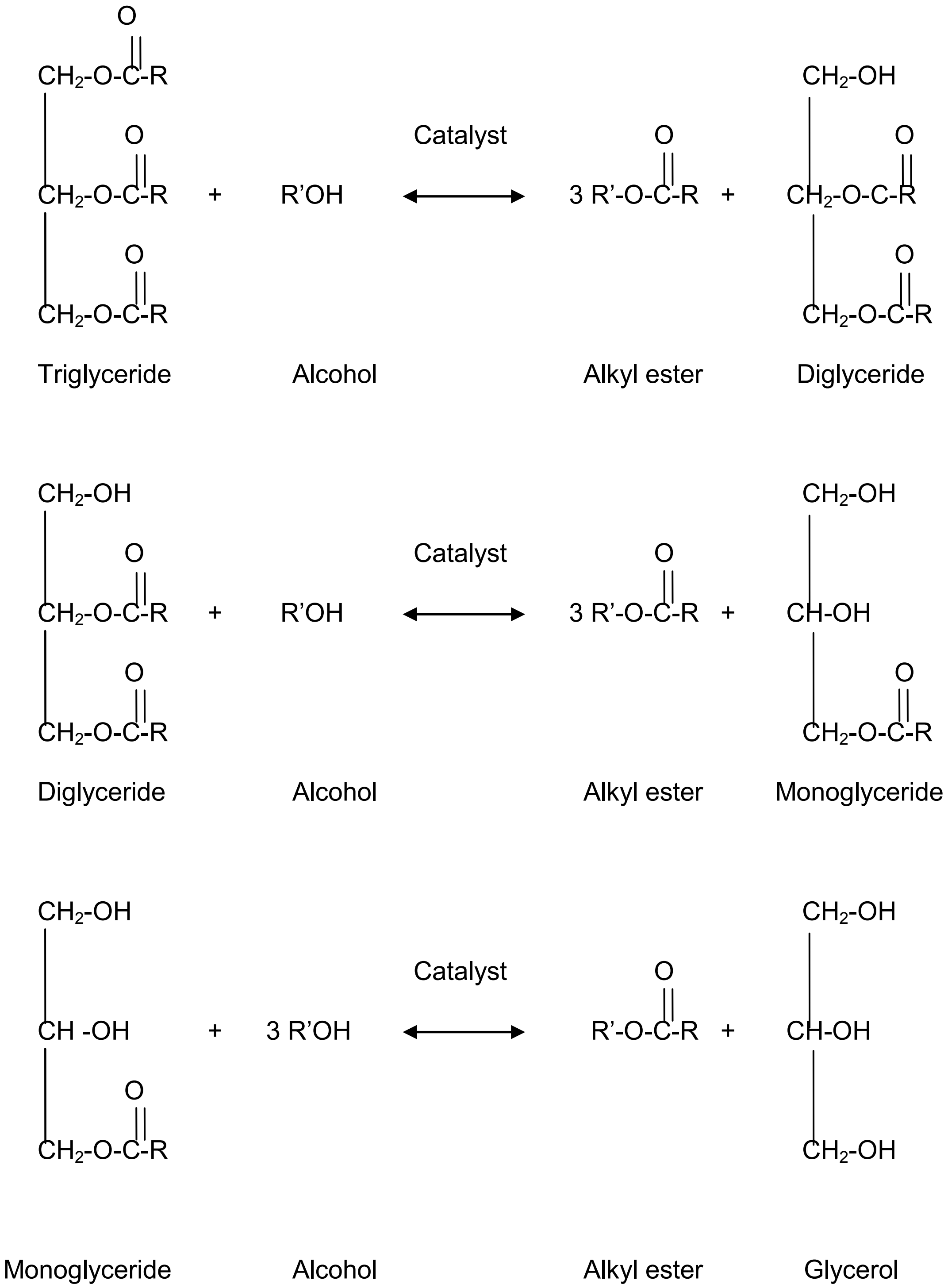
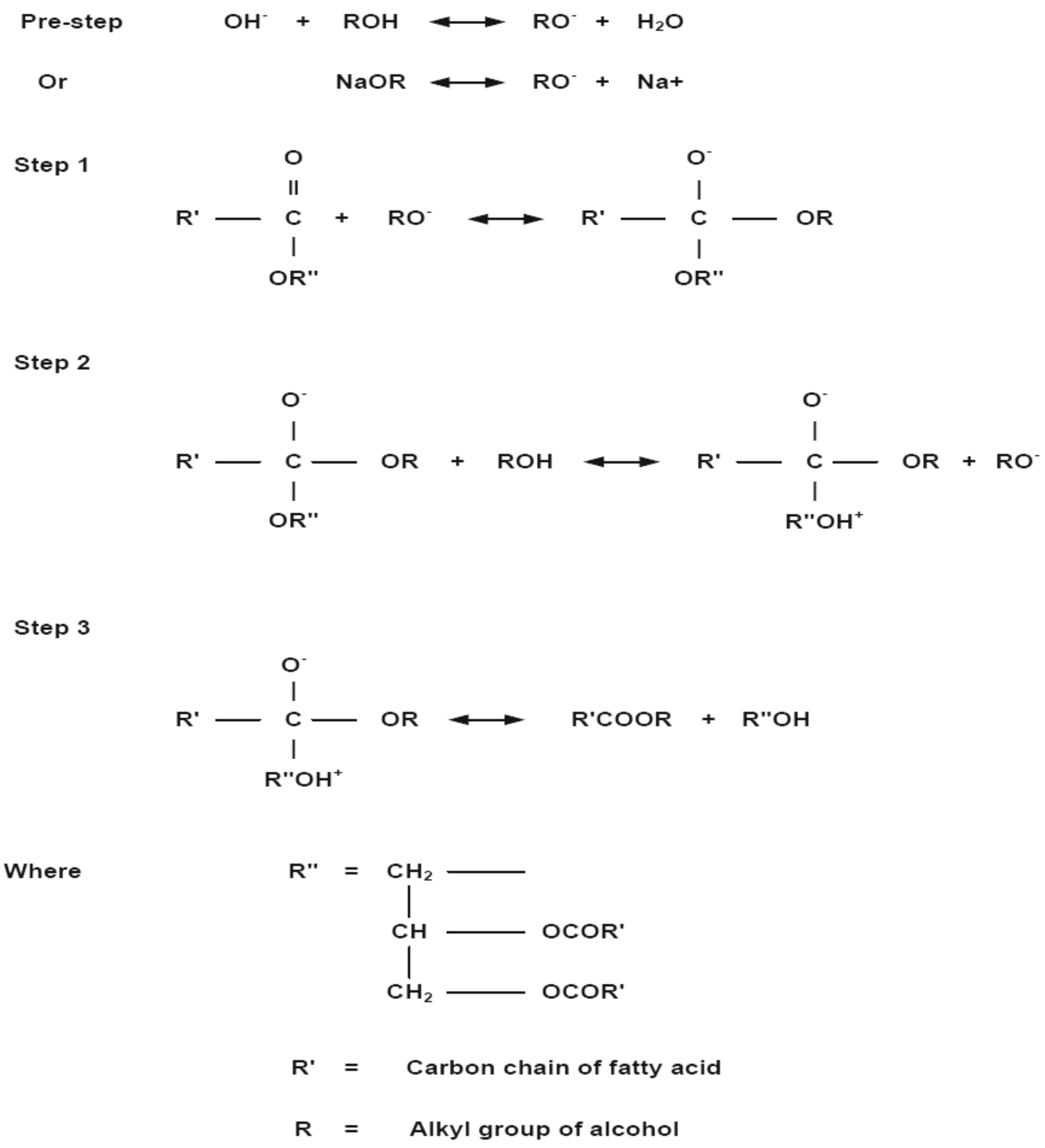


Figure 3.3 Three Step Transesterification Reaction



Pre-step $OH^- + ROH \longleftrightarrow RO^- + H_2O$

Or $NaOR \longleftrightarrow RO^- + Na+$

Step 1

$$R' - \underset{\underset{OR''}{|}}{\overset{\overset{O}{\|}}{C}} + RO^- \longleftrightarrow R' - \underset{\underset{OR''}{|}}{\overset{\overset{O^-}{|}}{C}} - OR$$

Step 2

$$R' - \underset{\underset{OR''}{|}}{\overset{\overset{O^-}{|}}{C}} - OR + ROH \longleftrightarrow R' - \underset{\underset{R''OH^+}{|}}{\overset{\overset{O^-}{|}}{C}} - OR + RO^-$$

Step 3

$$R' - \underset{\underset{R''OH^+}{|}}{\overset{\overset{O^-}{|}}{C}} - OR \longleftrightarrow R'COOR + R''OH$$

Where

$$R'' = \begin{array}{l} CH_2 - \\ \;| \\ CH - OCOR' \\ \;| \\ CH_2 - OCOR' \end{array}$$

R' = Carbon chain of fatty acid

R = Alkyl group of alcohol

Figure 3.4 Mechanism of alkali catalysed transesterification reaction

(Eckey. 1956)

3.5 Saponification

The formation of soaps as a side reaction complicates the downstream processing of the biodiesel. In order to achieve maximum biodiesel yield, it is necessary to reduce the soap. A molecule of soap is amphiphilic and has both a polar head and non polar tail. Figure 3.5 shows the molecule structure of the soap.

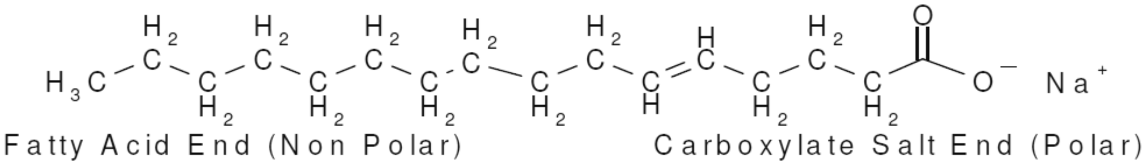


Figure 3.5 Molecular structure of Soap (Myint, 2007)

Soap is formed in biodiesel through saponification of triglycerides and by neutralisation of free fatty acids. It was reported by Zadra (2006) that the presence of water facilitates the reaction between alkali catalyst and triglycerides to form soap se Figure 3.6.

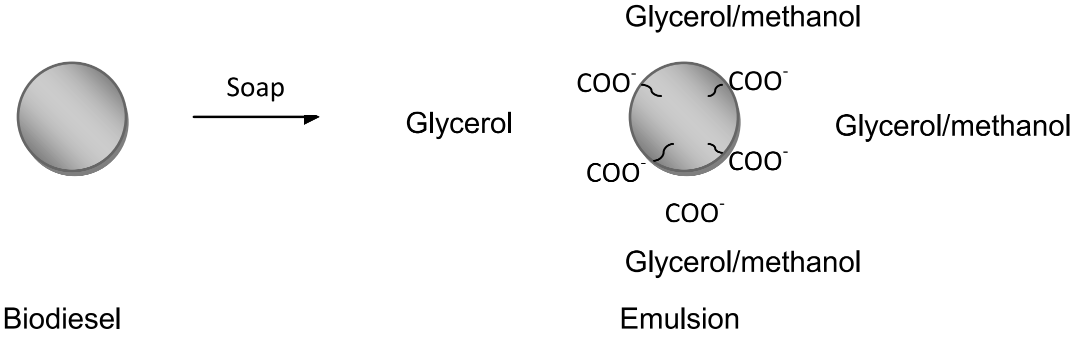


Figure 3.6 Emulsion of Biodiesel in the polar phase in the presence of soap

The polar head of the soap could attach or dissolve in the polar glycerol/methanol phase and the non-polar tail in the biodiesel, thus forming an emulsion. This increases the solubility of FAME in the polar glycerol/methanol phase thus reducing the yield (Van Gerpan et al. 2005; Vincente et al. 2007). In order to achieve highest biodiesel yield, it is necessarily to have a very low FFA content in the feedstock.

3.6 Biodiesel Production Process

3.6.1 Alkali catalysed transesterification

A schematic diagram of alkali catalysed transesterification is shown in the figure 3.3. The overall process includes the transesterification reaction, separation of glycerol from Fatty acid alkyl esters, purification of fatty acid alkyl esters, recovery of methanol and finally recovery of glycerol as a high grade by-product.

The reaction is usually carried out under constant agitation to facilitate greater contact between the immiscible phases, oil and methanol (OS Stamenković, 2007). The alkali catalyst in the form of methoxide ion is dissolved in the alcohol and the reaction is carried out at mild temperature and pressure. The reaction is usually given a residence time of 1 hour before collecting the product stream and gravity settled to separate the heavier fractions. Glycerol is usually collected at the bottom owing to the difference in the density and is a characteristic of its low solubility in fatty acid alkyl esters. Amphiphilic impurities like monoglyceride, di-glyceride can continue to be suspended in both the phases. Any unreacted alcohol and catalyst is dispersed in both phases.

The bottom layer is removed and the separated fatty acid alkyl ester phase is then washed with water to removed polar impurities like catalyst and glycerol. Finally, the methanol and water are recovered by distillation and evaporation respectively (Jehad et al. 2010).

3.6.2 High FFA feedstock

As seen earlier, alkali catalysed transesterification is not desired when the feed stock is high on free fatty acid content (> 2 wt %) due to the formation of soap thus reducing the biodiesel yield. It also complicates the downstream purification process increasing greatly the economics of water washing steps. It is hence necessary to pre-treat feed stocks high in FFA content before using them in the alkali catalyzed process. Figure 3.7 shows the pre-treatment process for feedstock's high on FFA content. The oil high on FFA is fed into the reactor with methanol and sulphuric acid. Canakci and Van Gerpan (2003) reported the typical reaction conditions which includes a molar ratio of methanol to FFA of 40 to 1 with sulphuric acid concentration of 5% by weight of FFA. The temperature is maintained at 60 ℃. The reaction proceeds until all the FFA's are converted to esters. The reaction mixture forms a two phase system of unreacted methanol and oil. The methanol can be recovered by distillation (West et al. 2008) and the oil which is now very low on FFA content can be used in base catalysed transesterification with subsequent process systems similar to a normal alkali catalysed transesterification.

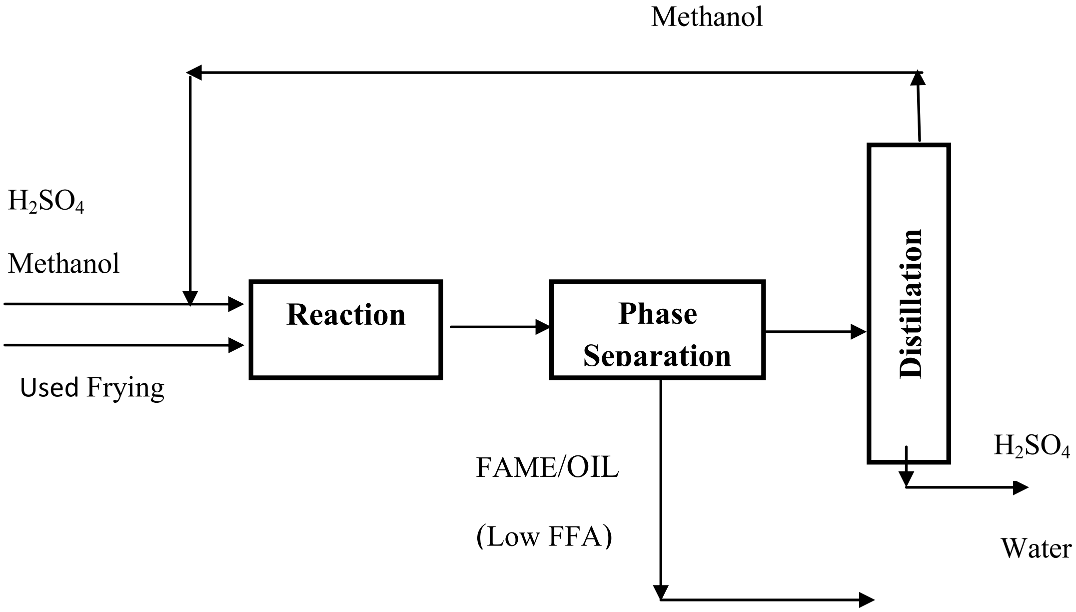


Figure 3.7 Acid esterified pre-treatment for high FFA feedstock

3.7 Biodiesel Purification

The purity of biodiesel is an important factor that affects the performance of a diesel engine. Impurities like monoglycerides, sterols, diglycerides, soap, methanol and catalyst can have adverse effects on the engine apart from affecting the properties of biodiesel. For instance, biodiesel high on saturated monoglycerides can lead to significant increase in the cloud point and contribute to filter plugging (Chupka et al. 2011). A high concentration of catalyst in biodiesel may damage the injector pump and accelerate corrosion in the engine. High levels of methanol lower the flash point and also deteriorate the rubber linings. The presence of significant amounts of glycerol can cause problems during long term storage (Jehad et al. 2010; Ma et al. 1998). In order to produce high quality biodiesel, a series of purification steps are necessary which include – gravitational settling, centrifugation, water washing, ion exchange and distillation.

Fatty acid alkyl esters are hydrophobic and can be separated from hydrophilic impurities by water washing. This step allows the removal of soap, alkali catalyst and small amount of mono and di-glycerides (Jehad et al. 2010; Becher 2001). Gravity settling is another way to separating the polar and non-polar phases. The separation is based on density differences and usually less effective when dealing with emulsions. Centrifugation is also used with waster washing to accelerate the phase separation; however the major disadvantage is the initial cost and the need for regular maintenance.

3.8 Gas Chromatography Analysis

3.8.1 Analysis

GC analysis is performed in order to determine the quantity of a class of contaminants in methyl esters (Jehad et al. 2010). The sample mixture injected into the GC column eludes mainly due to differences in boiling point and chemical structure. It was reported by Van

Gerpen (2004) that often it is the larger particles that have longer retention times in the GC. The free hydroxyl group are of esters are silylated with N-methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) prior to analysis to increase their volatility (Jehad et al. 2010). Two internal standards, butanetriol for the determination of free glycerol and tricaprin for the determination of glycerides, are used in the calibration process as well as in the analysis. ASTM method D6584 is to be used for this purpose (Jehad et al. 2010). Table 3.4 gives a list of GC standards.

Table 3.5 List of standards used for GC analysis

Standards (CAS number)	**Concentration (µg/mL in pyridine)**
Glycerol (56 – 81 – 5)	500
Monoolein (111 – 03 – 5)	5000
Diolein (2465 – 32 – 9)	5000
Triolein (122 – 32 – 7)	5000
Butanetriol (Ref ST # 1), (42890 – 76 – 6)	1000
Tricaprin (Ref ST # 2), (621 – 71 – 6)	8000

The samples to be tested by GC are first water washed and evaporated at 100 mbar at 95°C to remove methanol and water. After the GC analysis, the areas of pre-determined peaks are calculated and the mass of each component determined by method ASTM D6584-00.

3.8.2 Gas Chromatography

A GC, a Varian CP-3800, was used to determine the concentration of monoglycerides, diglycerides and triglycerides in FAME corresponding to individual samples by ASTM method. A 15 m x 0.32 mm x 0.1 µm column from Restek (MXT – Biodiesel TG) was used with a guard column of 2 m x 0.53 mm. Calibration curves for the GC were generated using two internal standards (butanetriol and tricaprin) and four references namely glycerine, monoolein, diolein, and triolein. Three replicate injections at 5 separate concentrations were performed to yield a glycerol calibration curve, $R^2 > 0.99$ to meet the ASTM requirement (Jehad et al. 2010).

The operating conditions for the column oven were 50°C for 1 min before ramping 15°C/min to 180°C, 7°C/min to 230°C and finally 30°C/min to 380°C. The oven was kept at 380°C for 10 min. The carrier gas, helium was held at a constant flow of 3.0 mL/min, flame ionization detector (FID) was held at 380°C, Hydrogen flow was kept constant at 35 mL/min, air flow rate was at 350 mL/min, and Helium flow rate was at 30 mL/min (Jehad et al. 2010).

Chapter 4

Study on transesterification kinetics through continuous elution reactions in a membrane reactor for speciation of Saturated Monoglycerides

Chapter 4

Study on transesterification kinetics through continuous elution reactions in a membrane reactor for speciation of Saturated Monoglycerides

Abstract

The addition of biodiesel to petro diesel can cause issues in cold-weather operations, because certain of its constituent compounds can form precipitates in the fuel. This issue has been attributed to the presence of impurities (mostly saturated monoglycerides, diglycerides, soap etc) in biodiesel and has been discussed in the literature. In addition to purity, the degree of saturation of the associated fatty acids in FAME affects the cloud point and pour point of the resulting biodiesel. This was aimed at studying the possibility of using the reaction kinetics of the transesterification to affect the continuous speciation of the biodiesel produced in a membrane reactor. The effect of selective transesterification of oil as a function of alcohol, temperature and catalyst concentration was investigated. At the conditions tested, the results showed very little specificity in the selection of fatty acid types in the transesterification reaction. We also found that the amount and type of monoglycerides present in the biodiesel is reflected by the relative amount of fatty acids types present in the oil. In biodiesel derived from Canola oil, a preponderance of monoolein was found for all runs and monolinolein as in the case of Soy bean oil.

Keywords: Fatty acid profiles, saturated monoglycerides, membrane reactor, elution studies

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4.1 Introduction

The development of renewable energy sources to replace fossil fuels such as oil, coal and natural gas can prevent depletion of the available energy resources and environmental pollution. However, despite these advantages, the production and usage of biodiesel has still not reached peak consumption as it is plagued with cold weather operability issues. This necessitates the requirement to blend biodiesel with conventional diesel fuel for better performance and to mitigate issues arising due to cold weather.

Blending petroleum diesel with biodiesel at concentrations of B20 or B5 has been largely problem free, where B20 is a mixture of 20% biodiesel and 80% petroleum diesel and B5 is a mixture of 5% biodiesel and 95% petroleum diesel (Chupka et al. 2011). However, the presence of higher melting saturated fatty acid methyl esters (FAME) and impurities mainly saturated monoglycerides in biodiesel still pose a threat of filter plugging in cold weather. Van Gerpen et al. observed that the final melting temperature for biodiesel spiked with saturated monoglycerides (SMGs), was 25 °C higher than the cloud point. (Van Gerpen et al. 1997).

Biodiesel contains impurities such as mono- and diglycerides that result from incomplete reactions. There is approximately 2% unsaponifiable matter in any feedstock. Soy oil feedstock for example contains about 1.6 w/w % unsaponifiable matter (Pfalzgraf et al. 2007).Unsaponifiable are non- lipid materials present in the oil feedstock and can include plant sterols, tocopherols, hydrocarbons, pigments, and minerals (Alleman et al. 2008; Chupka et al. 2010).

Total glycerin consists of bound and free glycerin. Bound glycerin is in the form of mono-, di-, and triglycerides (Alleman et al. 2007). Mono- and diglycerides are limited in ASTM D6751 by controlling the allowable level of 0.24 w/w %. It was reported by Van

Gerpen et al. (1997) that the fatty acid composition of the monoglycerides mirrors that of the parent fat or oil. Thus, in the case of soybean oil, palmitic acid (C16:0) would make up 7−11% of the fatty acid chains, while stearic acid (C18:0) would make up 3−5% of the fatty acid chains. Also, studies carried out on the saturated monoglyceride content of soy biodiesel observed that the concentrations of monopalmitin and monostearin to be about 11% and 5% of the total monoglyceride concentration. On the basis of this information, Chupka et al reports that the concentration of monopalmitin in soy biodiesel meeting ASTM standards would typically be about 0.026 w/w % and the concentration of monostearin about 0.01 w/w % (Chupka et al. 2010). Also it can be seen that, oil high on saturated fatty acid content would contain high amount of saturated monoglycerides. For example, Palm oil biodiesel could contain up to 45% palmitic acid chains and 4% stearic acid and thus might contain 0.108 w/w % monopalmitin and 0.01 w/w % monostearin.

Filter plugging issues have been a source of several studies. Although, the saturated content in the FAME is cited as one of the main reasons for poor weather operatability, study on the effect of other impurities like monoglyceride, soap, tocopherols etc also have been carried out extensively. Pfalzgraf (2007) examined the role of sterol glucosides (SG), monoglycerides, and water on filtration time after a cold temperature soak. The studies resulted in a positive correlation with higher filter times. Tang and co-workers cooled biodiesel blends to 4 °C, significantly above the expected cloud point, and noted the presence of precipitates after a storage time of 24 h (Tang et al. 2008). The precipitates on analysis showed a significant presence of saturated monoglycerides, monoglycerides and a combination of both in some feedstocks. This provides valuable information on the species contributing to the cold weather operatability issues and the need to remove all monoglycerides from the biodiesel. Moreau et al. examined 24 samples from various places in the biodiesel supply chain (Moreau et al. 2008). It was found that solids in these samples consisted primarily of saturated monoglycerides and other plant sterols. These studies suggest that SGs are mainly responsible for filter plugging above the CP.

Selvidge et (2007) al also reported that the use of a cold soak filtration test is effective at identifying biodiesel exhibiting precipitate formation above the CP and can contribute in lowering the incidents of fuel filter plugging (Selvidge et al. 2007).

In addition to this the profile of the fatty acid associated within the FAME affects the cold flow properties of the biodiesel. The melting point of methyl stearate (C18:0) is 39.1 ℃ while that of methyl oleate (C18:1) is -20 ℃ and methyl linoleate (C18:2) is -35 ℃ (Gunstone et al. 1994). It is easily seen that obtaining a biodiesel having less saturated FAMEs in an ester mix is desirable. This can be obtained by cold weathering of the fuel where a mixture of FAMEs is cooled below its cloud point and filtered to remove saturated FAMEs. In this current work, we have explored a new way of speciating the monoglycerides by exploiting the difference in the reaction kinetics of saturated vs unsaturated lipids.

4.2 Objectives

In this present study, a membrane reactor was employed to study transesterification kinetics through continuous elusion reactions to investigate the concentration of Fatty Acid Methyl Esters as a function of time for various vegetable oils, with an objective of speciating saturated monoglycerides namely monopalmitin and monostearin.

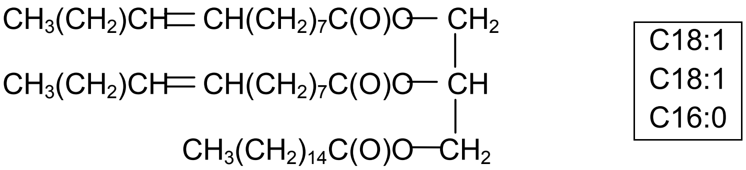
4.3 Approach

4.3.1 Understanding Triglycerides, Di-glycerides and Monoglycerides

The distribution of esters has a great deal of effect on the properties of biodiesel, which include density, cetane number, cloud point, melting point etc (Van Gerpan et al. 2005). Since, different feed stocks contain different concentration of fatty acids, the choice of feed stock generally characterises the fuel properties.

Glycerol contains three hydroxyl groups that can combine with up to three fatty acids to form monoglycerides, diglycerides, and triglycerides. If all the hydroxyl groups are esterified by fatty acids, we get triglyceride. Two esterified groups represent diglyceride and one esterified hydroxyl group represents monoglyceride (Zamora, 2012).

Triglycerides are the main constituents of vegetable oils and animal fats. Triglycerides at normal room temperatures may be solid or liquid based on the fatty acid content in the feedstock. A triglyceride is a chemical compound formed from one molecule of glycerol and three fatty acids. (Van Gerpan et al. 2005; Zamora, 2012).



$$\begin{array}{r} \mathrm{CH_3(CH_2)CH{=}CH(CH_2)_7C(O)O{-}CH_2} \\ | \\ \mathrm{CH_3(CH_2)CH{=}CH(CH_2)_7C(O)O{-}CH} \\ | \\ \mathrm{CH_3(CH_2)_{14}C(O)O{-}CH_2} \end{array}$$

Triglyceride

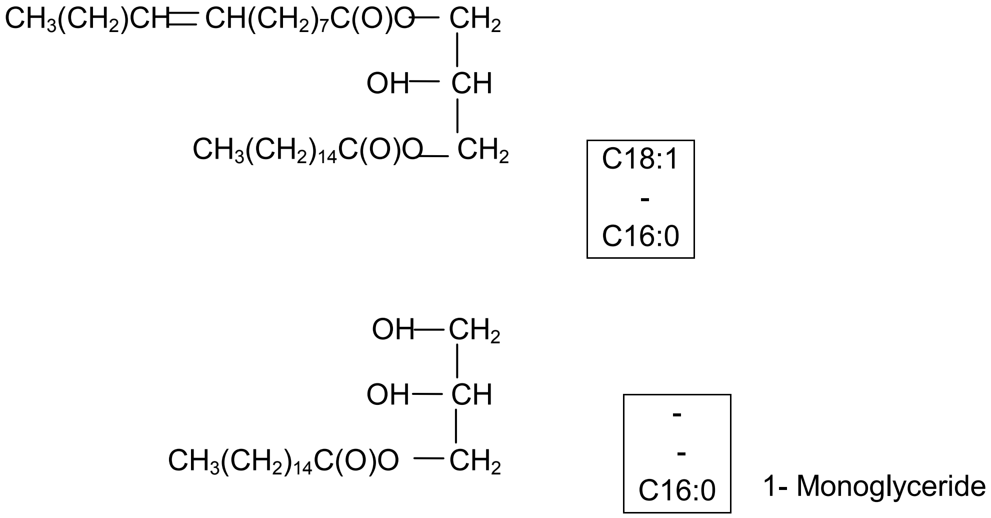


Figure 4.1 An example of Tri, diglyceride and monoglyceride molecules.

The triglyceride structural formula in Fig 4.1 on the left consists of two radicals of oleic acid (C18:1) and one of palmitic acid (C16:0) attached to glycerol.

A diglyceride molecule has two of the carboxyl groups joining other the other two hydroxyl groups to form an ester linkage and usually exists in the 1,2 or 1,3 form. A monoglyceride has only one fatty acid radical per molecule of glycerol. The fatty acid may be attached to carbon 1 or 2 of the glycerol molecule. The fatty acid distribution in various oils and fats is listed in Table 4.1.

Table 4.1 Fatty acid composition of some common edible fats and oils.

Oil or Fat	**Fatty Acid [C-O-O-R] Composition (Wt %)**					
	C14:0	**C16:0**	**C18:0**	**C18:1**	**C18:2**	**C18:3**
Canola		4-5	3.8-7	55-63	20-31	9-10
Coconut	13-18.5	7.5-10.5	1-3	5-8.2	1.0-2.6	
Corn	1-2	7-13	2.5-3	30.5-43	39-52	
Palm	0.6-2.4	32-46.3	4-6.3	37-53	6-12	
Soybean		2.3-11	2.4-6	22-30.8	49-53	2-10.5
Lard	1-2	28-30	12-18	40-50	7-13	0-1
Butter	7-10	24-26	10-13	28-31	1-2.5	0.2-0.5
Sunflower		3.5-6.5	1.3-5.6	14-43	44-68.7	

4.3.2 Triglyceride profiles of fats and oils

Zamora (2012) reports that the percentages of fatty acid contents reflect the overall proportions of the fatty acid radicals in the triglycerides. Going by this understanding, for example, 33 representative molecules of soy oil triglycerides would contain, on average, 11 radicals of palmitic acid (C16:0), 6 radicals of stearic acid (C18:0), 22 radicals of oleic acid (C18:1), and 52 radicals of Linoleic acid (C18:2) and 10 radicals of Linolenic acid (C18:3). These fatty acid radicals would be distributed randomly among the 33 triglyceride molecules. The typical soy oil triglyceride molecule would have one or two radicals of Linolenic acid and one radical of palmitic acid or stearic. It is rare that one would encounter triglycerides with only palmitic and stearic acid radicals as seen by carpenter et al (1976) (Carpenter et al. 1976; Zamora, 2012). Saturated molecules have only sigma bonds, which are very stable and hard to break. Unsaturated molecules, however, have pi bonds, and they are weaker. They deform the orbitals slightly and are more strained. Therefore, they will react faster and offer more reaction possibilities than their saturated counterparts.

The idea is to exploit the low reactivity of saturated fatty acids, thereby retaining saturated monoglycerides in the reactor as the unsaturated chain would react first and detach itself from the glycerol skeleton. The overall process of transesterification consists of three consecutive, reversible reactions to give diglycerides and monoglycerides as intermediates, however the actual reaction is lot more complicated. Stavarache et al. investigated the concentration of fatty acid methyl esters of various vegetable oils as a function of time through ultrasonic assisted transestefication. There has been not much discussed in the literature concerning continuos elution studies and speciation of monoglycerides using a membrane reactor and this work is first to look into this line of study. The intent is to gradually elute a reacted mixtuire out of a membrane reactor initally loaded with oil and measure the degree of saturation of the resulting permeate. The oils employed in the study were chosen primarily on their fatty acid composition targetting lipids low on saturated content as it is evident that the feedstocks with high saturated content have cold flow operatability issues.

4.4 Experiment

4.4.1 Feed Stock and Reagents

Refined Bleached and Degummed Canola oil and Soy bean oil was used in this study. Lard oil was used for batch scale experimental runs. The acid used for neutralization was hydrochloric acid (Assay: 36.5-38%, Fisher Scientific, Canada). The alcohol used for reactions was methanol (Fisher Scientific, Canada) and the catalyst was 25 wt% Sodium Methoxide in methanol (Sigma- Aldrich, Canada)

4.4.2 Experimental Setup

In the present study, a UF membrane setup was employed as shown in Fig.1. A membrane loop was utilized to perform all runs.

(a) The loop was equipped with a shell and tube heat exchanger to maintain the temperature of the fluid at a constant value.
(b) A water bath was used to control the water temperature, which was the heating supplying fluid.
(c) A platinum resistance temperature detector (RTD) was used in the membrane loop to measure the temperature of the mixture at any given time.
(d) Three pumps were used in the system: two gear pumps were used to pump methanol and oil separately into the loop and a centrifugal pump was used to circulate the reaction mixture in the loop.
(e) The system was operated in a semi-continuous mode, where a desired amount of oil and methanol was loaded in the loop at the beginning of the run and only methanol was fed to the loop during the run.

(f) Provision was given through a separate line to backflush/backwash the membrane with methanol between two subsequent runs to ensure that no fouling or oil deposition remained on the membrane surface and inside the pores.

(g) The process control software named Labview® (National Instruments), was used to control the methanol feed pump, temperature, operational cycle and TMPs in all runs.

(h) Balances placed under the methanol and oil tanks were used to control and record flow rates. TMPs were recorded during each run by a differential pressure gauge.

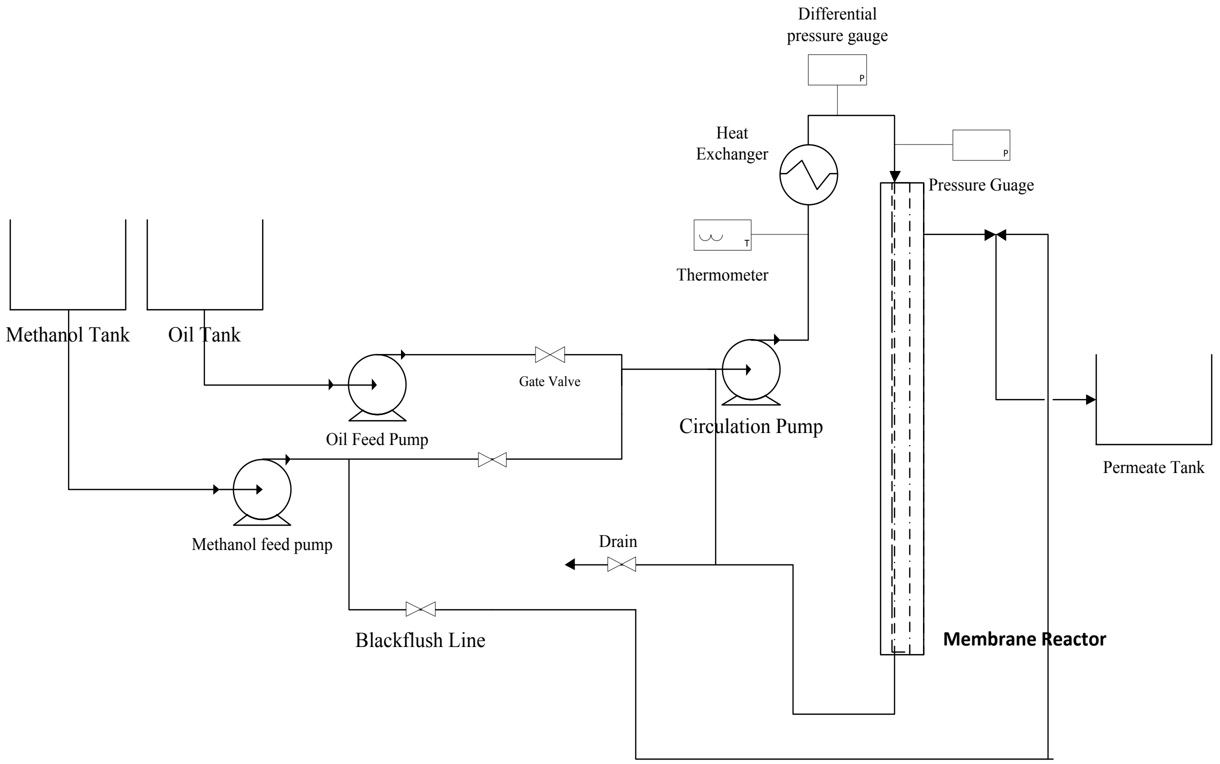


Figure 4.2 Schematic representation of membrane reactor setup for elution studies and first stage reactions

4.4.3 Membrane

A single tube 10 mm x 50 cm ceramic membrane from INOPOR was used in all runs. The membrane pore size was 0.05 microns.

4.5 Experimental Procedure and Analytical Method

4.5.1 Procedure

A series of runs with different variables were performed and analysed. Table 2 gives a list of runs that were performed to study the elution as a function of time. The free fatty acid content of the feedstock (Soybean and Canola) was estimated before feeding it into the reactor. This was used to determine the minimum catalyst concentration that was needed to be maintained in the reactor.

(a) The membrane reactor was backflushed with pure methanol to remove any residual oil and fouling deposits on the membrane walls from previous runs.

(b) Permeate and the backflush lines were closed.

(c) Initial weight of the oil and methanol was recording from the balance. Labview software was started to record the run information.

(d) The feed valves pertaining to oil were opened, and the oil was fed into the reactor.

(e) Oil was circulated to reach a desired temperature.

(f) Methanol was fed into the reactor and the circulation pump was started.

(g) After a residence time of 15 minutes, methanol was continuously fed into the reactor with a constant predetermined flow rate for the remainder of the run.

(h) Permeate was collected every 5 minutes and neutralised immediately to inhibit further reaction.

(i) Samples were collected till all the oil in the reactor was consumed.

(j) Circulation was stopped and the samples were sent for analysing.

4.5.2 Analysis

The samples to be analysed, have to be first free from any catalyst, glycerol and methanol. In order to obtain pure biodiesel, a series of processes are usually required. These can include: gravitational settling, centrifugation, water washing, adsorption and distillation.

The most common method for purification of the biodiesel is water-washing. FAME and unreacted TG are essentially non-polar and insoluble in water, while soap, methanol and glycerol are polar and readily soluble in water. Therefore, adding water to the non-polar phase is usually the first and the most common step in purifying biodiesel for GC analysis. Similar method of water washing was employed to wash the samples from the elution runs and is illustrated below.

(a) 30 ml of biodiesel sample is taken in a vial.

(b) 10 % by weight distilled water is added to the vial.

(c) The contents are shaken well and centrifuged for 10 min at 5000 rpm.

(d) The bottom phase is removed and the procedure is repeated again.

(e) The sample is then evaporated for trace amounts of methanol and water for 30 min at 100 mbar.

(f) The sample is ready for analysis.

4.5.3 Analytical Methods

A GC, a Varian CP-3800, was used to determine the saturated and unsaturated methyl ester concentration in the FAME corresponding to individual samples by ASTM method. A 15 m x 0.32 mm x 0.1 μm column from Restek (MXT – Biodiesel TG) was used with a guard column of 2 m x 0.53 mm. Calibration curves for the GC were generated using two internal standards (butanetriol and tricaprin) and four references namely glycerine, monoolein, diolein, and triolein. Three replicate injections at 5 separate concentrations were performed to yield a glycerol calibration curve, $R^2 > 0.99$ to meet the ASTM requirement.

Each sample was prepared for analysis by weighing 100 mg of FAME in a 10 mL septa vial. 100 µL of butanetriol, tricaprin and MSTFA were then added to the vial and shaken. The vial was left to stand for 15 min at room temperature. Approximately 8 mL of n-heptane was then added to the vial. 1 µL of the prepared sample mixture was then injected into the cool on-column injection port. The operating conditions for the column oven were 50°C for 1 min, 15°C/min to 180°C, 7°C/min to 230°C, 30°C/min to 380°C, hold 10 min. The carrier gas was helium at a constant flow of 3.0 mL/min, the detector was a flame ionization detector (FID) held at 380°C, H_2 flow was at 35 mL/min, air was at 350 mL/min, and He (make-up) was at 30 mL/min.

To get a detailed fatty acid methyl ester profile, a Perkin Elmer (PE) Auto system GC was used. A 30m long 0.32 mm ID column from Restek (FAME WAX) was used to generate chromatograms. The operating condition for the column were, 50°C for 5 minutes, 10°C/min to 120°C and held for 25 minutes. The temperature was ramped to 250°C at 15°C/min and held for 5 minutes. The plots from PE and Varian GC are discussed in the next section.

4.6 Results and Discussions

When a triglyceride molecule reacts with an alcohol, in a transesterification reaction, the fatty acid chains are released from the glycerol backbone to recombine with alcohol to give fatty acid alkyl esters. The left over skeleton forms di and mono glycerides before forming a glycerol molecule.

4.6.1 Trigycerides as a function of time

The amount of triglycerides decreased rapidly indicating that over 90% TG's reacted in the first 10 minutes of the reaction. The TG concentration in the case of higher oil to methanol ratio, showed a gradual decrease with time before reaching equilibrium. This can be attributed to compatibilisation dynamics. At high oil to methanol ratio, as glycerol is formed in the reactor, it decompatibilises oil (non-polar phase) and causes it to permeate through the membrane. However, in the case of low oil to methanol ratios, the high concentrations of methanol compatibilises the glycerol and permeates the membrane as one phase and hence less permeation of oil through the reactor can be seen. As methanol was constant pumped into the reactor, the TG's begin to react and the concentration dropped. The methanol flow rate was maintained at a predetermined constant value such that there is always excess methanol in the reactor beyond the first 50 minutes of the run to ensure complete reaction of the oil. This gurantees no presence of unreacted oil, di-glyceride and monoglycerides in the reactor loop at the end of run cycle.

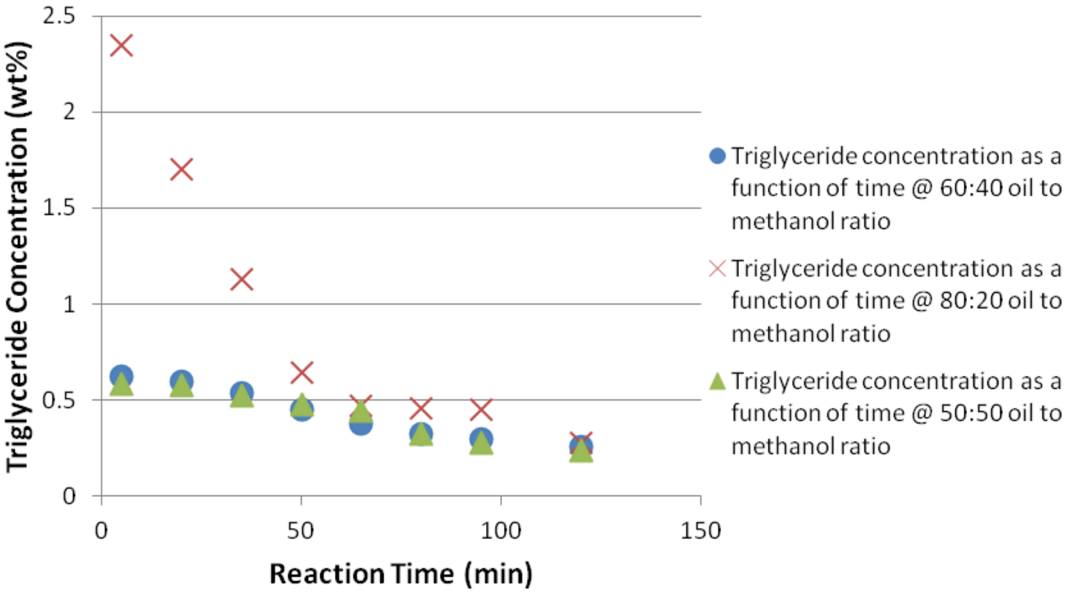


Figure 4.3 Triglyceride concentration as a function of time

As a result, the effect of oil to methanol ratio is accountanble for the first 50 minutes of the reaction. Figure 4.3 shows the triglyceride concentration as a function of time. It can be noted that, very little TG permeates through the membrane at low oil to methanol ratios as the TG concentration in the permeate is very low even in the first few minutes of the reaction. It eventually reaches a very low concenration of <0.3 wt% at the end of the runs.

4.6.2 Di-glycerides as a function of time

As seen in Figure 4.4, the amount of di-glycerides were low from the begining of the reaction and reducing gradually as the reaction proceeded. The only anamoly was again seen in the case of high oil to methanol ratio, where the concentration reduced gradually for the first 50 minutes, before reaching low values. The result was in agreement with stavarache et al 2007. The oil to methanol ratio did not have a significant effect on diglyceride reaction. Temperature did not account for significant differences.

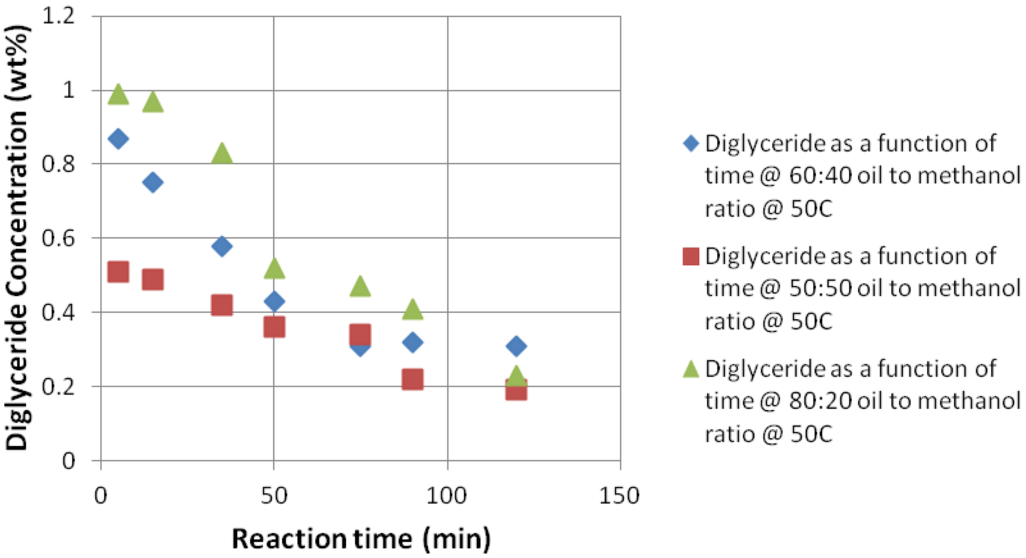


Figure 4.4(a) Diglyceride concentration at as a function of time at 50℃

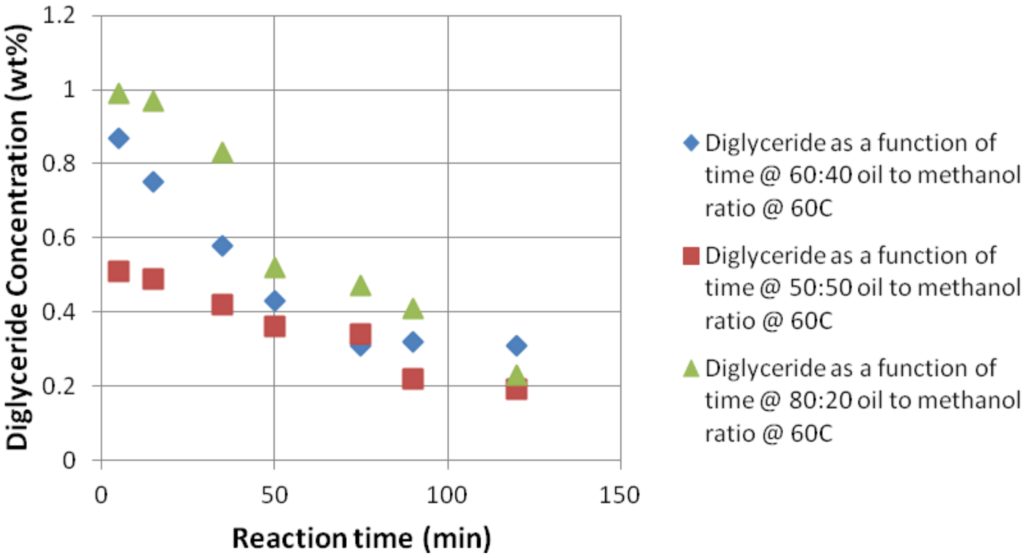


Figure 4.4(b) Diglyceride concentration at as a function of time at 60 ℃

4.6.3 Monoglycerides as a function of time

Unlike we expected, the concentration of saturated monoglycerides remained very low from the begining of the reaction. During transesterification, the amount of monoglycerides were larger than the diglycerides. This large concentration of monoglycerides was primarily contributed by unsaturated fatty acids, indicating that saturated fatty acids react almost fully very early in the reaction. A preponderance of monoolein was observed in the case of soy and monolinolein in the case of canola. The concentrations of monopalmitin and monostearing remained low and constant throughout the reaction. The effect of catalyst concentration, temperature and oil to methanol ratio did not have any significant effect on the speciation of saturated monoglycerides.

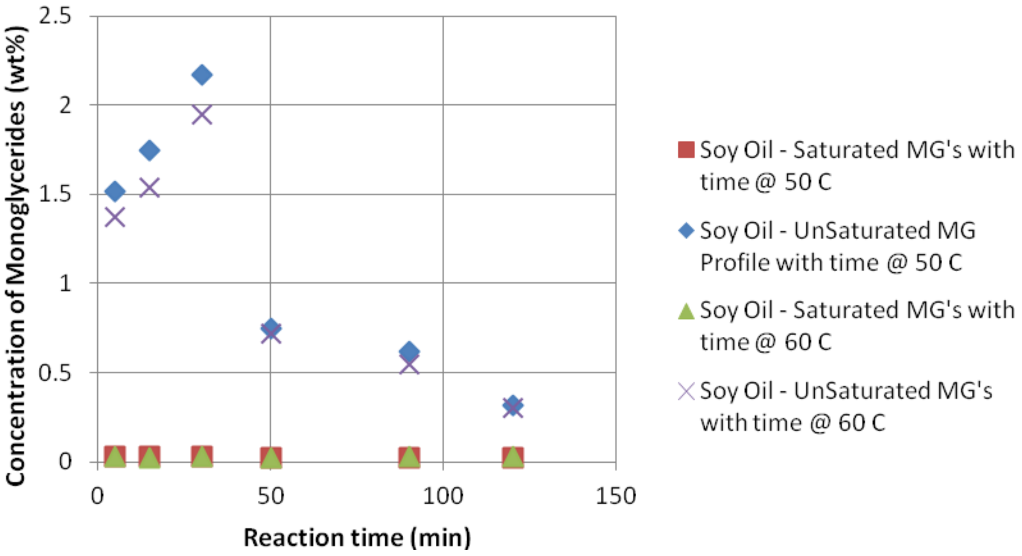


Figure 4.5 Saturated and Unsaturated monoglycerides of Soy ester as a function of time

4.6.4 Fatty Acid Methyl Ester concentration as a function of time

The saturated fatty acid methly esters in soy and canola (namely methyl palmitate C16:0 and methyl stearate C18:0) concentration remained same throughout the reaction. The unsaturated fatty acid methyl ester concentration increased before reaching a equilibrium. This confirms the understanding that fatty acid composition of monoglyceride mirror parent fat or oil. The catalyst concentration, temperature and oil to methanol ratio did not have significant effect on the saturated FAME concentration. Figure 4.6 shows the profile of fatty acid ester of soy oil as a function of time.

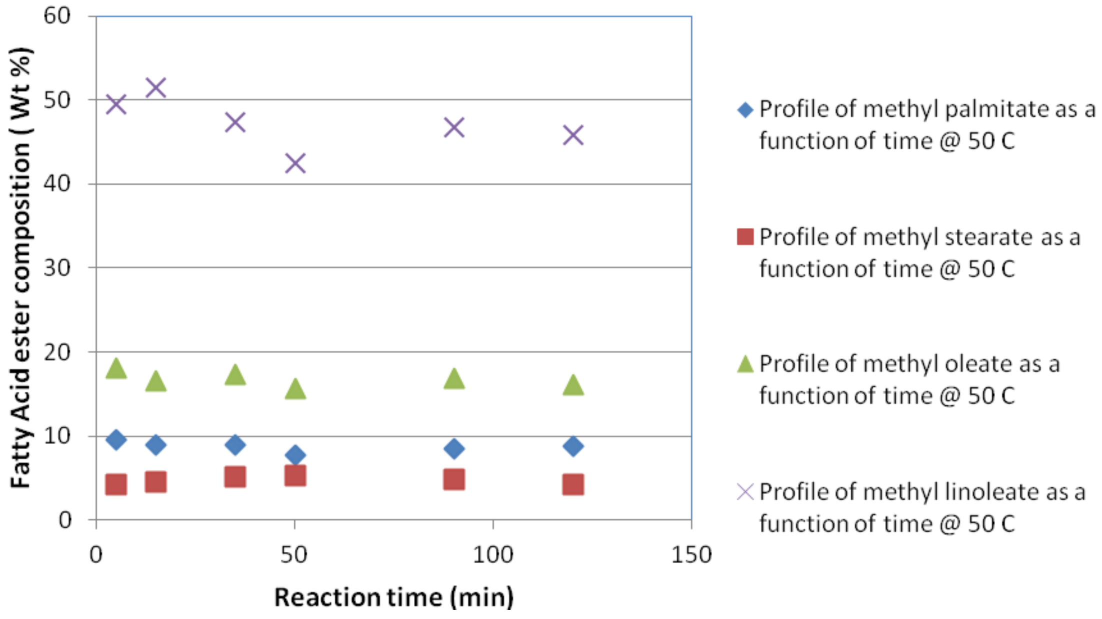


Figure 4.6 Fatty acid ester profile of soy oil as a function of time at 50 C at oil to methanol volume ration of 60:40.

These results suggest that saturated fatty acids are mostly transesterified at the begining of the reaction, while the amount of unsaturated fatty esters increases as a function of time before reaching equilibrium. This can be explained by examining the location of the saturated and unsaturated acid chains on triglyceride molecules. Table 4.2 below illustrates a geometric distribution of acid chains in soybean oil (Stavarache et al. 2007; Zamora 2012).

It is seen that, the positional distribution of saturated fatty acids in the sn-2 position is very rare (Carpenter et al.1976) The chains show a preponderence of oleic acid in different positions. Stearic acid is always in a sn-1 or sn-3 position. It is more accessible in this poosition and will react in the first or second reaction of the transesterification reaction. This explains the very low amount of saturated monoglycerides in the permeate and the preponderance of unsaturated monoglycerides in the same. It also explains the increase in unsaturated monoglycerides with time with Figure 4.5 before 50 min. The consequent increase in methyl stearate in Figure 4.6 up 50 min also illustrates this. These results indicate that transesterification is a function of positional distribution and positions sn1 and sn3 react the fastest and sn2 reacts the slowest thereby leaving mostly unsaturated monoglycerides in the reactor and agrees with the findings of stavarche et al 2007.

The samples collected up until 50 min in the 60:40 run would have a higher cloud point than the ones after 50 min. This suggests that further fine tuning of the technique could possibly lead to a speciation based on reaction kinetics and elution. The first trial of this technique while not a complete success and does indicate a way ahead in successfully implementing this process.

Table 4.2 Positional modelling of commercial soy bean oil

C18:0 C18:1 C16:0	C18:0 C18:1 C16:0	C18:2 C18:1 C16:0	C18:2 C18:1 C16:0	C18:2 C18:1 C16:0	C18:2 C18:1 C16:0	C18:2 C18:2 C16:0	C18:2 C18:3 C16:0	C18:0 C18:0 C16:0	C18:2 C18:2 C16:0	C18:2 C18:2 C16:0
C18:2 C18:2 C18:2	C18:2 C18:2 C18:2	C18:2 C18:2 C18:1	C18:3 C18:2 C18:1	C18:2 C18:2 C18:1	C18:3 C18:2 C18:1	C18:2 C18:2 C18:1	C18:2 C18:2 C18:1	C18:2 C18:1 C18:2	C18:3 C18:2 C18:1	C18:3 C18:2 C18:1
C18:2 C18:2 C18:1	C18:2 C18:1 C18:2	C18:2 C18:2 C18:1	C18:2 C18:1 C18:2	C18:3 C18:2 C18:1	C18:2 C18:1 C18:2	C18:2 C18:2 C18:1	C18:2 C18:1 C18:2	C18:2 C18:2 C18:1	C18:2 C18:2 C18:2	C18:2 C18:3 C18:2

4.6.5 Monoglycerides and polymorphysm.

As seen in the results above there is very little saturated monoglycerides in the FAME produced in this work. So we must turn to the possibility that unsaturated monglycerides can cause filter plugging. The melting point of various unsaturated monoglycerides is given in Table 4.3 below.

Table 4.3 Melting point of unsaturated monoglycerids and their possible polymorphic crystal forms Baldwin et.al (1944).

Monoglyceride Fatty acid chain	M.P (℃)	Polymorph Form I	Polymorph Form II
Monooleain (C18:1)	36	-	-
Monolinolein(18:2)	-10	-22.8	12.3
Monolinolenin(18:3)	-20	-13.5	15.7

As seen in the table unsaturated monoglycerides C18:1 has a melting point of 36 C and is of serious concern for cold flow issues. In adidtion to this unsaturarted C18:2 and C18:3 monos can exhibit various crystaline forms (polymorphs) above 0 °C that can lead to precipitation. Many reports discuss the possibility of precipitates occuring when biodiesel is stored over a relatively short period. The presence of unsaturated monoglycerides in biodiesel fits the profile of a fuel that is clear on leaving a plant (-13.5 and -22.8 °C polymorphs) and then forms crystals over time (+12.3 and +15.7 °C polymorphs). This time dependent change is often observed in pharmaceutical products exhibiting polymorphycity (Aguiar et al. 1967). So all types of monoglycerides must be removed to produce effective cold weather biodiesel. This remains a considerable challenge which is addressed in the next chapter of this thesis.

4.7 Conclusions

The saturated monoglycerides in the permeate from the membrane reactor were very low and did not change over the course of the reaction. The saturated FAME was realtively constant throughout the reaction. This was attributed to positional reactivity, with fatty acid moeties in the sn1 and sn3 position reacting the fastest followed by slow reacting sn2 position. Saturated fatty acids naturally exist in sn1 and sn3 positions (Carpenter et al. 1976) and this explains constant saturated FAME concentrations from the begining of the reaction. The unsaturated fatty acids usually take the sn2 position and are slower to fully react. This causes a gradual increase in unsaturated FAME concentration as the reaction proceeds. The preliminary investigation shows some promise for the design of a process that uses the different kinetics of transesterification to obtain mixtures of FAMEs with different cold flow characteristics. It also indicates that unsaturated monoglycerides should be an important concern in the cold weather performance of biodiesel. Standards that single out saturated vs unsaturated monoglycerides will not improve cold flow issues and all monoglycerides must be minimized.

Chapter 5

Study on multi-stage transesterification reactions for production of high quality biodiesel.

Chapter 5

Study on multi-stage transesterification reactions for production of high quality biodiesel

Abstract

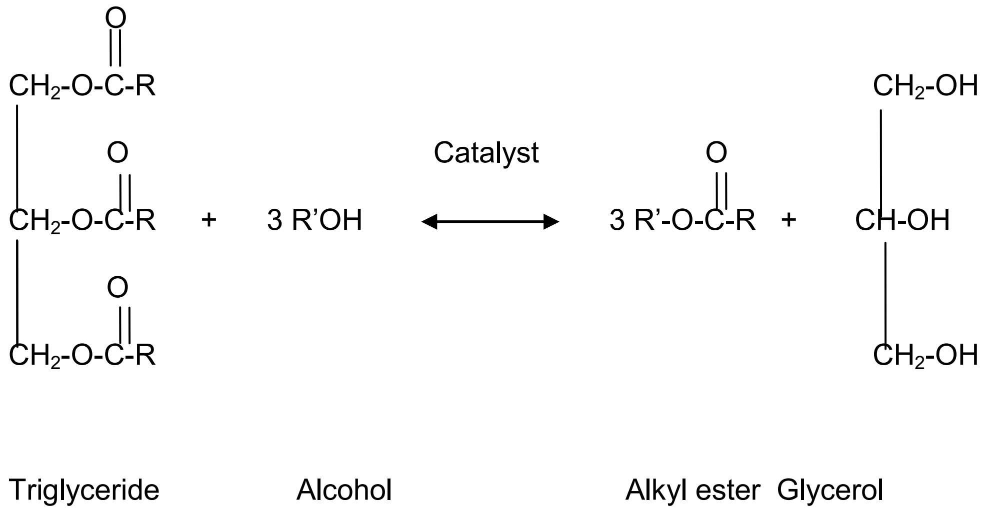
The work focuses on ways to greatly reduce monoglycerides (MG) in biodiesel with an optimized cost efficient approach by mitigating to a greater extent the possibility of side reactions (formation of soap). The effect of transesterification of oil as a function of alcohol, temperature and catalyst concentration was investigated over two and three stage reactions. Higher catalyst concentrations gave pure biodiesel with loss of yield. Three stage transesterification reaction was found to be the most effective in greatly lowering the monoglyceride concentration requiring least amount of catalyst and alcohol. The lowest monoglyceride concentration reached was 0.03 Wt% at a soap concentration of 120 ppm in the unwashed FAME phase.

Keywords: multistage, monoglycerides, yield, purity, membrane reactor, batch

5.1 Introduction

Biodiesel is defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. It can be used in diesel engines and heating systems (Mittelbach et al. 1983; Staat and Vallet, 1994). Biodiesel has numerous benefits in comparison with diesel fuel. It is a renewable, non-toxic and biodegradable fuel which has a significant low emission profile and can be used as an alternative to petroleum-based diesel fuel practically with no engine modifications. This implies less dependency on conventional fossil fuels and low impact on the environment. In this context, many scientific articles dealing with biodiesel production have been published. More recently, with the sharp inflation of petroleum based diesel fuel, the demand for biodiesel has increased. Furthermore, with advent of energy policy acts, the use of alternative fuels for transportation has received a great boost. (Vincente et al. 2007)

The most common way to produce biodiesel is by transesterification. In this reaction, triglycerides, as the main components of vegetable oils, react with an alcohol to produce fatty acid mono-alkyl esters and glycerol as shown in Figure 5.1. The stoichometry of methanolysis reaction requires 3 mol of methanol and 1 mol of triglyceride to give 3 mol of fatty acid methyl ester and one mole of glycerol. The complete reaction consists of three consecutive reversible steps with intermediate formation of monoglycerides and diglycerides. Methanol is generally used for transesterification reactions as it is cheaper than other higher alcohols. The biodiesel is then purified by water washing to remove glycerol, catalyst and trace impurities. The purified biodiesel is then used as a diesel fuel. The separated glycerol can be purified and used in pharmaceuticals and food industries (Claude 1999, Vincente et al 2007).



$$CH_2\text{-O-}\overset{O}{\overset{\|}{C}}\text{-R} \quad\quad CH_2\text{-OH}$$

$$CH_2\text{-O-}\overset{O}{\overset{\|}{C}}\text{-R} + 3\,R'OH \xleftrightarrow{\text{Catalyst}} 3\,R'\text{-O-}\overset{O}{\overset{\|}{C}}\text{-R} + CH\text{-OH}$$

$$CH_2\text{-O-}\overset{O}{\overset{\|}{C}}\text{-R} \quad\quad CH_2\text{-OH}$$

Figure 5.1 Transesterification Reaction (Van Gerpan 2005)

This transesterification is generally catalysed by a basic or an acid catalyst. The base catalysed transesterification is the most commonly used technique, because the process proves to be faster and the reaction conditions are moderate (Freedman et al. 1984). The most commonly used basic catalysts are sodium hydroxide and potassium hydroxide. However, the use of alkali catalysts in vegetable oil transesterification produces side reactions that are undesirable in a process. The most common side reaction is saponification of triglyceride and the neutralisation of free fatty acids to form soap as shown in Figure 5.2. Both soap formations are undesirable as they partially consume the catalyst, decrease the biodiesel yield and make the separation and purification steps cost intensive (Vicente et al. 2004).

$$\underset{\text{Fatty Acid}}{RCOOH} + \underset{\text{Sodium Hydroxide}}{NaOH} \longrightarrow \underset{\text{Sodium Soap}}{RCOONa} + \underset{\text{Water}}{H_2O}$$

Figure 5.2 Saponification reaction

Biodiesel does not contain 100 % fatty acid methyl esters; it can also contain significant amounts of mono, di- and tri-glyceride depending on the completion of the transesterification reaction (Van Gerpen 1997). These impurities can cause filter plugging issues and have been discussed extensively in the literature (Chupka et al. 2011). Pfalzgraf and co-workers studied the impact of sterol glucosides (SG) and monoglycerides on filtration time after a reduction in temperature of the biodiesel and found that all of the tested impurities could potentially contribute to higher filtration times (Pfalzgraf et al 2007, Chupka et al. 2011). This brings in the need to improve the purity of biodiesel. Many studies have been carried out on base – catalysed transesterification involving calculations on triglyceride conversion rates, product composition as a function of time (Feuge and Gros, 1949; Freedman et al. 1984, 1986; Schwab et al. 1987; Peterson et al. 1991; Mittelbach and Trathnigg, 1990; Ali et al. 1995; Chang et al. 1996; Mittelbach, 1996; Coteron et al. 1997; Boocock et al. 1998; Noureddini et al. 1998; Vicente et al. 1998; Darnoko and Cheryan, 2000). Most of these studies are related to fatty acid methyl ester concentration in the biodiesel phase i.e. purity of biodiesel. Although, the other important factor of transesterification process is the yield, it has not been discussed extensively in literature (Frohlich and Rice, 1995; Frohlich et al. 2000; Vicente et al. 2004). According to these authors, the loss of biodiesel yield is because of two major reasons, saponification of triglycerides and dissolution of fatty acid methyl esters in glycerol phase (Vincente et al. 2007).

5.2 Objectives

In this present study, multistage transesterification reactions were carried out to greatly reduce the monoglyceride concentration by minimising the yield lose due to soap formation. Different approaches were investigated with a motive to develop a process that uses lowest catalyst and methanol concentration to obtained desired results.

5.3 Methods

5.3.1 Feed Stock and Reagents

Refined Bleached and Degummed Canola oil (Spectra Foods brand) (Baie-d'Urfe, QC) was obtained from Tannis Food Distributors (Ottawa, ON) in a 16 L container and was used in this study. The acid used for neutralization was hydrochloric acid (Assay: 36.5-38%, Fisher Scientific, Canada). The alcohol used for the reactions was 99% pure methanol (Fisher Scientific, Canada) and the catalyst was 25 wt% sodium methoxide in methanol (Sigma-Aldrich, Canada). A complete list of chemicals used in the preparation of the biodiesel in this work is included in Table 5.1.

Table 5.1 Chemicals used to prepare biodiesel

Chemical	Supplier	Location	Purity
Methanol Optima Grade	Fisher Scientific	Fair Lawn, NJ	>99.9 %
Sodium methoxide solution, 25wt%	Sigma-Aldrich	Oakville, ON	23.5-26.5
Sulphuric acid, Certified ACS Grade	Fisher Scientific	Ottawa, ON	95-98
Hydrochloric acid, Certified ACS Grade	Fisher Scientific	Ottawa, ON	36.5-38

5.4 Experimental Setup

5.4.1 Membrane Reactor Setup

The experiment was carried out as two and three stage reactions. A UF membrane setup was employed as shown in Figure 5.3. Stage one reactions were performed in a membrane reactor.

1. The loop was equipped with a shell and tube heat exchanger to maintain the temperature of the fluid at a constant value.
2. A water bath was used to control the water temperature, which was the heat supplying fluid.
3. A platinum resistance temperature detector (RTD) was used in the membrane loop to measure the temperature of the mixture at any given time.
4. Three pumps were used in the loop: two gear pumps were used to pump methanol and oil separately into the loop and a centrifugal pump was used to circulate the reaction mixture in the loop.
5. The system was operated in a semi-continuous mode, where the desired amount of oil and methanol was loaded in the loop at the beginning of the run.
6. Methanol and oil were fed to the loop with predetermined flow rate during the run.
7. Provision was given through a separate line to backflush/backwash the membrane with methanol between two subsequent runs to ensure that no fouling or oil deposition remained on the membrane surface and inside the pores.
8. The process control software named Labview® (National Instruments), was used to control the methanol feed pump, the flux, temperature, operational cycle and TMPs in all runs.

9. Balances placed under the methanol and oil tanks were used to control and record flow rates. TMPs were recorded during each run by a differential pressure gauge.

5.4.2 Membrane

A tubular ceramic membrane manufactured by INOPOR having a 0.05 micron pore size was employed in all stage one reactions.

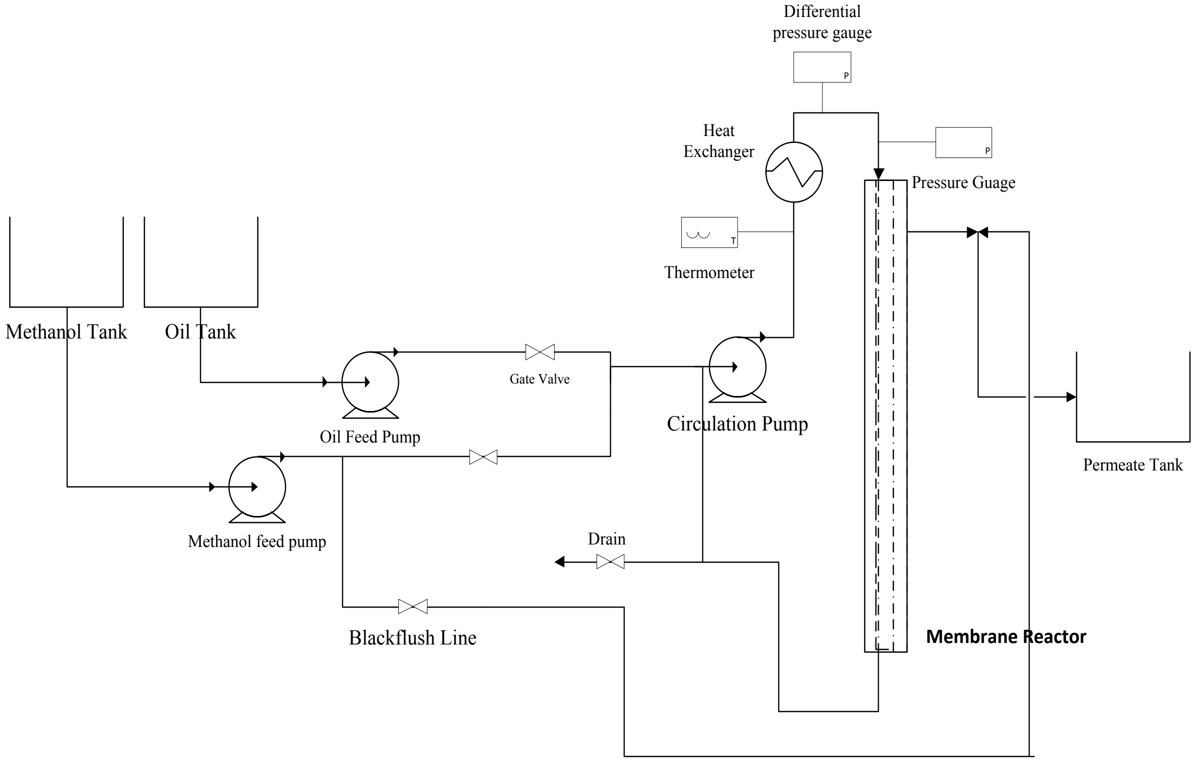


Figure 5.3 Schematic representation of membrane reactor setup for elution studies and first stage reactions

5.5 Batch Reactor

The second stage of the reactions was carried out in a batch reactor. The choice of batch reactor was to maximise the residence time and to contain the glycerol in the mixture. The reactions were carried out in a 500 ml three-necked round bottom flask, where the total volume of reaction mixture was 250 ml. The reactor was equipped with a reflux condenser to prevent loss of methanol by evaporation as shown in figure 5.4. The batch reactor was sealed with stoppers to mitigate any interaction of the reactants with water vapour. The reactor was immersed in a constant-temperature bath, which was placed over the hot plate. The hot plate was equipped with a magnetic stirring mechanism to cause agitation of the reaction mixture.

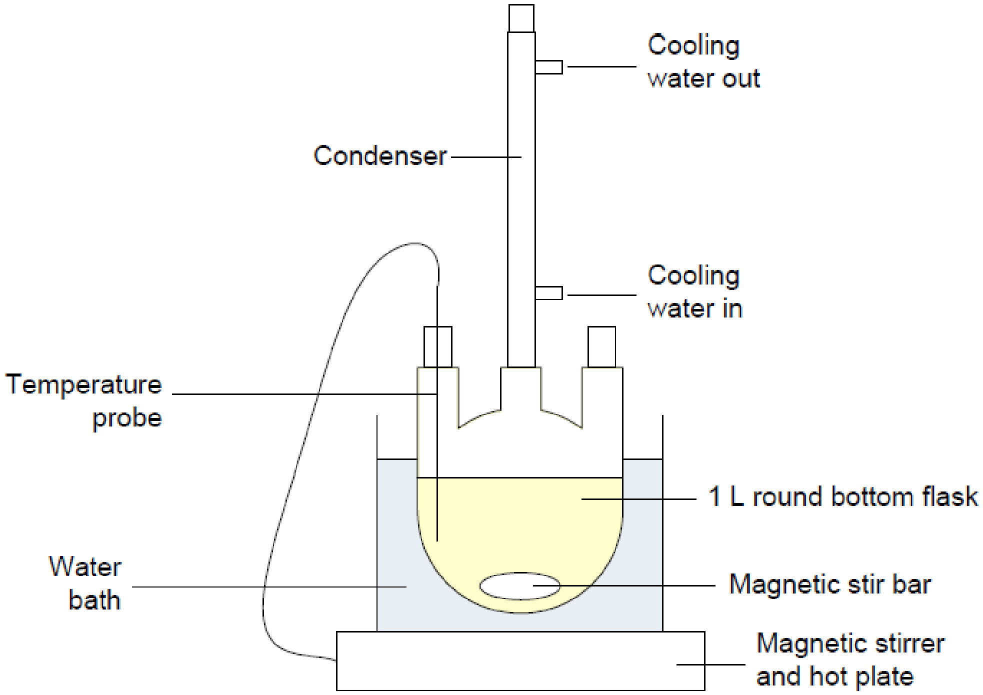


Figure 5.4 Batch reactor setup for biodiesel production

5.6 Experimental Procedure and Analytical Method

5.6.1 Procedure

Stage one of the transesterification reaction was carried out in a membrane reactor. The free fatty acid content of the feedstock (Canola) was determined by titration with catalysts before feeding it into the reactor. This gave us the correct estimate of the minimum catalyst concentration that needs to be maintained in the reactor. The reaction conditions are shown in the Table 5.3. The reaction was carried out at temperatures of 50 ℃ and 60℃, as below this the reaction rate is lower in agreement with the Arrhenius law (Mendow et al. 1969).

Table 5.2 Membrane reactor reaction conditions

Operating Parameter	Value
Feed Stock	Canola
Oil: Methanol ratio	8 : 1
Total catalyst concentration	0.33 wt% of the oil
Temperature	50℃ and 60℃
Oil titre	0.03 wt% of oil

Biodiesel was produced in the membrane reactor according to the following procedure:

a) The membrane reactor was backflushed with pure methanol to remove any residual oil and fouling deposits on the membrane walls from previous runs.

b) Permeate and the backflush lines were closed.

c) Initial weight of the oil and methanol was recorded from the balance. Labview software was started to record the run information.

d) The feed valves pertaining to oil were opened, and the oil was fed into the reactor.

e) Oil was circulated to reach a desired temperature.

f) Methanol was fed into the reactor and the circulation pump was started.

g) After a residence time of 60 minutes, methanol and oil was continuously fed into the reactor with a constant flow rate such that the predetermined overall molar ratio of 8:1 was maintained.

h) Permeate was collected after 60 minutes from the start of the run until end of the run.

i) A total of 16 L of biodiesel was produced for use in stage two reactions.

j) Circulation was stopped and the shut down procedures were followed as mentioned in the appendix A.

5.6.2 Analysis

The samples to be analysed, must be free from any catalyst and methanol. In order to obtain pure biodiesel, a series of processes are usually required. These can include: gravitational settling, centrifugation, water washing, adsorption and distillation Karaosmanoglu et al. (1996).

The most common method for purification of the biodiesel is water-washing. FAME and unreacted TG are essentially non-polar and insoluble in water, while soap, methanol and glycerol are polar and readily soluble in water. Therefore, adding water to the non-polar phase is usually the first and the most common step in purifying biodiesel (Clements et al. 2004). Similar method of water washing was employed to wash the biodiesel produced from transesterification reaction and is illustrated below.

a) 30 ml of biodiesel sample is taken in a vial.
b) 13 percent by weight 0.02M hydrochloric acid is added to the vial.
c) The contents are shaken well and spun in a centrifuge at 5000 rpm for 10 minutes.
d) The bottom phase is carefully removed.
e) 10 percent by weight distilled water is added to the vial.
f) The contents are shaken well and spun in a centrifuge at 5000 rpm for 10 min.
g) The bottom phase is carefully removed.
h) The sample is then evaporated for trace amounts of methanol and water for 30 min at 100 mbar.
i) The sample is ready derivatization and analysis.

5.6.3 Analytical Methods

A GC, a Varian CP-3800, was used to determine the concentration of monoglycerides, diglycerides and triglycerides in FAME corresponding to individual samples by ASTM method. A 15 m x 0.32 mm x 0.1 µm column from Restek (MXT – Biodiesel TG) was used with a guard column of 2 m x 0.53 mm. Calibration curves for the GC were generated using two internal standards (butanetriol and tricaprin) and four references namely glycerine, monoolein, diolein, and triolein. Three replicate injections at 5 separate concentrations were performed to yield a glycerol calibration curve, $R^2 > 0.99$ to meet the ASTM requirement (Jehad Et al. 2010).

5.6.4 Sample Preparation for Analysis

(a) Weigh 100 µL of FAME in a 40 mL septa vial.

(b) 100 µL of MSTFA, Butanetriol and Tricaprin were added in 5 minute intervals.

(c) The vial was then shaken to mix the contents and left to stand for 15 min at room temperature.

(d) Approximately 8 mL of n-heptane was then added to the vial.

(e) 1 µL of the prepared sample mixture was then injected in the GC.

The operating conditions for the column oven were 50°C for 1 min before ramping 15°C/min to 180°C, 7°C/min to 230°C and finally 30°C/min to 380°C. The oven was held at 380°C for 10 min. The carrier gas, helium was held at a constant flow of 3.0 mL/min, flame ionization detector (FID) was held at 380°C, Hydrogen flow was kept constant at 35 mL/min, air flow rate was at 350 mL/min, and Helium flow rate was at 30 mL/min (Jehad Saleh et al. 2010).

5.7 Batch reactions

The permeate from the membrane reactor was collected to perform further reactions. Figure 5.5 below gives the list of runs that were performed as stage 2 and stage 3 transesterification reactions.

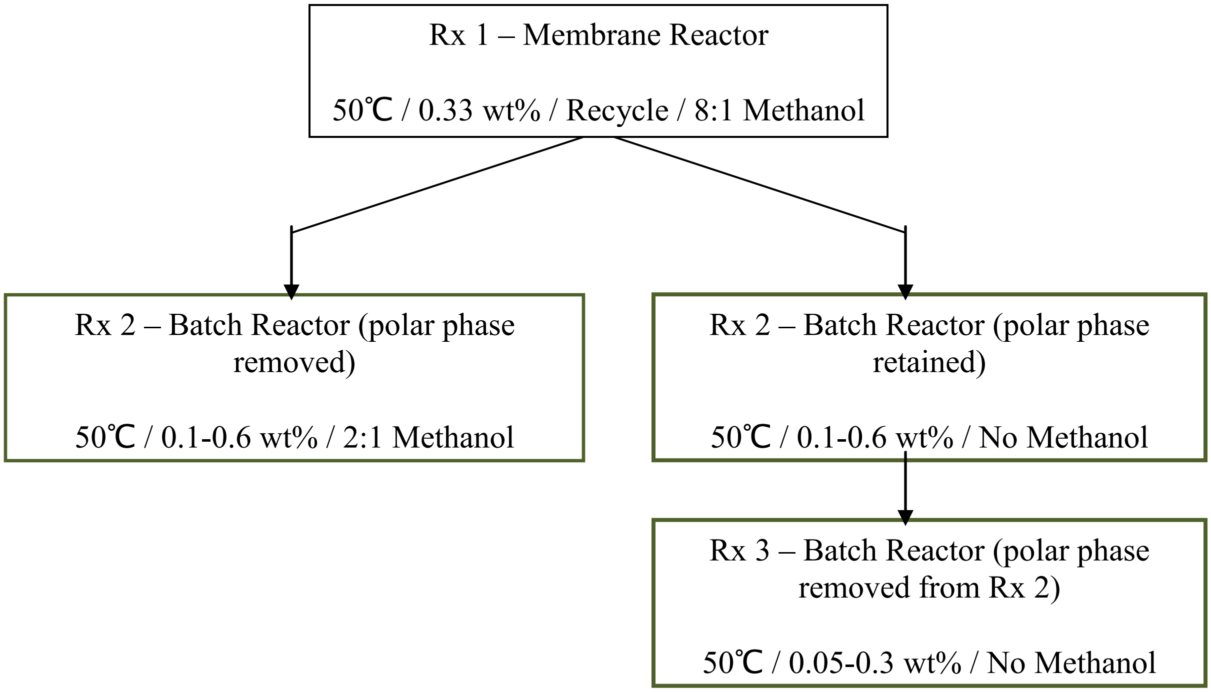


Figure 5.5 List of runs performed in a batch reactor

5.8 Reaction Stages

The main priority is to develop a multistage approach which runs on moderate operating temperature, low methanol to oil ratio and very low catalyst concentrations thereby giving best biodiesel purity (> 99.8%) and high yield and also which is viable economic point of view. The following approaches discussed below were carried out by varrying the temperature, catalyst concentration and methanol to oil ratio.

5.8.1 Stage two reactions with polar phase removed

The first set of stage two reactions were performed by removing the polar phase (glycerol) from the permeate as shown in Figure 5.6. The motive of separating the glycerol from the permeate stream was to mitigate mass transfer limitations.

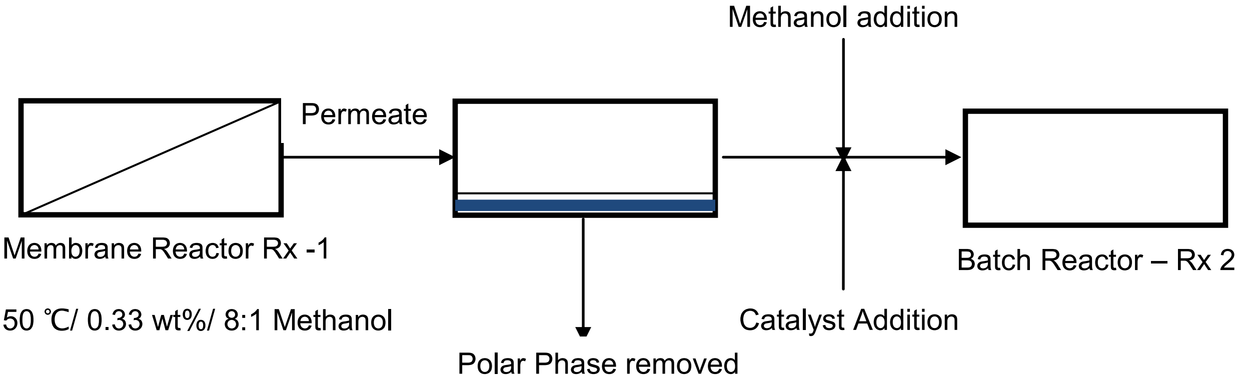


Figure 5.6 Aproach 1 for multistage reactions

It is postulated that, monoglycerides with two hydroxyls, tend to stay with glycerol, thus forming a boundary layer around them and limiting catalyst and methanol interations. This causes incomplete reaction thus reducing the purity (Tremblay et al. 2007). The second reaction was carried out at various catalyst concentrations and temperatures by adding 2:1 by mole of methanol with respect to oil. The influence of variables, methanol to oil ratio, catalyst concentration and temperature on the purity has been analysed.

5.8.2 Stage two reactions with polar phase retained

The second set of stage two reactions were performed by retaining the glycerol phase. The motive of retaining glycerol phase was to utilise unused catalyst and methanol. Considering their polarity, methanol and catalyst would go into glycerol phase. Thus, retaining the phase would cut down the need for adding more methanol. Also, glycerol would contain the soap formed in the reaction thus lowering the amount of soap in the FAME phase. The reactions were carried out adding the catalyst solution and keeping all other parameters constant as shown in Figure 5.7. The biodiesel from stage two was then reacted again as stage three, with addition of catalyst.

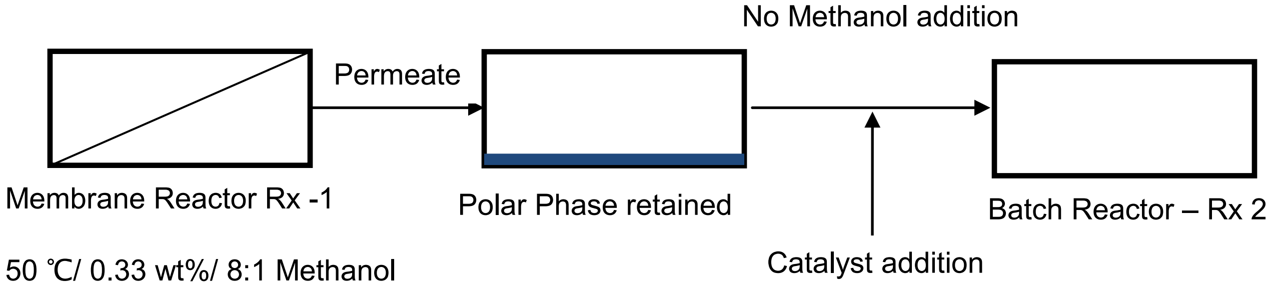


Figure 5.7 Approach 2 for multistage reactions

5.8.3 Stage three reactions with polar phase removed post stage two

In this variation, the total catalyst was divided between reaction 2 and 3 as shown in Figure 5.8. The approach further lowers the need of addition additional methanol and also lowers the overall soap in the FAME phase.

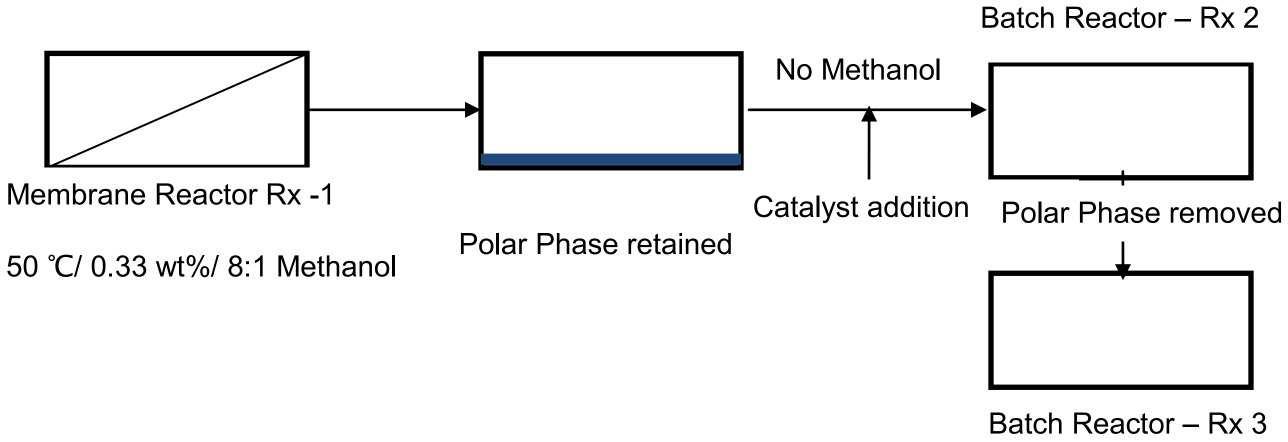


Figure 5.8 Approach 3 for multistage reactions

5.9.Results and Discussions

5.9.1 Effect of catalyst concentration, temperature and methanol to oil ratio on soap formation

Regarding the yield, the most important factor is the catalyst concentration. The second most important factor is the temperature. Both have a negative impact on the biodiesel yield. Therefore, any increase in temperature and catalyst concentration will reduce the biodiesel yield (Vincente et al. 2007). Figures 5.9 shows the soap concentration as a function of catalyst.

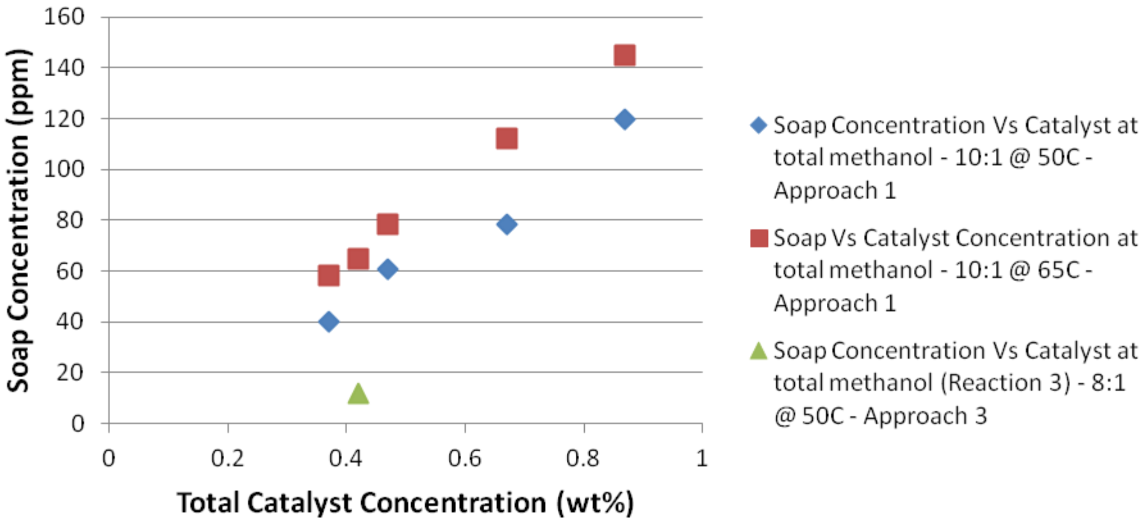


Figure 5.9 Catalyst concentration vs soap at different temperatures – Stage 2 polar phase removed (Approach 1)

As it can be observed, the influence of temperature on low catalyst concentration is not substantial but at the same time cannot be ignored. Saponification is favored at high temperatures and catalyst concentrations. This side-reaction produces sodium soap thus, decreasing the biodiesel yield and results were in agreement to Vincente et al. 2007.

The reaction with no addition of methanol produce less soap in the FAME phase as seen by comparing Figures 5.9 and 5.10. Owing to their polarity, the soaps dissolved into the glycerol phase during the separation stage after the reaction. In addition, the dissolved soaps increased the methyl ester solubility in the glycerol, causing additional yield loss when the phases are separated (Vincente et al. 2007). The concentration of soap in the glycerol phase seen in Figure 5.10 was much greater than the FAME phase as expected due to the polarity of the soap molecules.

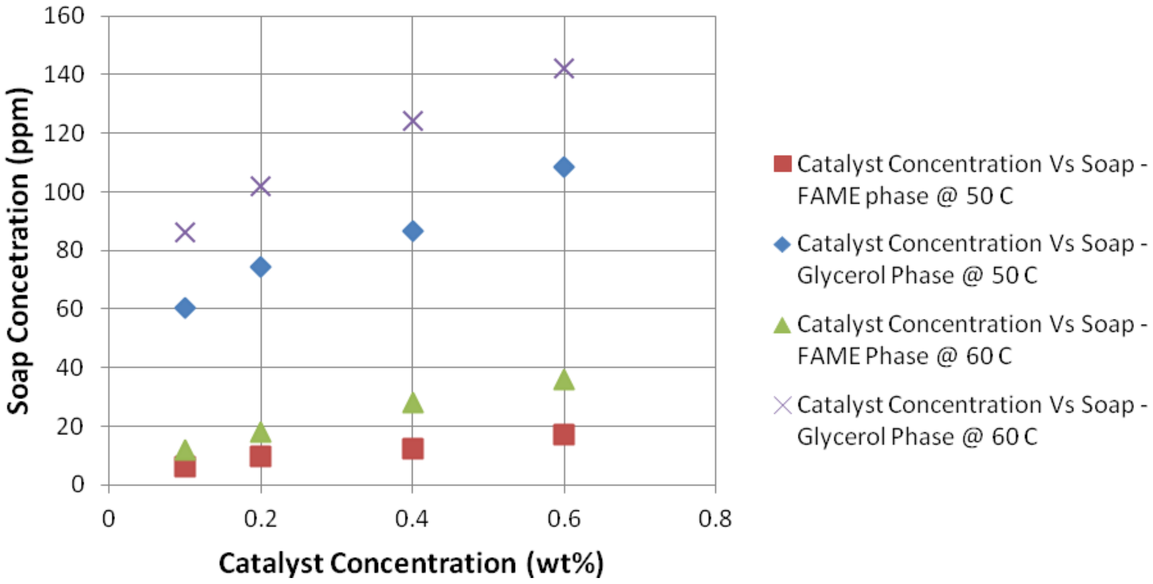


Figure 5.10 Catalyst concentration Vs Soap - stage 2 with polar phase retained (Approach 2)

5.9.2 Effect of catalyst concentration, temperature and methanol to oil ratio on purity

The initial catalyst concentration, methanol: oil molar ratio and temperature are the most important factors and all of them have a positive effect on the biodiesel purity. In other words, biodiesel purity increases with increase in the variables and agreement with the results of Vincente et al 2007. There was a significant increase in biodiesel purity with increase in methanol to oil ratio in the stage two as shown in Figure 5.11.

The monoglyceride concentration reached ultra low levels of 0.053 wt% at 50 ℃ with 2:1 methanol in the second reactor at 0.63 wt% catalyst concentration. It was also seen that, temperature at a constant methanol to oil ratio and catalyst did not have a very significant effect on biodiesel purity Figure 5.11.

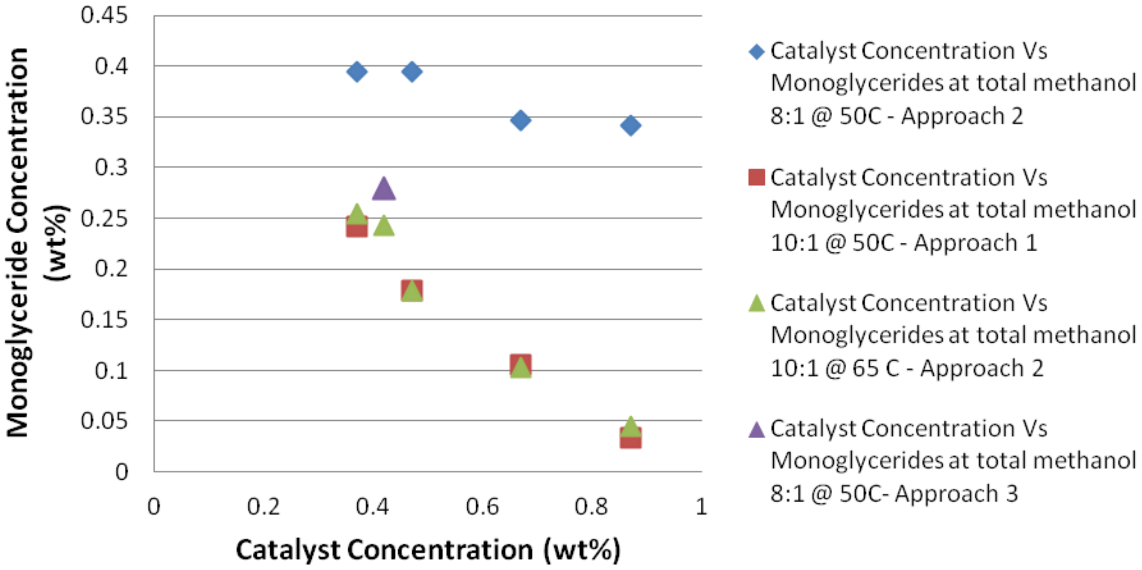


Figure 5.11 Monoglyceride concentration as a function of catalyst concentration

The FAME from reaction two was further reacted by adding 0.05 wt% catalyst. The monoglyceride concentration reached a low value of 0.28 wt% with a soap concentation of 12 ppm in the FAME phase.

5.10 Conclusions

The following set of conclusions can be derived from the study.

- The most effective way of reaching ultra low concentration of monoglycerides is by carrying out multi-stage transesterification.
- It can be postulated that, the stage one of the reaction can be performed to react the position 1 and 3 of the triglyceride molecule and further esterification can be carried out to react position 2.
- The factors affecting the biodiesel purity are catalyst concentration, methanol to oil ratio and the temperature. All of them have a positive effect on the biodiesel purity and therefore the biodiesel purity increases when the values of these variables increase, the results which were in agreement with Vincente et al 2007. The most significant effect was seen in the case of catalyst concentration.
- The most important factors affecting the biodiesel yield is catalyst concentration, methanol ratio and the temperature. Catalyst concentration has the greatest effect on increasing soap formation while the temperature range studied had less of an effect, the results which were in agreement with Vincente et al 2007.
- From the priliminary runs, it was also observed that conversion from the membrane reactor plays a very important role in bringing down the monoglyceride and soap concentrations in the further reactions. It is desirable to achieve higher conversion from the reactor one to achieve significant lower concentrations of MG and lower soap concentrations.
- The knowledge derived from the priliminary runs was that the three stage transesterification reaction is the most suitable approach to bring down the

monoglyceride and soap concentration in the FAME phase with lowest catalyst and alcohol consumption.

- The three stage reaction gave a purity of 0.28 wt% and low soap formation of 12 ppm at moderate temperature of 50 ℃, at a total methanol concentration of 8:1 and low catalyst concentration of 0.45 wt% . Furtherwork is currently underway to analyse other approaches in producing pure biodiesel and in turn mitigating the loss of yield and will be a matter of subsequent publications.

Chapter 6

6.1 Overall Conclusions

There is an increasing global concern surrounding the dwindling reserves of fossil fuels. With newer oil wells hard to reach, and global warming being a significant challenge, the scientific fraternity has started to focus on production of Biofuels for a sustained fuel source. Biodiesel of all the Biofuels has gained extra attention because of its striking similarities with petro diesel. However, the issues related to cold flow operatability plague the wide spread use of the biodiesel. There has been substantial work carried out to determine the impact of monoglycerides on the cloud point. Monoglycerides, which are a result of incomplete reaction, have been identified as the major source of issues pertaining to filter plugging. Monoglycerides have a very high melting point and could start to crystallise at temperature well above cloud point. Hence, it calls for more stringent norms and methods to greatly reduce monoglycerides to tackle cold flow issues and to facilitate widespread use of biodiesel as an alternative to petro diesel.

Chapter 4

In this project, a membrane reactor was employed to speciate saturated monoglycerides through continuous elution reaction. Series of experiments were performed to speciate saturated monoglycerides as the reaction proceeded. The effect of variables, temperature, catalyst concentration and methanol to oil ratio was also investigated.

From the preliminary results, there was no significant difference in the amounts of saturated monoglycerides as a function of time. The saturated monoglycerides remained low throughout the reaction.

From the results, it was realised that the positional distribution of fatty acids plays a significant role in the reaction kinetics. The fatty acid chain in the second position is hard to reach and reacts the slowest. Saturated fatty acids rarely occupy the second position, thus explaining the results of high amount of unsaturated monoglycerides in the permeate stream. The results were in agreement to stavarache et al 2007. Also, there was no significant difference in the saturated monoglyceride content with change in temperature, catalyst concentration and methanol to oil ratio. It was seen that unsaturated monoglycerides were the dominant factor in biodiesel and that the saturated monoglycerides are not present in great amounts as reports in the literature.

Chapter 5

As a part of my thesis, a novel two stage transesterification process was developed to greatly reduce the monoglycerides. The effect of catalyst concentration, methanol to oil ratio and temperature were analysed over multi stage transesterification reactions. The first stage of the reaction was carried out by a membrane reactor and the second stage in a batch reactor. The two stage system was successful and represented ultra low monoglyceride concentrations. The system was studied to obtain low monoglyceride concentrations at low catalyst and methanol concentrations. The effect of these variables on the yield was also investigated. The initial results were in agreements with Vincente at al 2007. The yield decreased with increase in catalyst concentration and temperature. High methanol ratio too resulted in decrease in yield due to mutual solubility. Purity on the other hand, had a positive impact on the catalyst concentration and methanol ratio. The runs were performed with three major configurations. The first configuration of retaining polar phase in the second stage, was not every effective in reducing the monoglyceride concentration over two stages. This can be attributed to the mass transfer limitations due to micelle formation. However, it was observed to be the best approach over three stages. The product was further reacted as reaction three after removing the polar phase. A low concentration of 0.28 wt % with 17 ppm of soap in FAME phase was achieved. The total methanol to oil ratio was at 8:1, the temperature at 50^{O}C and the total catalyst concentration was 0.42 wt %. This is a novel result as not much work has been carried out in the literature pertaining to two stage reactions with an idea to lower monoglycerides. The third configuration at 10:1 alcohol gave 0.03 wt % monoglyceride concentration. However, it was not considered the best approach as there was considerable yield loss due to formation of soap. The soap concentration in the FAME phase was 120 ppm.

6.2 Recommendations

Very little is covered in the literature pertaining to the work carried out in this thesis. The elusion study is a novel way of speciating saturated monoglycerides during the reaction. Further work can be carried out to understand the chain positioning for various feedstocks and the positional affinity to react faster. Enzymes can be used to selectively react saturated fatty acid chains based on positional distribution. Also, the impact of unsaturated monoglycerides on the cold flow properties can be analysed.

There is a great scope of work in the second project carried out. It would be interesting to see the effect of low catalyst concentrations in the stage one of the process. The methanol to oil ratio can be investigated over two or three stages by maintaining the total ratio constant. There is also scope of investigating soap formation and monoglyceride conversion to FAME. The process can also be investigated over higher alcohols and different feedstocks. The multistage transesterification can be analysed over a continuous stirred, membrane and batch reactors.

Chapter 7

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Appendix

Appendix A: Gas chromatography (GC) operation guide

(ASTM D6584 – Cold on column injector)

Sample Preparation

(All steps written below are done under nitrogen in the glove compartment)

1. Weigh 100 mg of sample into a 10 ml septa vial.

2. Add 100 µl of each Butanetriol (internal standard 1), Tricaprin (internal standard 2), and MSTFA into the sample vial. Both internal standards are located in the refrigerator in room D403 - ***Make sure you put the standard solutions back in the refrigerator after you're done***.

3. Shake the vial and let it set for 20 minutes at room temperature.

4. Add 8 ml of high grade n-heptane into the vial and shake for a few seconds.

5. Remove approximately 1 ml of the sample mixture into GC auto sampler vials.

6. Label the 10 ml vial and the auto sampler vial accordingly.

Getting Ready

1. Check that gas filters are still 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 helium, air, and hydrogen tanks. Verify that they are set to the appropriate pressures; if not, adjust the set-screw accordingly.

- Helium, carrier gas, set point is ~80 psi
- Compressed air, set point is ~60 psi
- Hydrogen, set point is ~40 psi

3. Always leave at least 400 psi residual gas in a depleted cylinder. As the cylinder pressure drops, the concentration of the impurities such as moisture and hydrocarbons increase which will lead to column damage. In addition, 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 data gathered.

Safety guidelines

- All Lab workers should take the WHMIS exam and Lab training prior to working in the Lab.
- All safety equipment i.e. lab coat, safety goggle and gloves should be used during these experiments.
- Both methanol and sodium methoxide (The homogenous catalyst) are extremely toxic. The MSDS of methanol and sodium methoxide should be carefully read beforehand.
- The reactor temperature should not exceed 67°C to avoid the methanol evaporation.
- Always lower the fume hood sash when working with methanol and sodium methoxide.
- Locate spill kit and pads.
- Reactor pressure should not exceed 50 psi. If it reaches this pressure, turn off all pumps and consult your supervisor.